A STATISTICAL STUDY OF BRAVOITE ZONING

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ABSTRACT

Bravoite-pyrite grains occur in sulfide ores of the Fredericktown area, Missouri, in the transition facies between the Lamotte sandstone and the Bonneterre dolomite. These ores also include galena, marcasite, siegenite, chalcopyrite and small amounts of sphalerite. Geopetal features displayed by sulfide agglomerations suggest their formation during diagenesis.

A systematic recording of specific characteristics of 4575 grains leads to a classification into eight zoning types. The internal regularities of the grains as well as their relationship to the surroundings are discussed.

Finally, the question of the possible causes for zoning is raised. Although no definite answer to the problem is reached, it is suggested that at the constant temperatures and pressures of formation other factors than these control such crystallization phenomena as zoning. Among the important factors are the surface properties of the crystallizing minerals.

INTRODUCTION

The incidence of bravoite in North America was first established in 1943 in an iron concentrate from the Fredericktown area in the southeastern part of the so-called "Lead Belt" of Missouri (Rasor, 1943). The Fe-Pb-Cu-Ni-Co-Zn-sulfide ores occur here in the shaly and glauconitic zone between the Lamotte sandstone and the Bonneterre dolomite. These upper Cambrian sediments were laid down on an irregular erosion surface of Precambrian granites, and these formations pinch out and lap up against Precambrian hills known as "granite knobs." The Fredericktown mining district is located between two of these knobs and alongside the larger of the two.

The paleogeographic positions of the sulfide-rich sedimentary layers are flat coastal areas of brackish water; glauconite and traces of hydrocarbons are abundant. Several geopetal structures are displayed by the sulfide agglomerations in the shaly sediments (Amstutz, et al., 1961). These features and certain geochemical considerations suggest a diagenetic age for the sulfides (Amstutz, 1959; Amstutz and El Baz, 1962).

The sulfides associated in variable proportions in these sediments are galena, marcasite and pyrite, siegenite and chalcopyrite, and small amounts of sphalerite and wurtzite. They occur in layers, layered disseminations, concretionary agglomerations and sulfide nodules.

SCOPE AND PURPOSE

Bravoite from the Fredericktown area, and that from most localities described in the literature, occurs as intergrowths with alternating zones of pyrite. The bravoite problem consists of the open question whether or not there are gaps in the solid-solution series between the bravoite (NiFeS₄) and pyrite (FeS₂) end members and, if so, under what conditions they occur.

There are two approaches to the solution of this problem—observations, measurements and analyses of natural material, on the one hand, and laboratory syntheses and phase-equilibrium studies on the other. The solution to the problem will probably develop from integration of both methods of investigation.

The present study is based on an analysis of certain observations on natural bravoite, on the assumption that there must be physico-chemical reasons for the features that can be observed in nature. Ultimately, a classification and evaluation of a great number of observations should allow us to draw limiting conclusions about the phase-relationships between two or more components and about other factors controlling the deposition of natural minerals. It will be interesting to compare the present study with the results of experimental work on bravoite done by Kullerud (pers. comm., 1962; Clark and Kullerud, 1960; Ramadan and Kullerud, 1961) and by Springer (pers. comm. D. Schachner, 1962).

LITERATURE REVIEW

Discovery and definitions. In their early investigations, several authors reported Ni and Co-rich varieties of pyrite (e.g. Hunt, 1866; Dana, 1871; Egleston, 1889; Penfield, 1893; Walker, 1894; Doelter and Leitmeier, 1926). Hillebrand (1907) appears to have been the first to describe and analyze bravoite. He found it in sulfide nodules from the vanadium mines of Mina Ragra, Peru, and proposed the name after J. J. Bravo, the Peruvian writer on the vanadium deposits of the same locality.
Strunz (1957) gives the formula \((\text{Ni, Co, Fe})\text{S}_2\) for bravoite, and defines it as occupying a solid-solution field between pyrite \((\text{FeS}_2)\), vaesite \((\text{NiS}_2)\) and catharite \((\text{CoS}_2)\). Ramdohr (1960) uses the same nomenclature, but puts more emphasis on the \(\text{FeS-NiS}_2\) side. He states (p. 749) that Hillebrand may have had material which actually consisted of "an unusual" \((\text{Ni-Fe-rich})\) violarite.

**Bravoite zoning.** Short and Shannon (1930; Short, 1940) recognized and analyzed two different internal zones in bravoite, one yellow and the other violet. According to their data, the violet zones contain more Ni and Co than the yellow ones. Schneiderhöhn and Ramdohr (1931) and Eskola (1946) refer to the remarkable zonal structure displayed by bravoite.

Kalb (1951, 1952) concluded from habit changes of zoned bravoite-pyrite grains from Mechernich that these minerals do not form a complete solid-solution series. The same conclusion was reached by Hegemann (1942).

An environmental mechanism causing zoning is suggested by Edwards (1960). Maucher and Rehwald (1961) picture zoned and unzoned bravoite grains. They describe different geometric forms in which these grains can occur.

**Reported zoned bravoite.** In addition to Rasor (1943), Kidwell (1946) lists bravoite among the minerals of the Fredericktown area. El Baz (1961) and Amstutz et al. (1961) describing zoned bravoite as one of the sulfides in the Cambrian sediments of the Fredericktown mine, attribute to these sulfides a diagenetic origin, based largely on geopetal features (Amstutz, 1959).

Extensive literature on experimental studies of the bravoite-pyrite group minerals, as well as other occurrences of bravoite, is available and will be reviewed at some later time.

**TECHNIQUES**

The methods used so far are microscopic only. X-ray microprobe analyses to obtain quantitative compositional information have been initiated.

A. Reflectivity measurements

Bravoite grains from the Fredericktown ores range from 5 to 200 microns in diameter. Most of them are, however, below 50 microns. Many of the grains show internal zoning, the individual zones averaging about 3 microns in width, so that none of the available photometers could be used. The reflectivity of the zoned portions had to be recorded by visual comparison with associated sulfides and gangue minerals. All variables of microscopic observation were standardized as much as possible, thus narrowing down the error of reflectivity estimates into a \(\pm 2\%\) to \(\pm 3\%\) range, justifying the choice of 10% reflectivity intervals in Figs. 11 and 12. The reflectivity in oil appears to vary from about 20 to about 40. Vachromeiev (1950, 1954) is the only one to give reflectivity values in air. His value of 41% is, of course, only an average.

**Observations and Results**

**Observations**—Bravoite occurrences in the Fredericktown sediments can be classified as follows:

1. Dark, isolated bravoite grains without any zoning or pyrite intergrowth; these are rare, and occasionally form colloform aggregates; they always occur in association with common rock-forming minerals.
2. Minute cores enclosed in bacterial-like disseminated pyrite spheres identical with the so-called bacterial pyrite grains of Mt. Isa (Allen et al., 1912; Love, 1938; Omera, 1961; and others).
3. Bravoite zones in layered intergrowths with pyrite or with transitional compounds and, in rare cases, locked to other sulfides such as siegenite and galena. The present study deals mainly with this property of zonal intergrowth.

The Fredericktown bravoites may be separated into eight zoning types. A total of 4575 zoned grains was recorded, including a few grains of the unzoned end member (type I, below). Figure 1 illustrates the eight essential zoning types arranged according to consecutive geometric differences. On the right side of the triangle are the types with abrupt zone boundaries, whereas on the left side most of the types display gradational zoning. The characteristics of the various types are as follows.

**Zoning type 1:** Grains that belong to this type show no internal zones. They display a slightly brownish tint and, as shown in Fig. 2, are always enclosed in siegenite and/or galena.

**Zoning type 11:** Bravoite grains included under this type also show a slightly brownish tint. They are either free or locked to other sulfides, and in most cases bravoite occupies the center of the grain, as shown in Fig. 3. Pyrite grains with a core of bravoite are usually slightly darker than those free of bravoite. Reflectivity differences in such cases may range from 2 to 4%. In Fig. 4 a bravoite grain with a core of pyrite is shown. It must be mentioned that the bravoite layer closer to the pyrite region is the darkest of all zones. This is not an optical illusion, as the difference in tone remains even when the pyrite zone is covered up.

**Zoning type 111:** Grains of this type are irregular modifica-
A classification of the zoning types of bravoite-pyrite grains from the Federicktown sulfide ores, subdivided into non-gradational or abrupt zoning and gradational or solid solution zoning.

Tions of similar grains of zoning type II. Most of them in this case are not intergrown with any other sulfides, but they always surround larger dolomite and/or quartz grains. They occur with the above-mentioned bacteria-like disseminations. Figure 5 shows an irregular geometric pattern displayed by bravoite. Central holes in the pyrite grains sometimes take the place of bravoite regions.

Zoning type IV: In this type, pyrite grains commonly occur with linear zonal structures. In many cases the lines separating these zones are represented by a hole 2 to 5 microns thick. In other rarer cases, this feature is displayed by bravoite instead of pyrite. Figure 6 shows a zoned bravoite grain where the intermediate zones consist of galena.

Zoning type V: Grains of this type are composed of bravoite in the center and a distinct pyrite rim. The bravoite region is always zoned. Individual zones in this case show clear changes of reflectivity, which are either abrupt or gradational. The zoning in such regions can be simple or intricate. Holes occur in or at the end of the darkest bravoite zones. In some cases they are occupied by galena (or possibly by cattierite, CoS₂). Intergrown grains are common to this type.

Zoning type VI: This type includes grains with linear broad zones of bravoite and pyrite. In many cases the bravoite regions show gradational zoning. Figure 7 is an illustration of the broad zones of bravoite, which show an internal set of
zones. Many of the grains classified under this type display a complex crystal form.

Zoning type VII: This type includes all grains which are formed of bravoite or "nickeliferous pyrite" layers showing definite gradational zoning. Bravoite generations displaying reflectivities from 20 to about 30% usually show a definite gradation from darker to brighter zones. The darkest bravoite generations are found at the rim of the grains, and surrounding holes in them. Parallel holes are also common and occur nearest to or within the darkest portions of the bravoite zones. Some of the holes are filled with galena or perhaps with cattierite. This mineral appears to be later than the dark type of bravoite. In many cases it fills these "crystallographic" holes. Galena is, on the whole, later in the diagenetic paragenesis of these holes. It fills, for example, cracks in bravoite as well as in most other minerals.

Zoning type VIII: Type VIII includes linear as well as massive disseminations of very tiny specks of bravoite and/or "nickeliferous pyrite" peppered over certain portions of pyrite crystals. The borders of the areas containing these disseminations can be either parallel or non-parallel to the boundaries of the enclosing pyrite crystal, as shown in Fig. 8. Bravoite patterns falling under this classification have been observed in sulfide nodules and in concentration products. They do not occur anywhere else in the area. In the sulfide nodules, they follow the contact boundaries of locked pyrite and marcasite, which occupy the central portions of these nodules.
Table 1. Classification of 4575 Bravoite Grains Counted in Fredericktown Ore, Missouri

<table>
<thead>
<tr>
<th>Zoning type</th>
<th>Size (microns)</th>
<th>Crystal habit</th>
<th>Dark zones</th>
<th>Bright zones</th>
<th>Holes</th>
<th>Direct locking</th>
<th>Enclosing rock</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>60% 5-20</td>
<td>simple</td>
<td>dark-brownish</td>
<td>absent</td>
<td>none</td>
<td># sg or py</td>
<td>dolomite or mixed facies</td>
<td>59 gr. 1.3%</td>
</tr>
<tr>
<td></td>
<td>40% 20-50</td>
<td>(Δh = 0)</td>
<td>(ΔR = 0)</td>
<td></td>
<td></td>
<td>(some # gn)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>45% 5-20</td>
<td>simple</td>
<td>dark-brownish</td>
<td>whitish-yellow</td>
<td>10%  with</td>
<td>free</td>
<td>dolomite or mixed facies</td>
<td>1275 gr. 28.0%</td>
</tr>
<tr>
<td></td>
<td>34% 20-50</td>
<td>(Δh = n)</td>
<td>(ΔR = 0)</td>
<td></td>
<td>90%</td>
<td>(or # gn, sg, mr, ct)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>21% 50-80</td>
<td>or = 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>38% 5-20</td>
<td>simple</td>
<td>violet-cream</td>
<td>whitish-yellow</td>
<td>30%</td>
<td>free</td>
<td>sandy dolomite or mixed facies</td>
<td>2272 gr. 50.0%</td>
</tr>
<tr>
<td></td>
<td>56% 20-50</td>
<td>(Δh = n)</td>
<td>(ΔR = 0 or n)</td>
<td></td>
<td>70%</td>
<td>(or # mr, cp, ct)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4% 50-100</td>
<td>or = 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>2% 100-150</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>IV</td>
<td>10% 5-20</td>
<td>simple</td>
<td>absent</td>
<td>whitish-yellow</td>
<td>100%</td>
<td>free</td>
<td>mixed facies or dolomite</td>
<td>380 gr. 10.1%</td>
</tr>
<tr>
<td></td>
<td>75% 20-50</td>
<td>(Δh = 0)</td>
<td></td>
<td></td>
<td></td>
<td>(or # gn, mr)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15% 50-100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>15% 5-20</td>
<td>simple</td>
<td>lavender</td>
<td>whitish-yellow</td>
<td>50%</td>
<td>free</td>
<td>dolomite</td>
<td>490 gr. 8.4%</td>
</tr>
<tr>
<td></td>
<td>26% 20-50</td>
<td>(Δh = 0)</td>
<td>(ΔR = 0 or n)</td>
<td></td>
<td>50%</td>
<td>(or # gn, ct)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38% 50-100</td>
<td>or = 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15% 100-150</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>6% 150-200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>33% 5-20</td>
<td>simple</td>
<td>dark-brownish</td>
<td>absent or whitish-yellow</td>
<td>85%</td>
<td># gn</td>
<td>mixed facies</td>
<td>33 gr. 0.7%</td>
</tr>
<tr>
<td></td>
<td>15% 20-100</td>
<td>(Δh = 0)</td>
<td>(ΔR = n)</td>
<td></td>
<td>15%</td>
<td>(or mr, sg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>32% 100-200</td>
<td>or = 0</td>
<td></td>
<td></td>
<td></td>
<td>some free</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>From 175 to 200</td>
<td>complex</td>
<td>dark-brownish</td>
<td>absent</td>
<td>100%</td>
<td># gn (or mr, sg, ct)</td>
<td>mixed facies</td>
<td>45 gr. 1.0%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Δh = 0)</td>
<td>(ΔR = n)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>200 or more</td>
<td>variable</td>
<td>spotted lavender</td>
<td>whitish-yellow</td>
<td>disseminated</td>
<td># mr only</td>
<td>sulphide nodules</td>
<td>21 gr. 0.5%</td>
</tr>
<tr>
<td></td>
<td>(Δh = 0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Δh = habit changes; ΔR = gradational change in reflectivity; # means “locked to”; sg = siegenite, py = pyrite, mr = marcasite, gn = galena, ct = cattierite, cp = chalcopyrite; gr = grains observed.

Results

Table I represents the results of the statistical recording of the characteristics of the 4575 bravoite grains. The columns of the table list the parameters of importance to this study, and are here briefly discussed.

Grain size: Grains showing simple zoning (types I to IV) are usually small. Most of them fall below the 50 micron limit. However, grains of types V to VIII are large, averaging about 100 or more microns in diameter.

Crystal habit: There is a change of habit (Δh) in types II and III only. Fig. 9 shows various forms that display such a change. Most of the drawings represent bravoite-pyrite grains from the Fredericktown ores. The two typical types in the lower right are drawn after Kalb (1951). Kalb interprets the habit changes as proof of a solid-solution gap. Habit changes are common, even from one generation of pyrite to another, and therefore can hardly be taken as proof of a gap in the bravoite-pyrite solid-solution series.

![Fig. 9. Various habit changes of bravoite-pyrite grains from Fredericktown and as reported from Maubach-Mechernich.](image-url)
Dark zones: The dark zones in the grains show variable characteristics. The darkest bravoite areas are found in the first two types and as rims of type VII grains. Violet-cream and lavender zones are common in larger grains. Usually they show gradational zoning. Gradational changes of reflectivity (BR) can be found mainly in types VI and VII. Two illustrations in Fig. 10 show gradational zoning. The gradational color slopes trend towards the Fe-rich member. Reversed slopes have never been observed with certainty.

Bright zones: When intergrown with bravoite, pyrite layers appear to be darker than those free of bravoite, as mentioned above. This might be due to a certain content of Ni and/or Co. The relationships between dark and bright zones of the bravoite-pyrite grains can be seen on the reflectivity profiles (see four examples in Fig. 10.) The components of all measurements made on the reflectivity profiles are shown in Fig. 11. Separate histograms are drawn here for each zoning type. Proceeding from type I to type IV, there is a tendency of area decrease on the side of bravoite and an increase on the side of pyrite. In types V to VIII a maximum shows up in the area of intermediate reflectivity, i.e., in the range from 20 to 35%.

Figure 12 is a histogram made by compiling data from the eight drawings of Fig. 11. Note that there are three maxima. Also, within the accuracy of the methods used so far, there does not seem to be any compositional gap between the bravoite and the pyrite.

Holes within the grains: The distribution of holes in the grains belonging to the eight zoning types is shown in the 6th column of Table I. These holes are regarded as natural rather than as produced by polishing, for the following reasons:
1. They always run parallel to crystallographic growth planes.
2. They occupy definite positions in certain zones.
3. They generally display smooth linear boundaries.
4. Frequently, their place is taken by galena and possibly by cattierite.
5. Since we are dealing with zonal structures, we may expect periods of interruptions during the growth of the grains.

Direct locking: Bravoite grains of types II, III and IV are mostly not intergrown with other sulfides. Grains of other types are commonly locked to siegenite, galena and marcasite.

Enclosing rock: Relations to the enclosing rock are listed in the 8th column of Table I. Types from I to IV occur in dolomites as well as in rocks of mixed facies, i.e. in finely interbedded shaly, sandy, glauconitic and dolomitic layers,
or variable mixtures of these rocks. Type V occurs in dolomites only. Types VI and VII occur in rocks of mixed facies, and type VIII occurs in sulfide nodules which are common in black shales, and in cavities in the Bonneterre dolomite.

Quantitative counting: With regard to their abundance, grains of types II and III comprise 78% of the total, and types IV and V constitute about 18%. The rest make up the remaining 4%, half of which represents grains of types VI and VII displaying clear gradational zoning, while the other half consists of grains that belong to types I and VIII.

**Possible Causes for Zoning**

The different observations and measurements discussed above illustrate various types of zoning in bravoite. Zoning is produced by compositional differences between successive crystal layers. It appears that conventional theories on zoning factors (Niggli, 1941, p. 608; Eitel, 1954, pp. 83 and 711; Buckley, 1951, p. 403) do not apply in this case. The coexistence of abrupt and gradational zoning, with many subvarieties in the same rock, suggests that factors other than straight pressure-temperature equilibria may play a substantial role. Possible factors that might be responsible for producing zones are these:

a) Possible internal factors
   - Lattice energy.
   - Electric properties of the crystallizing surfaces.
   - Types of lattice defects.
   - Size and polarization effects.
   - Rate of unmixing.
   - Number and rate of nucleation.

b) Possible external factors
   - Excess or deficiency of cations.
   - Partial pressures of anions.
   - pH and Eh values of the environment.
   - Network modifiers (in a surrounding colloidal "matrix.")
Cation fixation and periodic release by organic complexes. Temperature and pressure of the depositing solutions.

It seems likely that a combination of one or more factors, of both internal and external parameters, constitutes the working hypothesis. Among other observations, the presence of both abrupt and gradational zoning within the same small laminae of sediments can hardly be attributed to the same process. Preliminary considerations appear to suggest that in addition to concentration changes, surface properties during crystallization may act as a "screen" responsible for the formation of abrupt zones in one case and gradational in another. These relationships are being investigated.

References


