

SPHALERITE COLOR BANDING: LACK OF CORRELATION
WITH IRON CONTENT, PINE POINT, NORTHWEST
TERRITORIES, CANADA

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ABSTRACT

Normal sphalerite coloration—colorless through yellows to dark red-brown—has generally been attributed to iron content. Electron microprobe scanning and analyses of individual thin “colloform” bands show that although total iron content (<3 percent) does vary with the banding, it cannot be correlated with band color in these samples. The true coloring mechanism is not known.

INTRODUCTION

Prior to this study it was generally accepted that the color of most natural sphalerite is essentially a function of the amount of iron substituting for zinc in the structure. This correlation is documented by a large number of analyses of natural sphalerite. With increasing iron content the color in hand specimen changes from white (pure ZnS) through yellows, oranges, reds, reddish browns, and finally to black (Palache, *et al.* 1944). The colors in transmitted light, in thin, doubly polished plates, and on the streak plate, prove that even the seemingly opaque “black” sphalerites generally are within a range of dark reddish browns and browns, the intensity of which is directly related to the iron content. Somewhat similar changes in the color and intensity of transmitted light occur with changes in thickness of the polished plate. In addition, absorption studies have shown that most of the iron is present as Fe^{2+} ions substituting for Zn^{2+} , and that the absorption of these ions in the blue near 26000 cm^{-1} , plus absorption in the red from much smaller amounts of Co^{2+} , cause the yellow color of natural low-iron sphalerite (Slack, *et al.* 1966, 1967).

In the course of an investigation of fluid inclusions in doubly-polished plates of minutely banded “colloform” sphalerite ore from various Mississippi Valley-type deposits, it was noted that the colors seemed too dark for the general range of iron content expected. Thus samples from Pine Point, Northwest Territories, Canada, contain individual elongated sphalerite crystals that are cross cut by many color bands ranging from colorless to dark reddish brown at a plate thickness of only 0.09 mm. As in most low temperature sphalerite, this material shows some evidence of polytypy, in that it exhibits low birefringence (0.002) and weak X-ray powder diffraction lines of some wurtzite polytypes. Color comparisons with much thicker sections of analyzed single crystals of low-iron sphaler-

ite from other localities, in which the color does vary systematically with iron content (and thickness), would indicate iron contents of zero to perhaps 30 weight percent in the Pine Point material. Iron contents as high as the latter are generally considered to be most characteristic of relatively high temperature ore deposits. Yet homogenization temperatures and hence formation temperatures of primary fluid inclusions in Pine Point sphalerite samples were in the range 51° to 96°C (Roedder, 1968).

ANALYSES FOR IRON

To investigate this discrepancy, electronprobe analyses for iron were made of spots in relatively wide (28 to 117 μm) and uniform color bands, selected to represent the entire color range. A Materials Analysis Corp. probe was used, with an accelerating voltage of 20 kv., a specimen current of 0.02 μ amp., and an electron beam less than 3 μm diameter. These analyses only compounded the problem, however, because all showed low iron content (0.3 to 2.5 weight percent), with no apparent correlation between color and iron content. Manganese and cadmium were below the analytical limit (less than 0.1 weight percent) in all areas analyzed.

Electron beam scanning images were then obtained across several areas exhibiting a wide range of color bands in a recognizable pattern, as in Figure 1. The results for Fe $K\alpha$ radiation are shown in Figure 2, covering the same area as Figure 1. For control purposes, the area undergoing scanning was compared with the color banding (visible in transmitted but not in reflected light) by adjusting the intensity of light transmitted through the sample in the probe. With no transmitted light, the scanning beam was visible owing to fluorescence of the sphalerite under electron bombardment. Exact correlation of the areas covered by Figure 1 and 2 was achieved subsequently by photographing the section in transmitted light to reveal the color bands, and then in reflected light. The latter revealed the scanned area as a slight brownish surface stain. As some of the interfaces between bands are not perpendicular to the plane of the section, exact correlation between the color bands *within* the section (Fig. 1) and the *surface* analysis (Fig. 2) is not possible. It is evident, however, that the highest concentrations of iron are in narrow bands, about 8 μm in width, and each makes up only a part of a yellow or tan band. The relatively low-iron background includes bands varying in color over the entire range from colorless to dark reddish brown.

Analyses of specific areas along traverses across iron-rich band D, also using an electron beam less than 3 μm in diameter, yielded maxima of 2.3, 2.7, and 2.9 percent iron. The low-iron bands ranged from minimum of

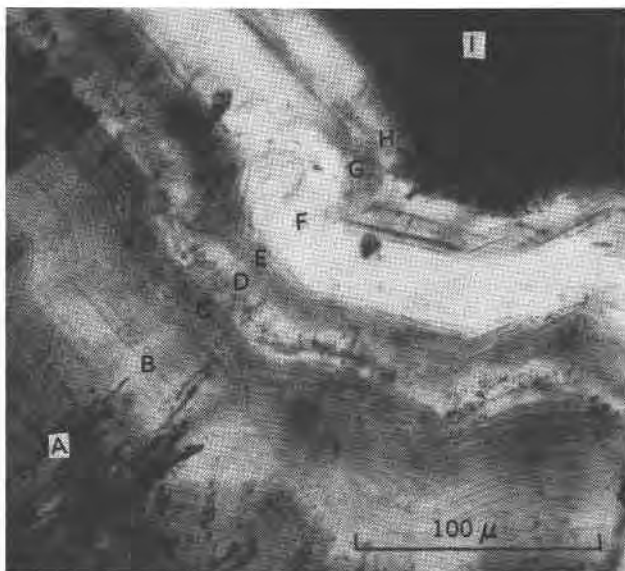


FIG. 1 Photomicrograph of polished plate, 0.09 mm thick, of banded sphalerite sample ER 65-99 in transmitted white light. Individual crystal faces, visible as straight segments, grew from lower left to upper right. The bands vary in color from almost colorless (F) through yellow (H), tan (B, D), orange (E, G) and red (C) to red brown (A). The dark spots in D that look like opaque mineral grains are actually minute fluid inclusions. Zone I is fine grained and almost opaque.

0.2 percent iron (three areas), to a maximum of 1.0 percent (near D), but no correlation of iron content with color could be found. From both sets of results it is obvious that the coloring mechanism in this sphalerite is not simply a function of the total iron content.

Previous chemical analyses of sphalerite from Mississippi Valley-type zinc deposits have shown rather low iron contents for material which appears very dark to black in hand specimen, e.g., from the Central Kentucky mineral district (Jolly and Heyl, 1964). The average of a series of analyses of iron in composite samples of multiply banded but generally dark sphalerite from the Upper Mississippi Valley district (Bradbury, 1961) was higher than that from adjacent earlier and later light colored zones, but still relatively low (0.83 vs 0.36 and 0.31% Fe). Many other elements are present in trace quantities in all natural sphalerites, and although occasional higher concentrations of these are probably responsible for some of the unusual colors, there is no evidence that they generally cause the "normal" range of yellows, oranges, reds, and browns. Yasinskaya (1955) found it impossible to determine the cause of coloration in natural sphalerite from spectral absorption curves.

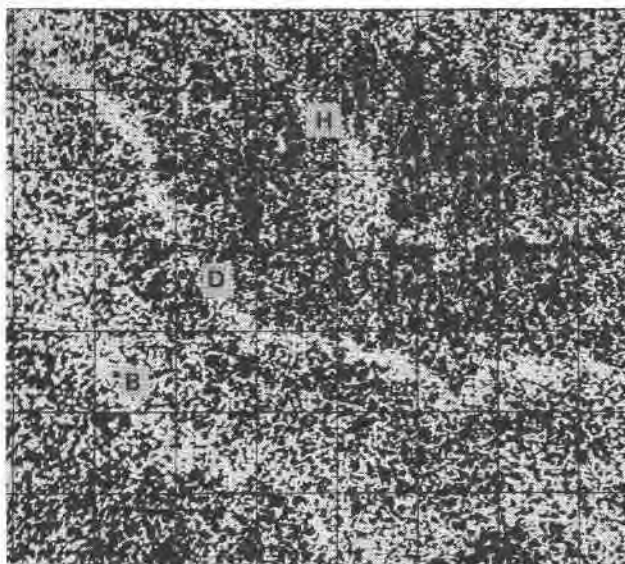


FIG. 2 Electron beam scanning of the identical area of Figure 1, in terms of Fe $K\alpha$ radiation. Parts of bands B, D, and H contain as much as ten times more iron than adjacent background.

INVESTIGATION OF OTHER CAUSES

Organic compounds in very low concentrations can cause intense colors and have been suggested as the cause for some mineral colors such as in certain fluorites, and organic matter of various types is common in the Mississippi Valley-type deposits including Pine Point (Campbell, 1967; Roedder, 1967). Even though the colorant molecules might not actually fit into the dense, closely packed sphalerite structure, they might be anchored by bonding to specific sites on the growing crystal surface and then enclosed. Electronprobe analyses for traces of carbon in such sphalerite would be of dubious value, owing to low sensitivity and the many possibilities of contamination. If the coloring is from organic compounds, it might be expected that heating could cause their breakdown. A portion of the Pine Point sample (including both polished plate and powder) was heated in vacuo, in the sequence: 200°C, 2 days; 325°C, 2 days; 400°C, 2 1/2 hours; 400°C, 3 days, 650°C, 2 hours. The first two heatings made no visible change in color. The third and fourth caused a slight darkening of the powder but no change in the polished plate. The last caused the sample to become black in bulk, but when sectioned, most of the sphalerite bands were almost colorless, with scattered opaque blebs mainly on grain boundaries. In certain bands, a few of the crystals still

had reddish color zones, but adjacent, contemporaneous crystals were completely (and inexplicably) bleached. Gross sample analysis for possible organic colorants would yield ambiguous data at best, because it would be difficult to distinguish between organic materials extracted from the sphalerite structure itself and from minute inclusions of liquid or solid organic compounds trapped in it. However, infrared absorption studies on the residue from a 1:1 HCl dissolution of a 35-gram piece of the same sphalerite specimen showed no organic matter, indicating that HCl-insoluble organic compounds, if present, must be less than perhaps 1 ppm. Some free sulfur was found in this residue, but its origin is uncertain, and it may be an artifact formed during the chemical processing.

In case the coloring might be a result of radiation-induced or radiation-sensitive color centers, another portion of the Pine Point sample (including both polished plate and powder) was irradiated with white x-rays from a platinum tube running at 50 kv., for a total of 15 minutes, and an approximate dosage of 3×10^7 roentgens. No detectable change was observed in the color of the powder or of any band.

Deviation from stoichiometric ZnS composition is also a possible cause of coloration. Thus Scott and Barnes (1967) believe that wurtzite is sulfur-deficient (or zinc-rich) relative to sphalerite, and mention a range of nonstoichiometry of about 1 (atom) percent. Gross variation in electrical and other properties of synthetic ZnS crystals grown in the presence of excess sulfur or excess zinc has been reported (Uchida, 1964; Galperin and Gurvich, 1964; Shalimova and Morozova, 1965; and Gavrillov and Shutilov, 1966), presumably indicating variation in composition, but generally without chemical analyses or statements about color. Nesterov (1961) reported 0.14 to 3.27 atom percent excess sulfur in natural sphalerite. Togari (1961) reported excess sulfur in almost all colored Japanese sphalerites, and states that the color changes, and its intensity increases, both with iron content and with degree of deviation from stoichiometric 1:1 metal:sulfur composition up to an excess of as much as 3 (weight ?) percent sulfur. Confirmation of these analyses would be desirable, as other evidence seems to indicate that ZnS (including both sphalerite and wurtzite) departs only immeasurably from a 1:1 metal:sulfur ratio. Thus Barton and Toulmin (1966, p. 834) found that in the system Fe-Zn-S, mixtures deviating only 0.1 atom percent either side of 50:50 metal:sulfur showed the appropriate extra phase in addition to sphalerite. Single chemical analyses of pure synthetic sphalerite and wurtzite reported by Pankratz and King (1965) yield the formulas $Zn_{50.00}S_{50.21}$ and $Zn_{50.00}S_{49.77}$, respectively, but there is no indication of the accuracy or reproducibility of these determinations. P. B. Barton,

Jr., who made these materials, reports that these two samples, as well as synthetic sphalerite and wurtzite grown in the presence of excess zinc or excess sulfur (Skinner and Barton, 1960) were essentially white powders (oral communication, 1967). An electron beam scan of the area of Figure 1 in terms of S $K\alpha$ radiation showed no recognizable variation in sulfur content, but the sensitivity of this test is not high. Current methods of analysis are probably not adequately sensitive to investigate stoichiometry as a possible cause of coloration in such minutely banded sphalerite, as very minute deviations from stoichiometry may cause intense color, for example in synthetic TiO_2 .

The problem of the cause of the color in any given sphalerite is obviously complex, but may well be of more than just academic interest, in view of the possible light it might shed on the environment and hence causes of ore deposition.

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REFERENCES

- BARTON, P. B., JR., AND PRIESTLEY TOULMIN, III (1966) Phase relations involving sphalerite in the Fe-Zn-S system. *Econ. Geol.*, **61**, 815-849.
- BRADBURY, J. C. (1961) Mineralogy and the question of zoning, northwestern Illinois zinc-lead district. *Econ. Geol.*, **56**, 132-148.
- CAMPBELL, NEIL (1967) Tectonics, reefs and stratiform lead-zinc deposits of the Pine Point area, Canada. In J. S. Brown (ed.) *Genesis of Stratiform Lead-zinc-barite-fluorite Deposits, a Symposium*. Econ. Geol. Publishing Co. Monogr, 3, Blacksburg, Virginia, p. 59-70.
- GALPERIN, E. L. AND A. M. GURVICH (1964) Phase of variable composition in the Zn-S system. *Russ. J. Inorg. Chem.* **9**, (7), 957-958.
- GAVRILOV, V. S., AND V. A. SHUTILOV (1966) Electron paramagnetic resonance in non-stoichiometric single crystals of ZnS. *Sov. Phys. Solid State*, **8**, (2), 501-502.
- JOLLY, J. L., AND A. V. HEYL (1964) Mineral paragenesis and zoning in the Central Kentucky Mineral district. *Econ. Geol.* **59**, 596-624.
- NESTEROVA, YU. S. (1961) Chemical composition of sphalerites. *Tr. Mineral. Muz., Akad. Nauk SSSR*, **1961**, (11), 65-102 in [Russian].
- PALACHE, CHARLES, HARRY BERMAN AND CLIFFORD FRONDEL (1944) *Dana's System of Mineralogy*, 7th ed., 1, John Wiley and Sons, Inc., New York, N. Y.
- PANKRATZ, L. B. AND E. G. KING (1965) High-temperature heat contents and entropies of two zinc sulfides and four solid solutions of zinc and iron sulfides. *U. S. Bur. Minncs, Rep. Invest.* **6708**.
- ROEDDER, EDWIN (1967) Environment of deposition of stratiform (Mississippi Valley type) ore deposits, from studies of fluid inclusions. In J. S. Brown (ed.) *Genesis of stratiform*

- lead-zinc-barite-fluorite deposits, a symposium*, Econ. Geol. Publishing Co. Monograph 3, Blacksburg, Virginia, p. 349-362.
- (1968) Temperature, salinity, and origin of the ore-forming fluids at Pine Point, Northwest Territories, Canada, from fluid inclusion studies. *Econ. Geol.*, **63**, 439-450.
- SCOTT, S. D., AND H. L. BARNES (1967) Nonstoichiometric phase changes in sphalerite and wurtzite. (abstr.) *Can. Mineral.*, **9**, 306.
- SHALIMOVA, K. V., AND N. K. MOROZOVA (1965) Effect of excess zinc on the crystal structure of ZnS. *Sov. Phys.-Crystallog.*, **9**, 471-472.
- SKINNER, B. J., AND P. B. BARTON, JR. (1960) Substitution of O and S in wurtzite and sphalerite. *Amer. Mineral.*, **45**, 612-625.
- SLACK, G. A., F. S. HAM AND R. M. CHRENKO (1966) Optical absorption of tetrahedral Fe^{+2} ($3d^6$) in cubic ZnS, CdTe, and $MgAl_2O_4$. *Phys. Rev.*, **152**, 376.
- S. ROBERTS AND F. S. HAM (1967) Far-infrared optical absorption of Fe^{2+} in ZnS. *Phys. Rev.*, **155**, 170-177.
- TOGARI, KENJI (1961) Mineralogical studies on Japanese sphalerite. *J. Fac. Sci. Hokkaido Univ., Ser. IV*, **10**, 703-733.
- UCHIDA, ICHIZO (1964) Fluorescence of pure zinc sulfide in correlation with deviation from stoichiometry. *J. Phys. Soc. Jap.*, **19**, (5), 670-674.
- YASINSKAYA, A. A. (1955) The color of sphalerite. *Mineral. Sbornik L'vovsk. Geol. Obshch. Lvovsk. Univ.*, **9**, 293-295 (in Russian).

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