The Canadian Mineralogist
Vol. 34, pp. 1211-1222 (1996)

SELF-ORGANIZED BANDED SPHALERITE AND BRANCHING GALENA IN THE PINE POINT ORE DEPOSIT, NORTHWEST TERRITORIES

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Abstract

Botryoidal arrays of banded-acicular sphalerite are intergrown with dendritic and branching galena at the Pine Point deposit, Northwest Territories. Scanning electron microscope (SEM) and electron-microprobe analyses (EMP) demonstrate that the banding in sphalerite is due to an alternation in Fe and Zn content. A time-series analysis constructed from the measurement of band widths in a doubly polished thin section is consistent with the hypothesis that the bands are self-organized as a result of the operation of a nonlinear chemical oscillator. The branching crystals of galena are shown to be another manifestation of far-from-equilibrium crystallization. Accordingly, a qualitative model is proposed that demonstrates how the interplay of reaction and diffusion kinetics can lead to the banding and branching. Models wherein the banding in sphalerite in Mississippi-Valley-type (MVT) deposits is solely considered to be an artifact of bulk chemical changes in the fluid within the system need to be re-examined.

Keywords: Mississippi-Valley-type deposit, MVT, sphalerite banding, zoning, branching galena, self-organization, nonlinear dynamics, reaction-diffusion kinetics, Pine Point, Northwest Territories.

Sommaire

Nous décrivons l'intercroissance d'amas bulbeux de sphalérite rubanée et aciculaire avec des dendrites et des ramifications de galène provenant du gisement de Pine Point, dans les Territoires du Nord-Ouest. Des analyses au microscope à balayage électronique et à la microsonde électronique démontrent que les rubans dans la sphalérite sont l'expression d'une variation de la teneur en fer. Une analyse de série temporelle construite à partir de la mesure des épaisseurs de bandes dans une section mince doublement polie concorde avec l'hypothèse que les bandes sont auto-organisées et le résultat de l'opération d'un oscillateur chimique non linéaire. Les cristaux de galène en branches manifestent également la présence d'une cristallisation hors d'équilibre. Par conséquent, nous proposons un modèle qualitatif de l'effet réciproque que peut avoir la cinétique de réaction et la diffusion sur la formation des ramifications et des rubans observés. Les modèles selon lesquels les rubans de sphalérite des gisements du type de la vallée du Mississippi seraient causés uniquement par des changements à vaste échelle dans la composition chimique des fluides hydrothermaux sont à revoir.

Mots-clés: gisements du type de la vallée du Mississippi, sphalérite rubanée, zonation, branchements de la galène, auto-organisation, dynamique non linéaire, cinétique de réaction et diffusion, Pine Point, Territoires du Nord-Ouest.

Introduction

The Pine Point deposits lie at the eastern margin of the Western Canada Sedimentary Basin, in a Paleozoic section approximately 500 m thick dominated by evaporite and carbonate rocks that overlie the Precambrian Shield in the southern Great Slave Lake area, Northwest Territories. The Pine Point deposits share characteristics with many lead–zinc deposits the world over, and are classified as members of the Mississippi Valley type (MVT) of deposits. In general, MVT deposits were formed by circulating low-temperature (50–100°C) hydrothermal fluids as fillings within carbonate rocks at shallow depths (<1 km). The ore occurs in breccias, solution channels or other voids, and may be accompanied by pyrite, fluorite, barite or

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bitumen. Many MVT deposits contain ore and gangue minerals that are banded. Banding in sphalerite of MVT deposits has been the focus of much attention, and its origin has been attributed to mineralization from pulses of hydrothermal fluids of variable composition over time (*e.g.*, McLimans *et al.* 1980).

In this paper, we examine the details of the sphalerite banding and its intergrowth with branching galena at Pine Point. We analyze the banding using modern methods of nonlinear dynamics, and conclude that both the sphalerite banding and the branching galena are due to crystallization under far-from-equilibrium conditions. We also propose possible models that consider the growth and banding as self-organizing processes resulting from the action of nonlinear chemical oscillators (Ortoleva 1994). We contrast the nature and origin of banding in sphalerite from MVT deposits with that of vein-type deposits.

Description of the Textures

In common with other MVT deposits, the banding in Pine Point sphalerite is characterized by alternation in the color of the zinc sulfide from clear to pale white,

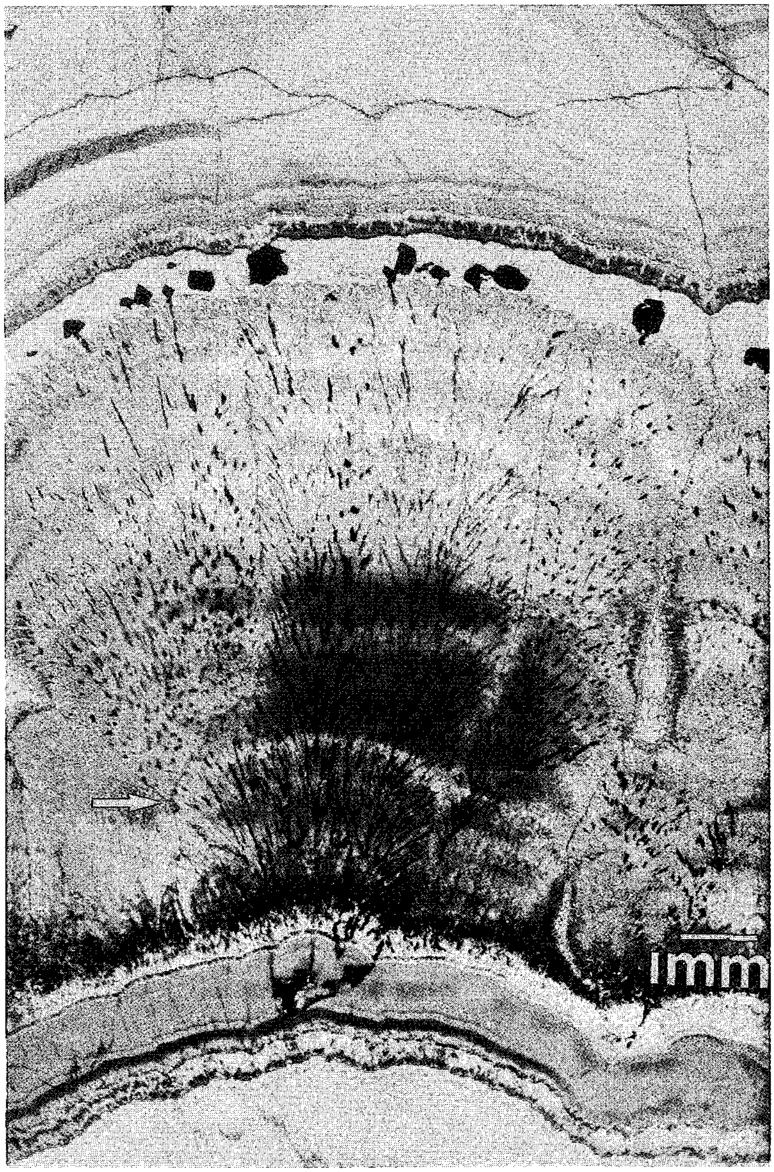

FIG. 1. Plane-polarized-light photomacrograph of part of a thin section showing sphalerite banding in a sample from the Pine Point deposit. The banding varies from clear, to pale white, to brown, to deep red-orange in color. The concentric bands form coalescent arcuate arrays that emanate from centers of growth. In three dimensions, these form the characteristic hummocky, so-called botryoidal textures. Note that some bands toward the top of the image do not correlate over the entire section. Black blebs and filigrees within the sphalerite bands are elements of what are interpreted to be a branching crystals of galena that radiate from the middle of the thin section. Although it appears discontinuous, in three dimensions, all parts are presumably connected. The arrow demarcates a point common to that of the more detailed Figure 3.

FIG. 2. SEM image captured from near the growth center of the galena using electron backscatter mode. The galena closest to the center of growth is dendritic and relatively thick in comparison to the later galena, which has a branching habit and is characterized by tip-splitting. The branching opens in the growth direction, toward the top of the figure.

to light brown, to red, to almost black. The bands consist of bulbous, so-called botryoidal arrays composed of sheaves of numerous acicular crystals oriented normal to the bands. Figure 1 illustrates a typical sequence of bands from core to rim of a doubly-polished thin section of a sphalerite sample from Pine Point. Note that the banding is discontinuous at the small scale, and that many bands are intergrown with branching and dendritic crystals of galena. These show evidence of tip splitting, and their branching opens in the growth direction (Fig. 2).

Close examination of the bands shows that they consist of networks of many acicular, platy and stubby crystals of sphalerite. Acicular crystals radiate from the inner margin to the outer margin of the band (Fig. 3). In addition to the color, both texture and grain size change between bands (Figs. 3, 4). Unlike the galena crystals, there appears to be no evidence of branching, *i.e.*, tip splitting. Some individual crystals can be traced across more than one band. Examination with a scanning electron microscope (SEM) and an optical microscope indicated that the sphalerite is intergrown

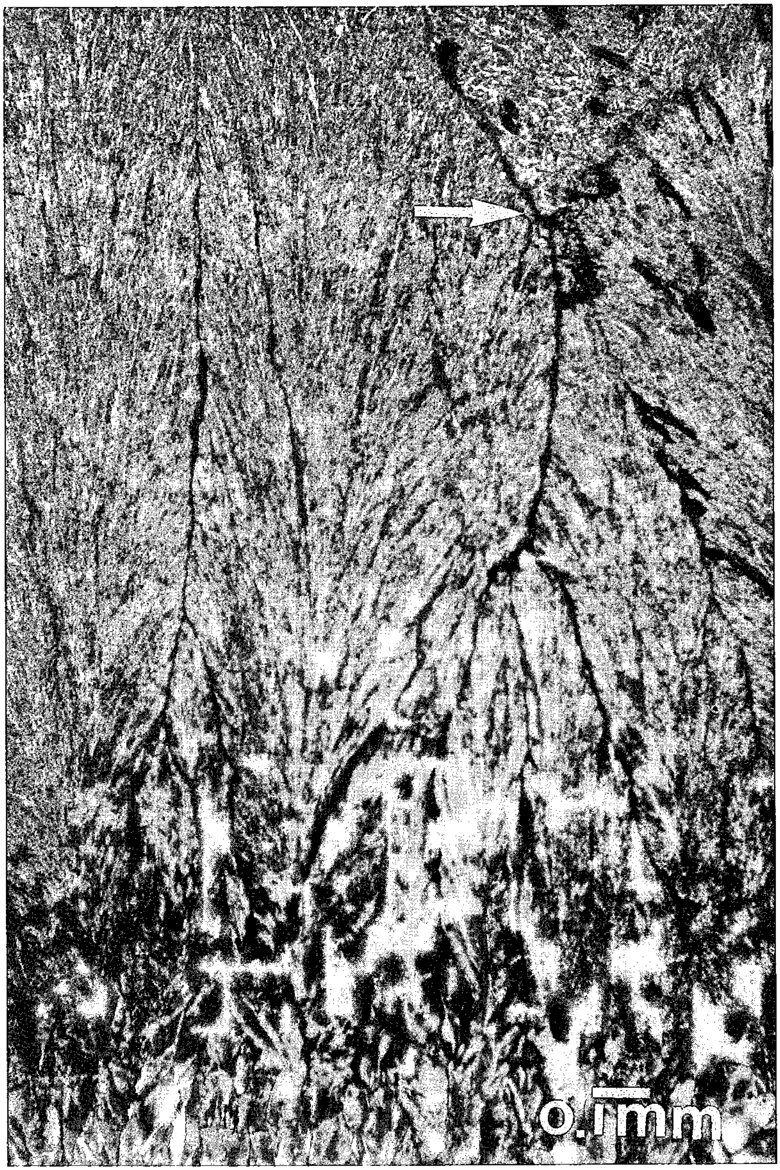

FIG. 3. Plane-polarized-light photomicrograph illustrating the growth habit of sphalerite. The arrow demarcates the same point as the corresponding arrow in Figure 1. In all bands observed, the sphalerite is composed of small acicular and platy crystals that are oriented normal to the banding. The relatively coarse sphalerite of one band is clearly shown to be arranged in a fasciculate texture (*i.e.*, bunches of crystals that radiate from a common area without evidence of tip-splitting).

with a hexagonal mineral, presumably the ZnS polymorph wurtzite. SEM evidence and electron-microprobe (EMP) analysis demonstrate that the banding correlates with a fluctuation in the content of Fe and Zn in sphalerite. For instance, SEM analysis of 56 bands yielded the following atomic concentrations for iron and zinc, respectively. For dark bands, the mean values are 6.0 wt.% and 61.2 wt.%, whereas for the light bands, they are 1.9 wt.% and 64.2 wt.%. Figure 4a, an Fe X-ray map, demonstrates the alternation in Fe content between the bands. Note that the banding is well characterized by the alternation in Fe content and that the distribution of Fe anticorrelates with that of Zn (Fig. 4b). Cu, Sn, Cd, Ni, and Co concentrations all proved to be below detection limits for the electron microprobe (500, 362, 321, 293 and 281 ppm, respectively).

INTERPRETATION OF THE TEXTURES

Intergrowths of sphalerite and galena form the botryoidal textures. The galena is characterized by dendritic and branching crystals. Under conditions close to equilibrium, galena forms equant euhedral cubic crystals. The mineral morphology observed here suggests far-from-equilibrium conditions of growth (*e.g.*, Fowler *et al.* 1989). As is typical in these circumstances, the interplay between rates of crystal growth, diffusion of solute, and surface tension results in self-organized patterns. Dendrites arise when a protuberance on a planar surface invades the solution, enhancing the local concentration-gradient. This augments the diffusive flux and, correspondingly, the rate of growth of the tip. However, surface-tension effects limit the growth process, and eventually the large cost in surface energy results in dissolution. Tip-splitting occurs when small protuberances (at the atomic scale) form on the growing tip. These protuberances are stabilized relative to their intervening embayments, as the probability of aggregation is highest at their tips (Nittmann & Stanley 1986). It is unlikely that diffusing (*i.e.*, random-walking) growth-species could penetrate between protuberances without striking them and sticking. Once initiated, the branches shield their embayments from growth-species, so that in-filling growth rarely occurs. The resulting pattern of growth is said to be self-organized in the sense that there is a pattern that is a spontaneous reaction to the growth conditions and not the result of growth on a pre-existing template *e.g.*, a unit cell (Ortoleva 1994).

Galena crystals such as those of Figures 1 and 2 are extremely delicate in that they are made up of a hierarchy of fine branches which, in three dimensions, are connected. The textures observed have three orders of branches. The fragile nature of the texture is evidence that they were formed in quiescent conditions.

Having recognized the acicular habit of the sphalerite crystals and the importance of far-from-equilibrium conditions for the formation of branching crystals such as the galena, we investigated the possibility that color banding in sphalerite also was the result of a self-organization process. The succession of dark and light bands that vary with Fe content suggests the existence of a nonlinear chemical oscillator. Chemical oscillators have compositions that fluctuate in time or space in response to feedbacks between reaction and transport rates. In one class of chemical oscillators, reactant solutions are pumped into reaction vessels at varying rates, and the nature of the products are monitored. Depending upon the particular rate of pumping, product compositions may be steady, or fluctuate in an oscillatory or chaotic manner (Gray & Scott 1990).

Deterministic nonlinear systems may exhibit complex irregular (chaotic) behavior. We can distinguish their output from purely random signals because there is an underlying order in deterministic nonlinear systems that is absent from random systems (Packard *et al.* 1980). In nature, systems are commonly both stochastic and nonlinear, but data analysis may allow us to deduce the relative importance of noisy and deterministic processes.

For this purpose, we performed time-series analyses on a measure of the sphalerite banding in order to test for nonlinear growth-modes. This was accomplished by measuring the thickness of successive bands of sphalerite. We found that the best way to observe the textures was through the use of doubly polished thin sections and an optical microscope. Nomarski phase-contrast microscopy using various etchants (dilute HCl, HNO_3, and NaOCl) was inferior to viewing in transmitted light in terms of the contrast between adjacent bands. Back-scattered electron images generated using the SEM also did not offer sufficient contrast. X-ray maps generated on the EMP have sufficient resolution, but are of such restricted areal extent that the technique is impractical.

Figure 5 illustrates the variation in band thickness across the botryoidal texture. Figure 6a is a return map produced by plotting the (n+1)th band's thickness as a function of the thickness of the previous one (nth). By plotting thicknesses of successive bands against each other, the return map monitors the influence of one event upon another, *i.e.*, determinism. Although it is difficult to detect a simple structure in the distribution of points, one can see a clustering near the origin, and the appearance of a degree of determinism. Indeed, a typical succession of points on the return map forms a cycle whereby a point in the upper part of the map is followed by one in the lower right corner and then by a point close to the origin. In contrast, Figure 6b shows the analysis of a series of uniform random numbers and results in uniform scattering of points across the return map.

We can further analyze the data using a predictor technique (Sugihara & May 1990, Fowler & Roach 1993), which searches for correlations within the series. Because systems may be described by numerous independent variables, a simple two-dimensional plot such as the return map may not be sufficient to resolve any underlying pattern within the dynamics. We examine the system in higher dimensions by searching for correlations within progressively higher vector space. In principle, this allows us to determine the embedding dimension, *i.e.*, the minimal number of dynamic variables sufficient to describe the evolution

FIG. 4 a. X-ray map showing the distribution of Fe across several bands. Brightness is proportional to Fe content. The image shows the same field of view as Figure 4b. Notice the anticorrelation with Figure 4b.

of the system. For instance, we can completely describe the dynamics of a periodically forced pendulum by monitoring two dynamic variables, the phase and its first time-derivative. Knowledge of these allows for calculation of other variables, *e.g.*, momentum, potential energy, kinetic energy, *etc.* The result of the sphalerite analysis is a plot of correlation coefficient *versus* embedding dimension. No significant correlations are expected for random systems. In contrast, near-perfect correlations are found for deterministic systems exhibiting low dimensional chaos (Fig. 7).

Figure 7 plots the results of 130 measurements of band thicknesses and demonstrates a maximum correlation (0.3) at embedding dimension 4. This means that there are only a few independent dynamic variables responsible for the banding. It also signifies that the complex pattern of banding is the result of the action of a nonlinear system. Stochastic systems, on the other hand, have so many independent dynamic

FIG. 4 b. X-ray map showing the distribution of Zn across several bands. Brightness is proportional to Zn content. The image shows the same field of view as Figure 4a. Notice the anticorrelation with Figure 4a.

variables that results of such analyses never yield any significant correlations (see line connecting × points in Fig. 7). Deterministic systems have high correlations because future values of the system are related to those of the past by fixed rules such as equations (see line connecting squares in Fig. 7). The analysis of the sphalerite data (Fig. 7) also demonstrates that in comparison to an exclusively deterministic nonlinear system, there is also considerable noise within the signal. This is likely due to random fluctuations in the growth parameters.

The best interpretation of the data based upon the return map and the predictor analysis is that the sphalerite banding, although noisy, is largely the result of a low-dimensional nonlinear deterministic process. In other words, we expect that the sphalerite modified the solution from which it grew, thus providing a feedback or nonlinearity in the growth conditions.

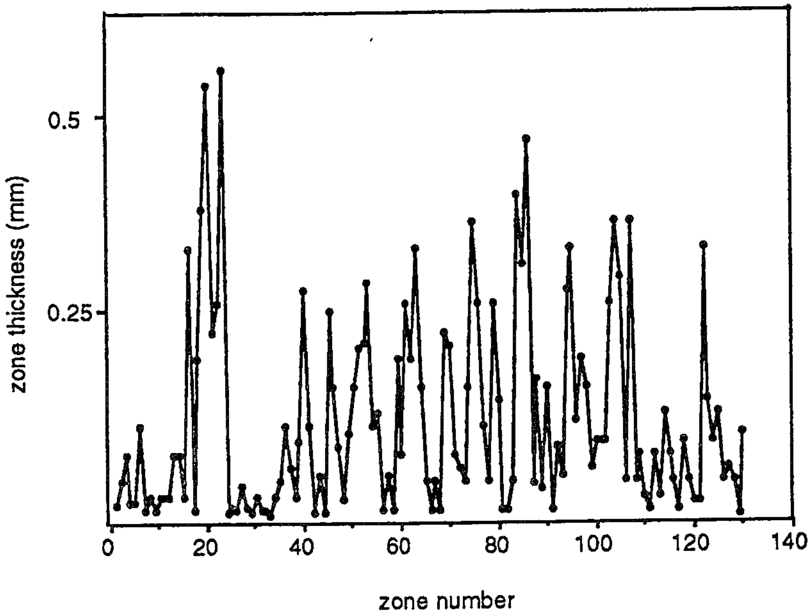

FIG. 5. Variation in thickness of sphalerite bands along the thin section shown in Figure 1a. The data are from 130 bands (abscissa). The scale of the ordinate (band thickness) is in mm.

DISCUSSION

Our analysis of the galena and the sphalerite textures imply that: 1) The crystals grew in an environment that was far from equilibrium, 2) the system was relatively quiet, *i.e.*, the fragile galena precluded turbulent mixing, 3) the sphalerite banding is described by alternations in Fe and Zn content at the ~0.1–1.0 mm scale, and 4) the organized deposition of the sphalerite and galena is likely dominated by a nonlinear far-from-equilibrium process.

Models for deposition of the sulfides in MVT deposits can be categorized into two broad types. In the first type, both metals and reduced sulfur are transported to the site of deposition in the same hydrothermal fluid (Anderson 1975). Metals could be precipitated by various processes (*e.g.*, changes in temperature, pH, pressure or concentration of reactant). In the second type of model, the metals are transported into carbonate host-rocks containing H_2S. The H_2S may be locally derived through the reaction of hydrocarbon gases and sulfate minerals (Anderson 1991) or could be transported to the site of deposition in another brine (Plumlee *et al.* 1994). We expect that the second class of model to be more conducive to the generation of far-from-equilibrium conditions, since such models require the mixing of very different solutions. The most recent findings are consistent with this idea (Haynes & Kessler 1994, Plumlee *et al.* 1994, Baines *et al.*1993, Anderson 1991, Samson & Russell 1987).

Models for galena and sphalerite growth in accord with the mixing hypothesis and our observations and data analysis are proposed. Branching galena can be linked to a process known as diffusion-limited aggregation (DLA) (Witten & Sander 1981). Here, growth is computer-simulated by the release of a random walker from a point far from a nucleus particle. When the walker eventually touches the nucleus it attaches, and a new walker is released. In-filling growth is rare, because the walkers can seldom penetrate between branches. The resulting aggregate is a pattern characterized by several orders of branching. DLA can be thought of as the interaction of a stochastic process (the Brownian motion of growth-species) and a potential field (*e.g.*, temperature, concentration, chemical potential) that obeys the Laplace equation (*e.g.*, Nittmann & Stanley 1986). Simply put, this means that the crystal grows in a chemical potential field that is constant and that the growth species diffuse down-field to randomly arrive at the growth front. Stirring, advection, turbulence or other flow would mean that the potential field no longer obeys the Laplace equation. Physically, one can envisage that such flow would enhance the flux of fresh growth-species at the growth front in a directed

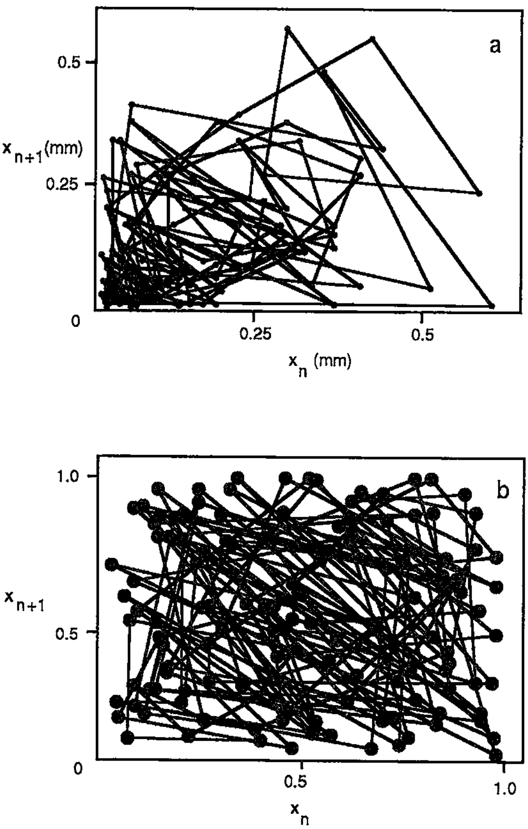

FIG. 6. a. Return map plotting the (n + 1) band thickness (in mm) as a function of the thickness of the previous one, the nth band. For the most part, the data are restricted to an area of the plot near the origin. They form a triangular pattern that spirals in a clockwise direction. In contrast, random data (Fig. 6b) scatter across the plot, and show no such pattern.

way, thus causing in-filling growth between branches. The growth of branching crystals can be driven by various potential gradients, *e.g.*, Cu electrodeposition driven by an electric potential (Brady & Ball 1984). This type of model is known to be relevant for branching growth of minerals and may be driven by a steep concentration or thermal gradient (Fowler *et al.* 1989, Fowler & Roach 1996). For the branching galena, we expect that growth was driven by a sharp gradient in chemical potential as a result of the introduction of metal-bearing brines into H_2S-rich carbonate rocks. During the branching growth, the potential fields must remain in a quasi-stationary state, *i.e.*, almost constant, so that the growth species aggregate by diffusion. This constraint allows us to infer that the growth conditions for the galena were quiescent, which is consistent with our interpretation of the fragile nature of the galena texture. Because the branching galena has a habit characteristic of patterns formed by diffusion-limited growth, we can also assume that its growth was diffusion-controlled.

Considering the (Fe,Zn)S system as a continuous solid-solution series, a model for the branching can be based on the coupling of reaction and diffusion kinetics during growth. This could lead to oscillatory patterns similar to those resulting from the constitutional undercooling model for plagioclase (L'Heureux 1993, L'Heureux & Fowler 1994). However, the banding is composed of aggregates of many crystals, in contrast to the single-crystal zoning observed in the plagioclase system, or indeed to the sphalerite of higher-temperature vein-type mineralization (*e.g.*, Pattrick *et al.* 1993).

A promising model for growth banding in sphalerite under far-from-equilibrium conditions is related to that of the Liesegang phenomenon (*e.g.*, Liesegang 1913) for precipitation from colloidal suspensions. In our model, an influx of Fe–Zn metal-bearing solution locally reacts with H_2S to produce nuclei of sphalerite, thus locally changing the supersaturation and the Fe:Zn ratio in the solute. These are not immediately restored to their bulk values by diffusive influx of new material. It is reasonable to assume that the nucleation rate changes rapidly with supersaturation (e.g,. Dee 1986). Consequently, the reaction may stop or be retarded, providing time for the subsequent replenishment of the reactant concentration. This succession of nucleated deposits can be linked to the observed variability in iron content. An order-of-magnitude estimate of the characteristic band-thickness L is estimated from $L \approx D/V$, where D is the diffusion constant, and V is the velocity of flow of the incoming fluid (Ortoleva 1994). Typically, D is approximately equal to $10^{-5} - 10^{-7}$ cm^2 s^{-1}, and a reasonable value for V could be 100 cm a^{-1} (Dewers & Ortoleva 1988). This simulation yields a band width L of approximately 1 to 10^{-2} cm, in good agreement with our observations. We are currently refining this model.

Models for the growth should invoke mechanisms in which the diffusion rates of growth-species for the galena and sphalerite are relevant. Indeed, the banded textures of many ore minerals led early investigators (Rogers 1917) to interpret them in terms of classic Liesegang experiments, in which bands are formed in a gel, which acts as a barrier to diffusion. They referred to the ore textures as colloform and suggested that ores were precipitated from sols. On the contrary, all evidence (*e.g.*, fluid inclusions) demonstrates that the metals were precipitated from aqueous solutions (brines). The limitation of diffusion in a liquid system can be achieved by invoking an interplay between growth rate and diffusion rate. Systems where the growth rate dominates over diffusion [*e.g.*, snowflakes:

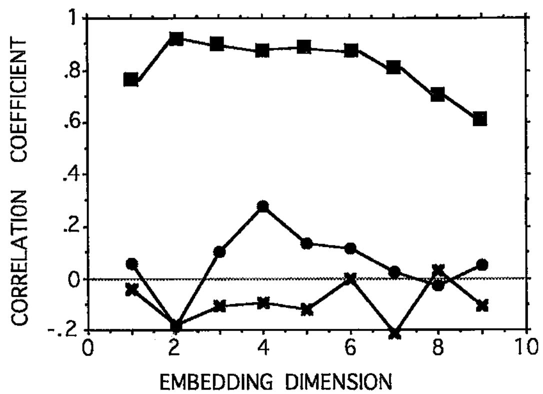

FIG. 7. Plot showing the result of the wimplex predictor technique for the data on the thickness of sphalerite bands (dots connected by lines). The graph plots the correlation coefficient determined for predictions made from points in the series about those elsewhere in the series, *versus* the embedding dimension. Good predictions result in correlations. Note that at embedding dimension (4), the correlation coefficients are positive and significant (for 130 samples at 2σ), suggestive of a deterministic though noisy "signal". In contrast, analysis of 130 uniformly distributed random data (× points connected by lines) shows no significant correlations, and unlike the case for the sphalerite analysis, the "correlations" are erratically distributed. The upper line (squares) is the result of analysis of chaotic data from the Lorenz system of equations (*e.g.*, Moon 1992). Although in time-series form the data are scattered, they were completely deterministically derived from a fixed set of equations, with no random inputs. The analysis shows very high correlations consistent with the data occupying a low-dimension deterministic attractor.

Ben-Jacob & Garik (1990)] will tend to form branching structures. In contrast, for polymers (plastics and silicate glasses), the sluggish rate of diffusion dominates the branching growth (Keith & Padden 1963). Analogously, the feedback between growth and diffusion rates should affect the sphalerite banding. Thus the interpretation of Roedder (1968) that the galena and sphalerite textures are due to rapid growth, and the older interpretation that they were the result of colloidal (*i.e.*, diffusion-limited) growth are both partly correct. We conclude that the sphalerite crystallized as a relatively open network of acicular and stubby crystals in response to far-from-equilibrium growth conditions.

It is commonly assumed that the banding in ores from the Mississippi Valley can be correlated over various scales (from hundreds of m to many km), and that the alternation in banding is due to changes in the bulk composition of the fluid on a broad scale (*e.g.*, McLimans *et al.* 1980). We reject this hypothesis as the direct cause for small-scale botryoidal sphalerite banding at Pine Point for several reasons. 1) Our analysis shows that the banding of adjacent clusters of sphalerite is not always correlated; indeed, examination of the figures of McLimans *et al.* (1980) shows that their correlations of ores from their area are by no means exact, and that there are numerous discontinuities. 2) Uncorrelated banding between adjacent growth-bands, splitting and rejoining of bands are hallmarks of chemical oscillators. 3) Furthermore, once the growth is initiated, a sudden change in fluid composition would destroy the quasi-stationary growth conditions required for branching growth in galena. 4) One would expect to see changes in the morphology or chemistry of galena at the contacts between bands in the sphalerite.

However, we recognize the importance of fluid mixing in the deposition mechanism of MVT deposits, which could be partly responsible for the isotopic variation observed in many other deposits (*e.g.*, Heyl *et al.* 1966, Deloule *et al.* 1986). Our work does not rule out the possibility of multiple sources of fluid or pulses of mineralization acting in concert with the far-from-equilibrium growth processes. Indeed, mixing of fluids could be necessary to initially trigger the growth. Our proposed models could easily include these effects. Although our analysis is inconsistent with each sphalerite band being related to a unique period of fluid mixing, mixing may be important for the initiation of the nonequilibrium conditions.

Finally, for completeness, we compare the banding of vein-type deposits to that in MVT deposits. The banding of crystals within vein deposits is parallel to the faces of individual equant crystals. Our observations of crystals occurring in vein-type deposits show the banding to be of two types, sector and oscillatory zoning. The zoning patterns are unique to individual crystals. In contrast, the crystal banding at Pine Point and other MVT deposits is observed across a multitude of acicular and radiating crystals aligned normal to banding. The banded sphalerite in vein-type deposits shows an alternation in Cu concentration between light and dark bands (Pattrick *et al.* 1993), which has not been reported for MVT deposits. This arises from a coupled substitution of Cu^{+} + In^{3+} for $2Zn^{2+}$, which is facilitated by the structural similarity between roquesite ($CuInS_2$) and sphalerite (Pattrick *et al.* 1993) and the higher solubility of Cu at the elevated temperatures typical of vein-type mineralization (Pattrick *et al.* 1993, Bente & Doering 1995). Indeed, our analyses show Cu to be below electron-microprobe detection limits (500 ppm) for the Pine Point samples. Therefore, we prefer a nucleation–diffusion model rather than a reaction–diffusion coupled-substitution model for the growth at low temperatures of botryoidal sphalerite in MVT deposits.

Conclusions

In this paper, Pine Point sphalerite–galena intergrowths were analyzed. Sphalerite has an acicular habit and exhibits an irregular alternation of differently colored bands correlating with Fe concentration. Nonlinear dynamic data analyses were performed on the band thicknesses, as observed from a doubly-polished thin section. Results of these analyses and the presence of branching dendritic galena allow us to conclude that the growth pattern is likely the result of non-equilibrium self-organization processes. A far-from-equilibrium growth model having the potential to yield spontaneously organized patterns is presented. Accordingly, the hypothesis that the small-scale bands in sphalerite can be correlated over large distances (*i.e.*, sphalerite stratigraphy) needs to be re-examined.

Acknowledgements

We acknowledge the continuing support of NSERC. We are grateful to Gary Ansell of the Geological Survey of Canada for providing one of the samples used for this study. The assistance of Peter Jones (SEM laboratory, Carleton University) and Glenn Poirier (EMP laboratory, McGill University) was greatly appreciated. We thank the referees for their useful comments.

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Received September 1, 1995, revised manuscript accepted May 2, 1996.