

ZONAL VARIATION IN BRAVOITE

DAVID J. VAUGHAN, *Department of Geology and Mineralogy,
Parks Road, Oxford, England.*

ABSTRACT

Zoned bravoites from Mill Close Mine, Derbyshire and Maubach, Germany, have been examined to determine variations in color, reflectivity and microhardness in relation to compositional variations. In both localities nickel and cobalt showed a sympathetic relationship in the zones, which was antipathetic to iron. Iron-rich members were found to be harder and have higher reflectivity than those rich in cobalt and nickel, in the former case this could be correlated with cell-size variations. The analyses suggested variable amounts of nonstoichiometry and the reflectivity also decreased with increase in total metals. Variations in the geometry of the zones were also considered. In some cases these are probably related to properties of the crystal surfaces. The zoning is probably the result of very local variations in conditions.

INTRODUCTION

The cubic disulphides pyrite FeS_2 , cattierite CoS_2 , and vaesite NiS_2 , exhibit solid-solutions between all three end-members, the intermediate form $(\text{Fe}, \text{Co}, \text{Ni})\text{S}_2$ being termed "bravoite." The problem of nomenclature arising in an isomorphous series of this type has been best solved by delineation of the end-members as those containing at least 80% of the total metals as either Fe, Co or Ni, leaving all intermediate compositions as bravoites.

Following the first description of bravoite from Peru by Hillebrand (1907), Short and Shannon (1930) described and analysed bravoite which showed two different internal zones. Bannister (1940) gave X-ray data and descriptions of two different bravoites from the Mill Close Mine in Derbyshire. El Baz and Amstutz (1963) made a statistical study of zoning in the Fredericktown, Missouri, bravoites and on the basis of this classified eight zoning types. They discussed the relationships suggested by these types and the factors controlling the formation of the zones. Although data were given by them on the physical properties of the zones, none were given on composition.

In 1964, Springer, Schachner-Korn and Long studied natural bravoite using electron-probe microanalysis in an attempt to discover whether the end-members FeS_2 , CoS_2 , NiS_2 form solid-solutions in all proportions. Dry melt experiments by earlier workers (Lundquist, Clark and Kullerud, Klemm) had shown large areas of immiscibility. However, according to Springer *et al.* (*op. cit.*), nearly all ratios of FeS_2 , CoS_2 and NiS_2 occur in nature and they assume that most of these compositions are metastable. It is believed that natural bravoite is precipitated from aqueous solution, and if it has not been held at high enough temperatures for an adequate

time no reequilibration occurs into the stable phases. These authors succeeded in producing zoned bravoite experimentally under controlled conditions in aqueous solutions.

INVESTIGATION OF MATERIAL

Previous studies, as described above, have dealt with variations in composition or with physical variations with no attempt to correlate the two. This is the object of the present work. Material was examined from the Mill Close Mine, Derbyshire and from Maubach, near Düren in Germany.

Mill Close Mine. Bravoite from Mill Close Mine occurs associated with chalcopyrite, pyrite and gangue minerals and it shows two distinct zones with, in some areas, one or more intermediate zones. The outer zone closely resembles pyrite but is not so highly reflecting; the inner zone is of a pale violet color and the intermediate zones are pale gray-brown. All three phases are nonpleochroic and isotropic.

The identification of this material as bravoite was confirmed by X-ray powder photography. The violet "bravoite" zone has data comparable to bravoite I of Bannister and the pyrite-like "nickelian pyrite" zone has values between those for bravoite I and pyrite. The cell parameters were determined from this data (Table 1).

The Vickers microhardness of the two major zones was determined and also that of the so called "pure pyrite" which was present in the sample. The instrument used for these determinations was the Leitz Durimet microscope with a Vickers diamond indenter, described in greater detail by Young and Millman (1964). The reflectivity of these areas was also measured using the Reichert reflex spectral microphotometer. This instrument is described in detail in a paper by Singh (1965). In all recorded values the reflectivity of the specimen was determined by comparison with a standard of known reflectivity. In this case a specimen of pyrite which had been calibrated by the National Physical Laboratory (NPL, 1915.1) was the standard used. This pyrite was a natural specimen from Elba with cell size determined by X-ray powder photography as 5.404 Å. Precise analyses of pyrite from this locality are quoted by Allen *et al.* (Fe—46.49%, S—53.49%). Its reflectivity directly measured, is 54.2 percent at 589 nm wavelength in air (Table 1).

All of these phases were then examined by electron probe microanalysis using a Cambridge Mk I microanalyser with an excitation voltage of 25kV and carbon-coated specimens. Allowance was made for background radiation and the results corrected for such errors as those caused by absorption, overvoltage, atomic number effect, characteristic fluorescence, background fluorescence etc. X-ray scanning images from the electron probe show the distribution of elements in the area selected for analysis (Fig. 1). Examination of

TABLE 1. REFLECTIVITY, MICROHARDNESS AND COMPOSITION OF MILL CLOSE BRAVOITIC PHASES

Cell-size μ	Phase	Microhardness range HV ₁₀₀ in kg/mm ²	Spectral reflectivity range R% air at 589 nm	Analyses in wt. %			
				Fe	Co	Ni	ΣMe
5.499 (± .001)	Bravoite	1,081 (± 182)	40.2 (± 0.4)	29.9	1.4	16.2	47.5
5.456 (± .008)	Nickelian pyrite	1,682 (± 294)	48.1 (± 0.2)	44.1	0	1.4	45.5
5.417 (± .005)	"Pure" pyrite	1,683 (± 373)	51.4 (± 0.2)	45.9	0	0	46.10 ^a

^a ~0.2% Cu content in this pyrite.

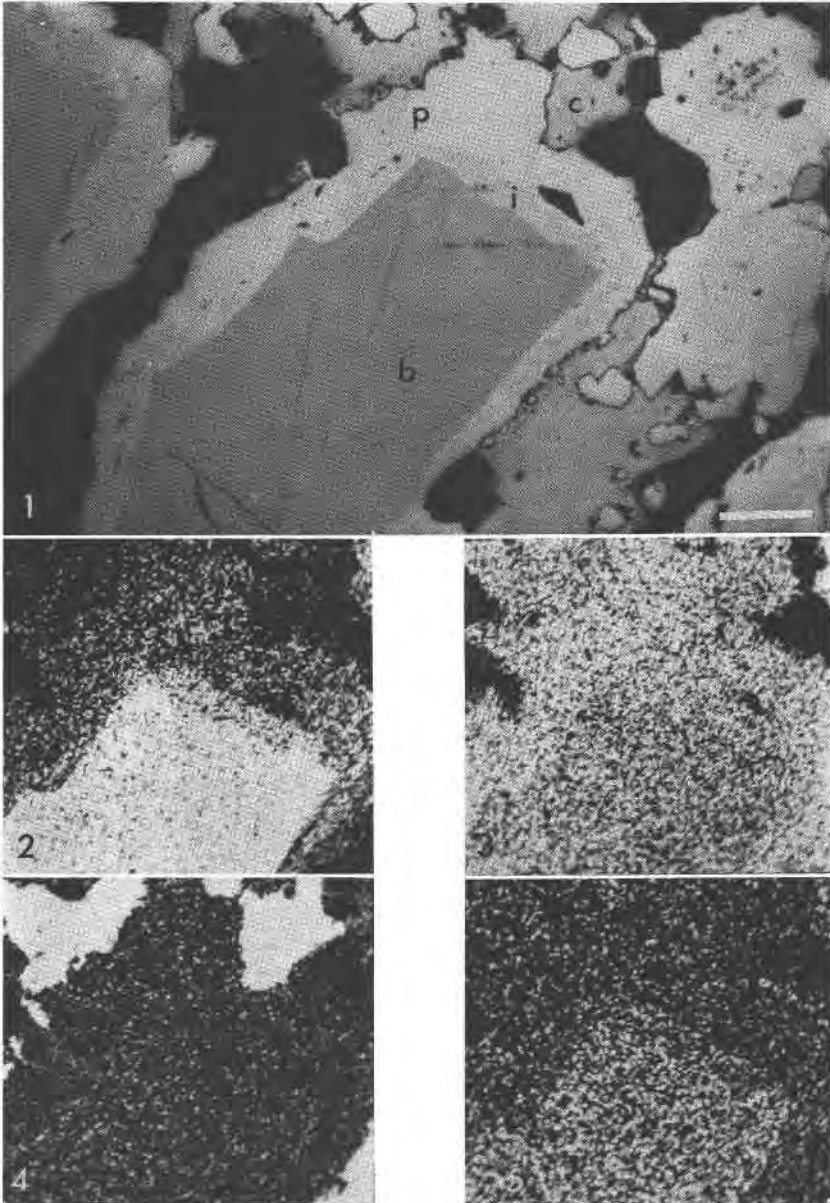


FIG. 1. Zoned bravoite from Mill Close Mine, Derbyshire. (1) Photomicrograph taken in reflected light showing a core of violet bravoite (b) surrounded by nickelian pyrite (p) and between them in some areas a thin band of intermediate composition (i). Chalcopyrite (c) and gangue minerals also appear in this section. X-ray scanning micrographs of this area: (2) NiK α ; (3) FeK α ; (4) CuK α ; (5) CoK α . Length of scale bar = 100 μ m.

these X-ray images shows more subtle zonal variations than were suggested by the quantitative point measurements, including a certain asymmetry of the zoning. Nickel and cobalt were noted to show a sympathetic relationship in the zoning, both antipathetic to iron. These photographs also substantiated the suspected lack of homogeneity in the intermediate phase. Although copper was not present in measurable amounts in the bravoite, the copper distribution photograph showed preferential concentration of trace copper in the cobalt-rich and nickel-rich areas of bravoite.


Maubach. A concentrate from this locality, containing considerable numbers of small (50–100 μm) bravoite crystals with some sphalerite and galena, was examined. Many of the bravoite crystals showed zoning of diverse and beautiful types. The properties of the bravoite in this specimen closely resembled those of Mill Close bravoite, except that at Maubach variation in zonal types (color, reflectivity etc.) was far greater and the zoning itself far more complex. In some cases it also assumed a colloform nature.

The identification of the bravoite was again confirmed by X-ray powder photography.

Owing to the diversity of color and reflectivity exhibited by the various zones it was decided to select one specific grain for intensive study of reflectivity variation with composition. In order to include variation in hardness as a third parameter, use was made of the Nomarski interferometer, since the zones were too narrow for indentation microhardness measurements to be made. Exceptionally, discrete areas of homogeneous unzoned "nickelian pyrite" and "violet bravoite" occurred. Two values for microhardness extremes were obtained from such areas (Table 2).

A photograph taken using the Nomarski interferometer is shown in Figure 2. The grain selected for study is shown in Figure 2; results of reflectivity measurements (at 589 nm

TABLE 2. REFLECTIVITY (AND HARDNESS) VALUES FOR ZONED BRAVOITE CRYSTAL IN RELATION TO COMPOSITION, MAUBACH, GERMANY

Reflectivity (R% air at 589 nm)	Zone number	Composition (in Wt. %)				Trend in Vickers microhardness (VHN ₁₀₀)
		Fe	Co	Ni	Metals ^b Total	
33.7	10 ^a	12.9	14.1	25.5	52.5	"Violet bravoite" VHN ₁₀₀ = 907 ± 194  "Nickelian pyrite" VHN ₁₀₀ = 1,332 ± 203
35.1	12	22.9	3.4	24.2	50.5	
36.8	2	24.7	2.1	22.8	49.6	
	4					
38.4	5	28.5	1.8	19.5	49.8	
	6					
38.8	8	28.4	0	15.1	43.5	
39.7	7	31.4	0.3	17.8	49.5	
40.1	3	28.0	2.0	19.5	49.5	
40.1	1	31.4	0.4	17.7	49.5	
41.4	9	28.7	0.2	19.1	48.0	
48.6	11	34.1	1.2	10.9	46.2	
52.2	13	47.9	0	0.1	48.0	

^a Formula calculated from compositions for this zone (Fe, Co, Ni)_{1.2}S₂.

^b Calculated values of Σ metals for the end members are: FeS₂ 46.6, CoS₂ 47.9, NiS₂ 47.8.

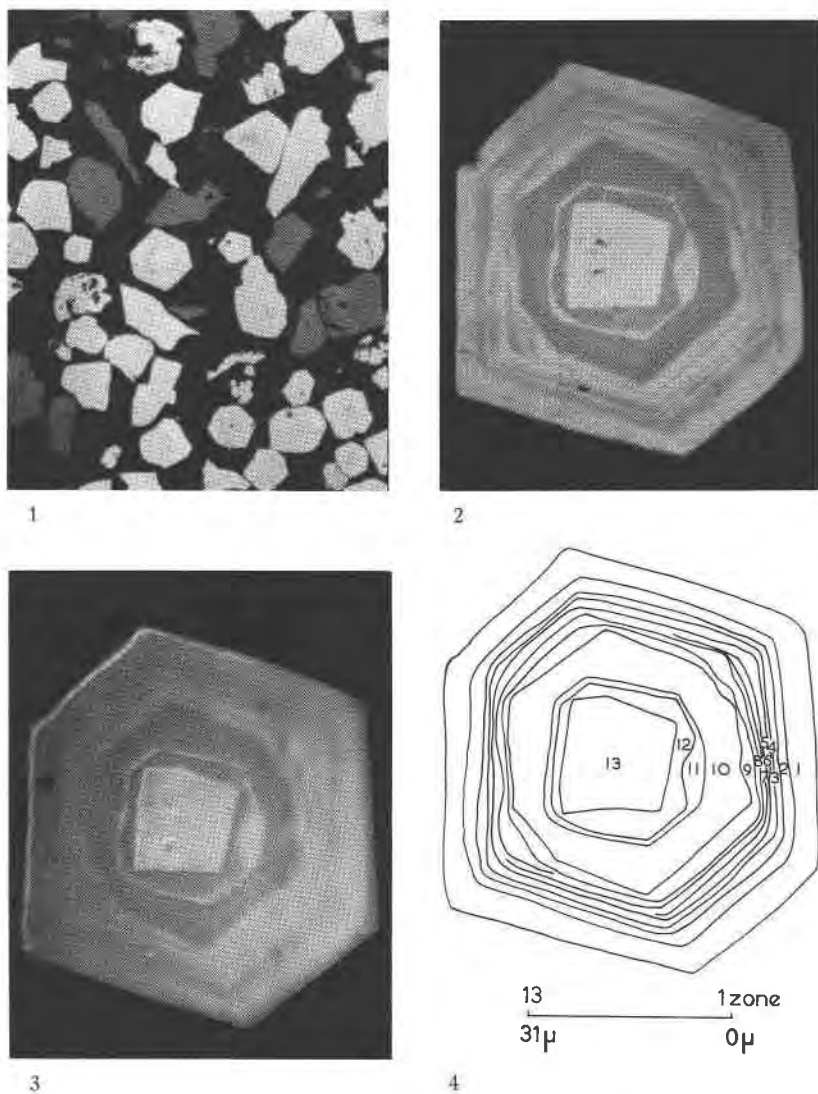


FIG. 2. Zoned bravoite selected for special study, Maubach, Germany. (1) Photomicrograph taken in reflected light showing the selected grain near the centre of the field. (2) The selected grain at higher magnification. (3) The selected grain photographed using the Nomarski interference contrast device. (4) Key to the bravoite zone numbers.

wavelength) are in Figure 3 and Table 2; quantitative probe results are also included in this table and qualitative probe data (X-ray images) are shown in Figure 4. A qualitative assessment was also made of the dispersion in reflectivity of nickel-rich zones in comparison with cobalt-rich zones in different parts of the spectrum. No remarkable differences were noted,

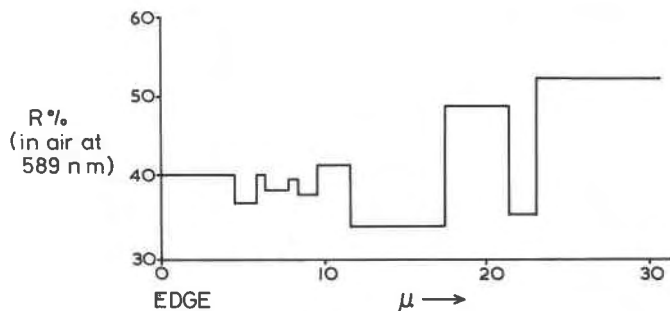


FIG. 3. Variation in reflectivity (at 589 nm in air) with zones, Maubach bravoite.

but maximum separation of the profiles takes place in the range of yellow light near the middle of the spectrum.

CONCLUSIONS

Variation in Vickers microhardness with composition was noted in both localities. The more iron-rich members tend to be harder, and the more nickel and cobalt-rich members are softer. This variation in microhardness can be correlated with the variation in cell-size. The trend in microhardness variation is also seen in the photomicrograph taken using the Nomarski interferometer (Fig. 2). However, in spite of the correlation between hardness and cell-size variation, the cell-size variations themselves are anomalous with reference to other Fe, Co, Ni sulphide groups, showing an increase from Fe→Co→Ni whereas in the others the reverse is the case. This may well be related to the unusual structure of pyrite minerals with "dumbbell shaped" polysulphide (S_2^{2-}) anions and divalent cations in a "sodium chloride type" array. The range in compositions is shown in Figure 5.

The reflectivity variations with composition were well substantiated in both localities. The high value for "nickelian pyrite" at Mill Close can be compared with zone 13 of the Maubach crystal which has a similar composition; similarly the "bravoite" of Mill Close can be compared to zone 3. Even lower reflectivity values are shown by especially cobalt-rich zones at Maubach. The reflectivity decreases with decrease in iron and increase in nickel and cobalt. Another broad trend is that of decreasing reflectivity with increasing content of total metals. The variation in total metals suggests a degree of nonstoichiometry which in zone 10 at Maubach would give a formula of $(Ni, Co, Fe)_{1.2}S_2$ whereas zone 11 would be almost stoichiometric bravoite. As these determinations involved only a single crystal, relative electron-probe microanalysis errors would be minimized.

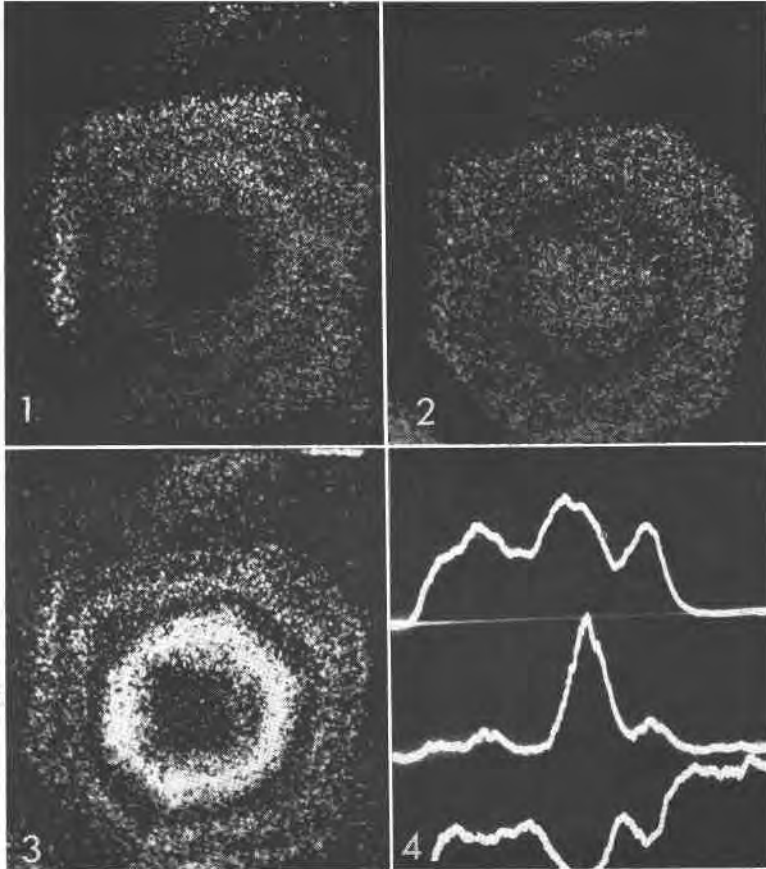


FIG. 4. Zoned bravoite grain selected for special study, Maubach. (1) X-ray scanning micrograph—nickel $K\alpha$. (2) X-ray scanning micrograph—iron $K\alpha$. (3) X-ray scanning micrograph—cobalt $K\alpha$. (4) A trace from the edge (left) to the centre of this crystal showing variation in metal content of $NiK\alpha$ (top), $CoK\alpha$ (middle) and $FeK\alpha$ (bottom).

In the Mill Close and Maubach zones, nickel and cobalt show a sympathetic relationship, antipathetic towards iron and in Mill Close an interesting concentration of copper is seen in the zones enriched in nickel and cobalt.

Interesting aspects of the bravoite study arose from a consideration of the zoning. In the simpler case at Mill Close, the iron-rich bravoite was probably earlier than the cobalt and nickel-rich bravoite, the latter arising through a subsequent change in the composition of the ore forming fluids. Areas where an intermediate zone is found between these two types could be due to either slight variation in the composition of the fluids or a

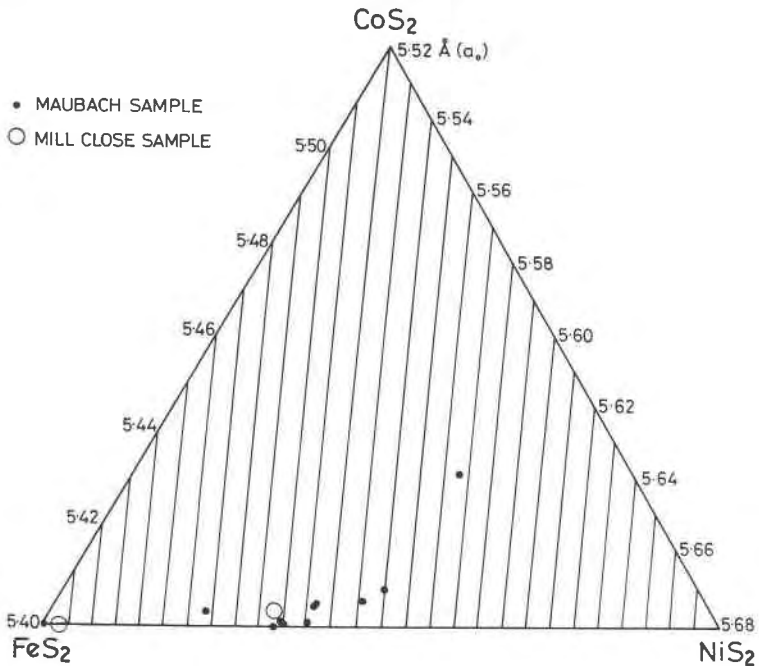


FIG. 5. Compositions of analyzed bravoites.

certain amount of replacement or diffusion of one type into the other. Bannister's distinction (based on Mill Close material) of Bravoite I and Bravoite II which is perpetuated by Berry and Thompson, seems to have been based on a variation of cell size with composition, not a change in structure, and is therefore unjustified.

The Maubach bravoite crystals exhibit a rhythmic zoning which is far more complex. The zones are usually concentric but not always complete. The variation in the geometric shape of successive zones was at first taken to indicate a change of habit with a change of composition. It was concluded, however, that no particular geometry could be ascribed to a certain composition. However, bravoite being of the pyrite class of the cubic system would crystallize in the form of pentagonal dodecahedra (as well as cubes), a figure which can give three- four- five- six- and eight-sided cross-sections. Hence many of the rather complex geometrical relations of successive zones could be explained in terms of sections through zoned pyritohedra. In even more complex zonal types, mixtures occur of normal crystal faces and colloform boundaries between zones and in some crystals a preferential concentration of (Co+Ni)-rich compositions occurred at the edges of crystals, and of iron on the faces. These phenom-

ena are probably related to the surface properties of the crystals. The reported occurrence of zoned and unzoned crystals in the same locality or from the same synthetic experiment suggests that the concentration changes leading to the zoning occurred very locally. Only in some environments is the metastable zoned character preserved.

ACKNOWLEDGMENTS

During the course of the work, which was carried out at Imperial College, London, the author was supported by a grant from the Natural Environment Research Council. The work was carried out under the supervision of Dr. A. P. Millman to whom grateful thanks are recorded. Mr. T. K. Kelly is thanked for advice regarding electron-probe microanalysis and members of the technical staff at Imperial College for preparation of the material.

REFERENCES

- ALLEN, E. T., J. L. CRENSHAW, J. JOHNSTON AND E. S. LARSEN (1912) The mineral sulphides of iron. *Amer. J. Sci., Ser. 4*, **33**, 169.
- BANNISTER F. A. (1940) Bravoite from Mill Close Mine, Derbyshire. *Mineral. Mag.* **25**, 609-614.
- BERRY, L. G., AND R. M. THOMPSON (1962) X-ray powder data for ore minerals. *Geol. Soc. Amer. Mem.* **85**.
- CLARK, L. A., AND G. KULLERUD (1959) The Fe-Ni-S system; The phase relations between pyrite and vaesite in the presence of excess sulphur: *Carnegie Inst. Wash. Year Book* **58**, 142-145.
- EL BAZ, F., AND G. C. AMSTUTZ (1963) A statistical study of bravoite zoning. *Mineral. Soc. Amer. Spec. Pap.* **1**, 190-197.
- HILLEBRAND, W. F. (1907) The vanadium sulphide patronite and its mineral associates from Mina Ragra, Peru. *Amer. J. Sci., Ser. 4*, **24**, 151.
- KLEMM, D. D. (1962) Untersuchungen über die Mischkristallbildung im Dreieck-diagramm $\text{FeS}_2\text{-CoS}_2\text{-NiS}_2$ und ihre Beziehungen zum Aufbau der natürlichen "Bravoite." *Neues Jahrb. Mineral. Monatsch.* **1962**, 76-91.
- LUNDQUIST, D. (1947) X-ray studies on the ternary system Fe-Ni-S. *Arkiv. Kemi. Mineral. Geol.* **24A**, 1-12.
- SHORT, M. N., AND E. V. SHANNON (1930) Violarite and other rare nickel sulphides. *Amer. Mineral.* **15**, 1-22.
- SINGH, D. S. (1965) Measurement of spectral reflectivity with the Reichert microphotometer. *Trans. Inst. Mining Met. (London)*, **74**, (Part 14) 901-916.
- SPRINGER G., SCHACHNER-KORN D., AND J. V. P. LONG (1964) Metastable solid solution relations in the system $\text{FeS}_2\text{-CoS}_2\text{-NiS}_2$. *Econ. Geol.* **59**, 475-491.
- YOUNG, B. B., AND A. P. MILLMAN (1964) Microhardness and deformation characteristics of ore minerals. *Trans. Inst. Mining Met. (London)* **73**, (Part 7) 437-466.

Manuscript received, December 23, 1968; accepted for publication, February 28, 1969.