

*Bravoite from Mill Close mine, Derbyshire.*

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with chemical analysis by M. H. HEY, M.A., D.Sc.

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(With Plate XXVIII.)

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EARLY this year Mr. Arthur Russell brought me a small specimen of ore from Mill Close mine, Wensley, Derbyshire, for identification. An X-ray powder photograph pl. xxviii, fig. 3, showed that the mineral has the pyrite structure with unit-cell edge  $a$  5.49 Å., and a chemical analysis of a small sample of specific gravity 4.82, yielded Ni 16.69, Fe 29.30, S 53.40 % (see table 1). These data identified the specimen as bravoite, a rare mineral new to the British Isles. At a later date Professor W. G. Fearnside interested himself in our preliminary work and kindly provided me with further specimens of bravoite and accessory minerals from the Mill Close mine. These also have been investigated.

Prior to W. F. Hillebrand's analysis in 1907<sup>1</sup> of an iron nickel sulphide from the vanadium ore of Minasragra, Peru, the nickel content of pyrite had never been reported to exceed 6 %. Hillebrand found that the nickel content of the minute grains of sulphide picked from the vanadium ore was 15.7 %. 'Should it seem proper to give it a specific name later, *bravoite* is suggested', after Señor José J. Bravo, the Peruvian writer on the vanadium occurrence at Minasragra. A. F. Buddington<sup>2</sup> has described Alaskan bravoite containing 19.6 %, and P. B. Nye<sup>3</sup> bravoite from Tasmania with 25.42 %, Ni. Only W. F. de Jong and H. W. V. Williams<sup>4</sup> have previously published X-ray data on chemically analysed bravoite.<sup>5</sup> This mineral with unit-cell edge 5.57 Å. comes from Mechnich, Rhenish Prussia, and contains as much as 24.73 % Ni and 3.28 % Co.

As far as I can judge from the descriptions in the literature and the

<sup>1</sup> W. F. Hillebrand, Amer. Journ. Sci., 1907, ser. 4, vol. 24, p. 149.

<sup>2</sup> A. F. Buddington, Econ. Geol., 1924, vol. 19, p. 521. [M.A. 2-447.]

<sup>3</sup> P. B. Nye, Tasmania Geol. Surv. Bull., no. 39, p. 22. [M.A. 4-229.]

<sup>4</sup> W. F. de Jong and H. W. V. Willems, Zeits. Anorg. Chem., 1927, vol. 160, p. 189. [M.A. 3-339.]

<sup>5</sup> G. Kalb and E. Meyer, Centralblatt Min., Abt. A, 1926, p. 26. [M.A. 3-154.]

comparison of a small amount of Hillebrand's original bravoite and a specimen of bravoite from Mechernich in the mineral collections of the British Museum, the bravoite from Mill Close mine, although not abundant, occurs in much finer specimens than elsewhere.

The largest of the specimens presented by Professor Fearnside comes from a cavern below the second toadstone at the 170-fathom level of the northern extension of the Mill Close mine. The bravoite has been deposited on the toadstone (altered at the contact mainly to granular quartz) in radiating nodular layers up to  $1\frac{1}{2}$  inches thick. On a fresh fracture the mineral exhibits a bright silvery lustre with a yellow tint like calaverite. Weathered surfaces are tarnished to a pinkish tint. The crystal terminations on the nodular surface of the bravoite crusts show pyritohedral faces close to (210) rather than octahedral terminations commonly seen on pyrite nodules. The bravoite intergrown with calcite is succeeded by a compact mass of chalcopyrite intergrown with tetrahedrite and a little galena. The chalcopyrite-tetrahedrite ore is enclosed by a vein of large scalenohedral crystals of calcite and nodular pyrite encrusted with fine-grained marcasite. The calcite crystals are filled with marcasite inclusions. Mr. Russell tells me that purple fluor spar also has its place in this mineral sequence. It is to be hoped that in due course Mr. Russell will himself contribute a more satisfactory account of the bravoite occurrence at Mill Close mine.

The material detached from Mr. Russell's specimen for chemical analysis and X-ray work was carefully examined on fractured surfaces and also when coarsely crushed for any inclusions of other minerals. Polished sections prepared by Dr. W. R. Jones in the Royal School of Mines from bravoite specimens collected by himself with Mr. Russell at Mill Close mine fail to show any trace of enclosures and the mineral is completely homogeneous. It is also obvious from the good summation of Dr. Hey's semimicro-analysis in table 1 and the fair agreement of the observed and calculated specific gravity that he analysed uniform material free from admixture with pyrite or chalcopyrite. The analyses of bravoite from other localities including Hillebrand's are also given in table 1 for comparison.

X-ray work on Hillebrand's material from Peru shows that the specks of bravoite enclosed in carbonaceous shale have the pyrite structure. They are not single crystals, however. They give only a weak powder pattern with broad high-order diffractions which show that the mineral is very fine-grained or imperfectly crystallized. The lines approximate in position to those of the Mill Close mineral rather than to those of

pyrite, but an accurate cell-edge measurement is impossible. Both bravoites from Mill Close mine and Mechernich, however, yield sharply defined X-ray photographs and it has been possible to measure the corresponding unit-cell edges accurately.

X-ray and chemical work has also been carried out upon the pyrite from Mill Close mine. A polished specimen of pyrite detached from the large specimen described above

reveals a core of pale-yellow pyrite P (fig. 1) separated from an outer zone of a pinkish-grey mineral (dark-grey on the reproduction) by a thin vein of galena. This vein can be seen immediately to the left of P as a thin white line. The powder photograph of the pinkish-grey zone has been reproduced in pl. xxviii, fig. 4, and shows in contrast to the powder photographs of the single minerals pyrite and bravoite in figs. 2 and 3 double lines instead of single ones. This material consists of ad-

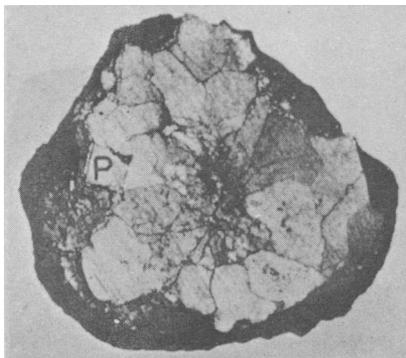


FIG. 1. Polished section of a nodule of coarsely granular pyrite (light-grey) with a veinlet of galena (white, seen to the left of P) surrounded by a minutely granular mixture (dark-grey) of pyrite and bravoite.  $\times 3$ .

mixed granular pyrite and bravoite. The granular bravoite, however, has a spacing of  $5.57 \text{ \AA}$ ., which is close to the value of the cell-edge for bravoite from Mechernich. Dr. Hey finds that the nickel content of this pinkish-grey granular zone is 12%. Assuming that this granular bravoite from Mill Close mine contains as much nickel as the Mechernich material, we have calculated that 43% of the bravoite would be needed in a mixture with ordinary pyrite to yield Dr. Hey's nickel figure. It is apparent that both the lines of each doublet in fig. 4 have about the same intensity, suggesting about equal amounts of bravoite and pyrite.

It is therefore very probable that two types of bravoite exist at Mill Close mine, the more abundant and well-crystallized nodular mineral containing 16.69% Ni (X-ray photograph pl. xxviii, fig. 3) and a much rarer zone of granular material containing about 28% Ni mixed with granular pyrite (X-ray photograph, fig. 4). Dr. Hey cannot detect even a trace of nickel in the pyrite core represented in fig. 1, and so far we have no evidence that any other members of the bravoite-pyrite

series exist at Mill Close mine. This is rather surprising in view of the known existence of nickeliferous pyrite from many localities usually containing not more than 6% Ni. Recently E. Thomson and J. S. Allen<sup>1</sup> have described a nickeliferous pyrite from Sudbury, Ontario, which contains Ni 6.5% and yet when X-rayed gives the normal spacings of common pyrite.

TABLE I. Analyses of bravoite, &amp;c.

	1.	2.	3.	4.	5.	6.	7.	8.
Fe ... ..	29.30	17.08	29.46	25.19	28.4	20.68	38.54	—
Ni ... ..	16.69	24.73	18.23	25.42	19.6	24.81	6.50	45.6
Co ... ..	trace	3.28	trace	0.35	—	—	—	—
S ... ..	53.40	51.15	52.31	49.04	[50.1]	54.51	51.39	54.4
Cell-edge ...	5.49	5.57	5.5 c.	—	—	—	—	5.74 Å.
Nickel atoms per unit cell	1.41	2.42*	1.48	—	—	—	—	4

\* Includes cobalt.

1. Mill Close mine, Derbyshire; on 80 mg. M. H. Hey, total 99.39. Sp. gr. of nodular mass 4.82, calc. 4.80.
2. Mechernich, Rhenish Prussia; also Cu 0.47 and insol. 0.40, total 97.11 (Kalb and Meyer, loc. cit.).
3. Minasragra, Peru; original analysis by Hillebrand recalculated to exclude  $V_2O_5$  4.31.
4. Main creek, Adamsfield district, Tasmania; recalculated omitting 7.80 insol. found by Nye (loc. cit.).
5. Spirit Mountain deposits, Canyon Creek valley, Lower Copper river valley, Alaska. Sulphur by difference; the recalculation made by Overbeck adds together the figures obtained by W. T. Schaller for material soluble and insoluble in HCl. Bull. U.S. Geol. Surv., 1920, no. 712, p. 97.
6. Same locality as 5. Analysed by A. H. Phillips (in Buddington, loc. cit., p. 525) and recalculated to exclude impurities.
7. Nickeliferous pyrite from the Denison mine, Sudbury district, Ontario; insol. 3.80, total 100.23. Thomson and Allen, loc. cit., p. 137.
8. Artificial nickel disulphide prepared by de Jong and Willems.

Fig. 5 shows the unit-cell nickel-content of bravoite specimens and also of artificial nickel disulphide (prepared and studied by de Jong and Willems, loc. cit., p. 185) plotted against the unit-cell edge. It is apparent from the direction of the curve that can be drawn through the known points that pyrite containing  $6\frac{1}{2}\%$  Ni, i.e.  $\frac{1}{2}$  atom per unit cell, should have a spacing of 5.42 Å. Thomson and Allen have either failed to detect the difference between this value and that of ordinary pyrite 5.405 Å., or there is a discontinuity in the series of known mixed crystals  $FeS_2-(Fe,Ni)S_2$ . Judging from the account of their optical data there

<sup>1</sup> E. Thomson and J. S. Allen, Univ. Toronto Studies, Geol. Ser., 1939, no. 42, p. 135. [M:A. 7-510.]

can be little chance of their results corresponding to a mixture of common pyrite and bravoite.

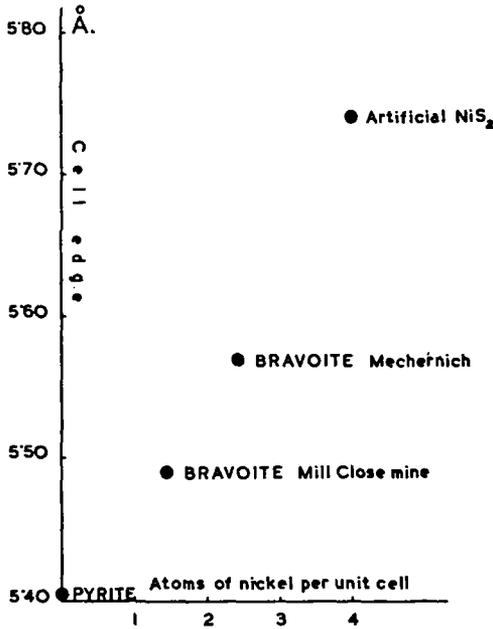


FIG. 5. Cell-edge dimensions and nickel-content of bravoite.

So far no bravoite has been described with a nickel-content exceeding about 25 %, and the suggestion that violarite<sup>1</sup> approaches nickel disulphide in composition and may therefore be a member of the pyrite-bravoite series can only be accepted if X-ray work yet to be carried out shows that the mineral has the pyrite crystal-structure and does not belong to the spinel type. Neither has a bravoite yet been described with nickel-content between 6.50 and 16.69 %, so that a discontinuity in the pyrite-bravoite series may exist in this region. The problem may be more of paragenetic than chemical interest. There is need for syntheses of artificial bravoites and pyrites with various nickel-contents up to pure nickel sulphide. It will be imperative not only to carry out X-ray measurements on analysed specimens but to prepare samples suitable for the preparation of polished sections to test for homogeneity.

<sup>1</sup> W. Lindgren and W. M. Davy, *Econ. Geol.*, 1924, vol. 19, p. 309. [M.A. 2-338.]  
M. N. Short and E. V. Shannon, *Amer. Min.*, 1930, vol. 15, p. 12. [M.A. 4-335.]

In this way it should be possible not only to check apparent discontinuities in the naturally occurring pyrite-bravoite series but also to decide whether the unit-cell edge of pyrite remains the same up to a nickel-content of  $6\frac{1}{2}\%$ .

#### EXPLANATION OF PLATE XXVIII.

X-ray powder photographs of pyrite and bravoite from Mill Close mine, Derbyshire, taken with unfiltered iron radiation  $\lambda = 1.934 \text{ \AA.}$ , and with the same cylindrical camera diameter 6.04 cm. A length of 15 cm. on all the original films is equivalent to 10 cm. on the reproduced figures.

FIG. 2. Pyrite, a standard photograph. The photograph of the pyrite from the nodule, fig. 1, was taken with a rotating fragment and is not so suitable for reproduction but agrees precisely with the standard.

FIG. 3. Bravoite containing 16.69% Ni.

FIG. 4. Granular mixture of about equal proportions of bravoite (about 28% Ni) and ordinary pyrite.

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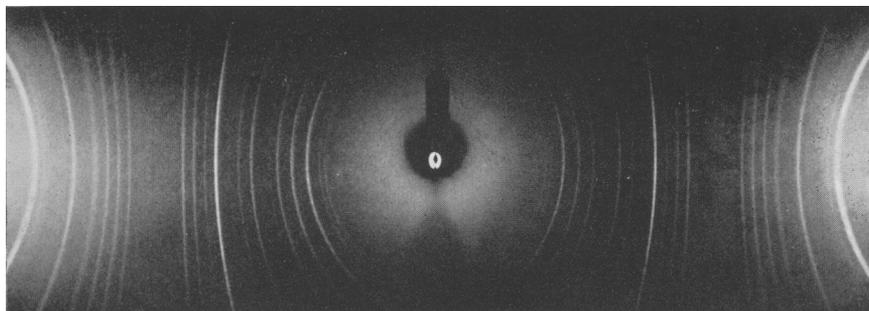


FIG. 2

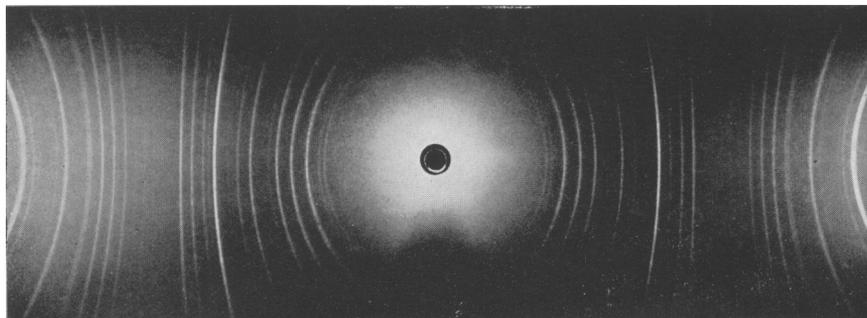


FIG. 3

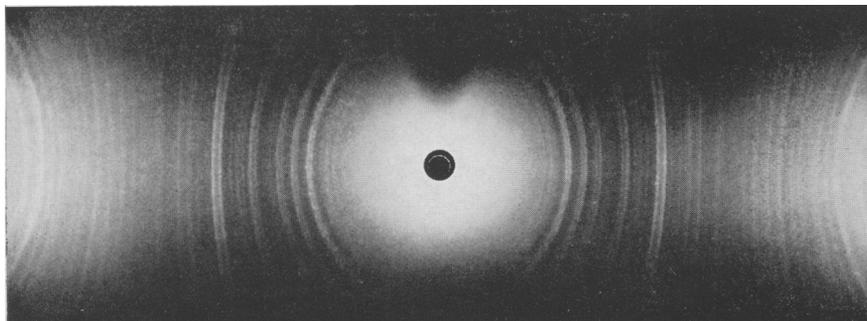


FIG. 4

F. A. BANNISTER : X-RAY PHOTOGRAPHS OF BRAVOITE AND PYRITE.