

CHARACTERISTIC OPTICAL DATA FOR COOPERITE, BRAGGITE AND VYSOTSKITE

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ABSTRACT

Reflectance spectra for cooperite PtS and braggite (Pt,Pd)S from the type locality at Potgietersrus, South Africa, were measured between 400 and 700 nm. These spectra, and qualitative descriptions of the grains, complete the characterization of the minerals made in 1932 by Bannister & Hey. The mineral association, optical properties and reflectance spectra of cooperite, braggite and vysotskite PdS from the Minneapolis Adit area of the Stillwater complex, Montana, are also described. The data for cooperite and braggite are compared with those for the type material; the data for vysotskite may, in the absence of appropriate data for the type material from Noril'sk, U.S.S.R., be considered characteristic for the mineral. Electron-microprobe data are provided for all of the grains measured in the reflectance study, and VHN for most of them. The extraordinary confusion that has surrounded the quantitative data and qualitative descriptions of these minerals is described. Reflectance spectra and color values demonstrate the falsehood of the long-standing belief that cooperite resembles pyrrhotine. The original descriptions (Schneiderhöhn 1929a,b) were not of cooperite but probably of the then unknown mineral braggite. This error was compounded when the reflectance 'spectrum' of pyrrhotine, from the supposedly cooperite-bearing concentrates, was mistaken for that of cooperite.

Keywords: cooperite, braggite-vysotskite, reflectance spectra, color values, optical characteristics, VHN, compositional range, Potgietersrus, Stillwater complex, platinum-group minerals.

SOMMAIRE

On a mesuré, entre 400 et 700 nm, le spectre de réflectance de la cooperite PtS et de la braggite (Pt,Pd)S de la localité type, Potgietersrus (Afrique du Sud). Ces spectres, ainsi que la description qualitative des grains, complètent la caractérisation des deux espèces amorcée en 1932 par Bannister et Hey. On décrit aussi l'association minéralogique, les propriétés optiques et les spectres de réflectance de cooperite, braggite et vysotskite PdS du secteur dit Minneapolis Adit du complexe de Stillwater (Montana). Les données sur la cooperite et la braggite sont comparées à celles des échantillons types; vu le manque de données pertinentes sur le matériau type de Noril'sk (U.R.S.S.), les observations ici consignées peuvent servir à caractériser la vysotskite. On présente les résultats d'analyses à la microsonde électronique pour tous les grains dont on a déterminé la réflectance, et la dureté VHN pour la plupart d'entre eux. On décrit la confusion extraordinaire qui émane des descriptions, tant qualitatives que quantitatives, de ces espèces. Les spectres de réflectance et l'évaluation des couleurs

montrent que cooperite et pyrrhotine ne se ressemblent pas. Les descriptions originelles de Schneiderhöhn (1929a, b) portaient non pas sur la cooperite, mais probablement sur la braggite, encore inconnue à l'époque. L'erreur s'est aggravée quand le "spectre" de réflectance de la pyrrhotine, extraite de concentrés censés contenir de la cooperite, fut attribué à la cooperite.

(Traduit par la Rédaction)

Mots-clés: cooperite, braggite-vysotskite, spectre de réflectance, évaluation des couleurs, caractéristiques optiques, VHN, intervalle de composition, Potgietersrus, complexe de Stillwater, minéraux du groupe du platine.

INTRODUCTION

Cooperite, braggite and vysotskite are important sources of platinum and palladium in many of the world's largest deposits of platinum-group minerals. It is thus surprising that their optical characteristics, particularly those of cooperite and braggite, have remained ill-defined since their discovery. At present, their identification with the microscope is uncertain, owing to erroneous and conflicting descriptive and quantitative data in the literature.

We first encountered this problem in 1980 when examining samples from the Minneapolis Adit area of the Howland Reef (Bow *et al.* 1982), Stillwater Valley, Montana. Here, unusually, all three minerals occur in close association but, during our initial investigation, we were unable to identify them without the aid of the electron microprobe. Indeed, at first, we believed cooperite to be a new mineral and braggite to be cooperite. Closer examination of the literature revealed that the earliest descriptions of *cooperite* (Schneiderhöhn 1929a,b) were on material of dubious authenticity. These descriptions, and in particular a suggested similarity to pyrrhotine, are completely misleading. Unfortunately, when cooperite and braggite were characterized (Bannister & Hey 1932), their optical characteristics were not determined. It remained for Edwards *et al.* (1942) briefly to describe the qualitative optical properties of a type specimen of braggite. The erroneous descriptions and reflectance data for cooperite (Schneiderhöhn 1929a, b, Schneiderhöhn & Ramdohr 1931, Frick 1930) and the incomplete data for braggite hindered the identification of the minerals by ore microscopy. Thus, although confirmation of their

identity was certain by X-ray diffraction and chemical analysis, the problem remained of identifying the right mineral in the first instance. As a result, until quite recently cooperite was regarded as a 'rarity' (Ramdohr 1980), and braggite was reported to be a 'very rare mineral' (Picot & Johan 1982).

Attention was first drawn to the 'conflicting and overlapping data' for braggite and cooperite by Leonard *et al.* (1969), who also noted that adequate quantitative data were lacking. The situation improved somewhat in the 1970s, when electron microprobes and microscope-photometers capable of measurements of spectral reflectance became more widely available. The first spectral-reflectance data, though restricted to four wavelengths that correspond to the perceived brightness and color of these minerals, were those of Cabri (1972) for braggite and Schweltnus *et al.* (1976) for cooperite and braggite. More complete spectra and descriptive information were reported by Picot & Johan (1977). Unfortunately, the spectra and descriptions for cooperite are transposed in their book and appear as for braggite (this mistake occurred at an editorial stage; Picot & Johan, pers. comm.). Their description of cooperite is also in error; it corresponds neither to cooperite nor to braggite. In 1981, Cabri reviewed the situation and concluded that the reflectance spectra of braggite needed confirmation, that those of cooperite needed redetermination, and that more work was required on the qualitative optical properties of vysotskite. The latter, despite the uncertain properties of braggite, had been characterized with minimal optical data in 1962 by Genkin & Zvyagintsev. In 1982, Picot & Johan published characteristic reflectance spectra and descriptive data for cooperite. Their *R* spectra for braggite are also characteristic, but their description of this mineral does not correspond to these spectra; in fact, it is almost identical to the description of Schneiderhöhn's *cooperite* that had previously been reiterated in various forms in the diagnostic texts of Farnham (1931), Ramdohr (1950 and all later editions), Schouten (1962) and Uytendogaardt & Burke (1971). Correct reflectance values determined at the four wavelengths recommended by the Commission on Ore Microscopy (COM) for braggite and cooperite from the Rustenburg mine, South Africa, were reported, together with brief descriptive notes, by Kingston & El-Dosuky (1982). These authors go some way toward resolving the confusion concerning the two minerals; however, their assertion that the incorrect description of the color of cooperite (that had become entrenched in the literature) is more applicable to braggite has introduced a new source of confusion. Further, their conclusion that the original source of the mistaken identity of cooperite arose from a description of braggite-cooperite intergrowths is one that we cannot support.

Clearly, a thorough re-investigation of all three minerals using procedures recommended by the COM was overdue. In particular, the confusion surrounding the color and brightness of the minerals required measurement of the dispersion of their reflectance throughout the visible spectrum and calculation from these spectra of unambiguous color-values. More than this, we considered it essential to relate these measurements to the composition of each grain that was measured and to obtain X-ray data for selected grains. We were fortunate in having at our disposal the type specimens of cooperite and braggite of Bannister & Hey (1932), as well as the intergrown grains of cooperite, braggite and vysotskite from the Minneapolis Adit. The latter, fortuitously, occur in a matrix consisting predominantly of pyrrhotine, pentlandite and pyrite; hence direct comparison of cooperite and pyrrhotine was possible. What follows, therefore, may be regarded as the completion of the characterization of braggite and cooperite, with additional and more complete data for vysotskite.

In addition to measuring the reflectance spectra, calculating color values, and measuring micro-indentation hardness (VHN) values, we examined in detail the apparent color, brightness, bireflectance and reflectance pleochroism of the minerals in plane-polarized light, and their rotation tints between crossed polars. This was done not only to complete their characterization but to determine whether the qualitative properties alone were sufficiently distinctive to be used as a means of identification.

EXPERIMENTAL PROCEDURE

All of the Pt-Pd-Ni-S-bearing samples from the Stillwater Valley examined (fourteen polished mounts, ten polished grain-mounts, and five polished thin sections) came from an unusually coarse-grained pegmatitic gabbro from the first cross-cut of the Minneapolis Adit. These samples were selected from a suite of specimens BM 1981, 134. The equipment and polishing procedure used for the mounts and grain mounts were described in Criddle & Stanley (1979). Comminution, separation and mounting procedures for the grain mounts are those described by Cabri & Laflamme (1976). The same polishing procedures were applied to the grain mounts of the type specimens from Potgietersrus as were used on the Stillwater samples.

The equipment and procedures used for measuring the reflectance of all the samples are as described in the Appendix to Cabri *et al.* (1981), except that $\times 16$ air and oil objectives, adjusted to provide effective numerical apertures of 0.2, were used. Micro-indentation hardness measurements were made at 100-gram force with a Leitz Miniload 2 hardness tester equipped with a Vickers indenter. The areas

selected for both sets of measurements were first checked for compositional homogeneity with the electron microprobe, a Cambridge Instruments Microscan IX, operated with an accelerating voltage of 20 kV and a beam current of 2.50×10^{-8} A on the Faraday cage. The pure elements Pt, Pd and Ni, as well as FeS, were used as standards. The results were corrected using the Cambridge Instruments ZAF programme V02B.

For the qualitative examination of the optical properties of the minerals we used a Leitz Ortholux Pol-BK microscope as well as the Zeiss MPM03 microscope-photometer. It was apparent that even when using the same lightbulbs, adjusted to the same voltage, and hence the same nominal color-temperature of ca. 3100 K, the relative brightness and the intensity of the rotation tints were greater with the Leitz than with the Zeiss equipment. This we ascribe to the longer light-path of the microscope-photometer (it includes a modulator that extends the light-path by some 16 cm). We recorded separately with both instruments our observations concerning the appearance of the minerals in plane-polarized light and the sequence of rotation tints between crossed polars and with the analyzer uncrossed by 3°. Allowing for slight differences in color percep-

tion and vocabulary between the two observers, the results were very consistent.

Initially, we were under the impression that the rotation tints differed between the two microscopes but, on checking our notes, it became clear that the difference was not in the color but in the relative intensity, or brightness. This phenomenon was most marked in the polymineralic Stillwater samples, where the eye was further confused by the rotation tints of the associated minerals. As a result, in the subjective terminology applied to the strength of anisotropy and rotation tints (Galopin & Henry 1972, p. 243), the anisotropy of the same mineral could be described, depending on orientation and association, as weak, distinct, or strong. We emphasize this point because rotation tints have recently been recommended as one of the most important diagnostic properties for ore minerals (Picot & Johan 1982).

OPTICAL PROPERTIES

Qualitative optical data for the type specimens from Potgietersrus

Five discrete and monomineralic grains of

TABLE 1. ANISOTROPY AND ROTATION TINTS

| CROSSED POLARS: | | COOPERITE | BRAGGITE |
|----------------------------|---|---|---|
| AIR | Potgietersrus | s. light greenish grey to mid-grey to yellowish brown | d. purplish grey to brownish grey |
| | Stillwater | s. greenish grey to bright whitish yellow to brown-grey to bright and pale brown | d. bluish/purplish grey to pinkish brown |
| OIL | Potgietersrus | s. greenish grey to bright whitish yellow to brown-grey to bright and pale brown | w/d. subdued purplish grey to mid-grey to slightly brownish dark grey |
| | Stillwater | s. greenish grey to bright whitish yellow to brown-grey to bright and pale brown | w/d. subdued purplish grey to pinkish brown |
| ANALYSER UN-CROSSED BY 3°: | | | |
| AIR | Potgietersrus | pale and metallic greenish white to slate or bluish grey | pale and bright purplish/bluish grey to pale and bright brownish grey |
| | Stillwater | pale greenish grey to brilliant, slightly creamy, white to mid-grey | slate or bluish grey to pale yellowish brown |
| OIL | Potgietersrus | pale yellowish or greenish brown to brilliant, slightly creamy, white to light pinkish grey to steel-grey | strong purplish/bluish grey to mid-grey to slightly reddish mid-grey to yellowish light grey to brownish mid-grey |
| | Stillwater | pale greenish grey to brilliant, whitish yellow to light pinkish grey to steel-grey to yellowish brown | slate or bluish mid-grey to slightly reddish mid-grey to light yellowish grey |
| CROSSED POLARS: | | VYSOTSKITE | PYRRHOTINE |
| AIR | w. dark brown to dark blue-grey | s. light greenish grey to mid-grey to dark grey | |
| OIL | v/w. very subdued dark brown to dark blue-grey | s. light greenish grey/white to mid-grey to purplish mid-grey to mauve to reddish brown | |
| ANALYSER UN-CROSSED BY 3°: | | | |
| AIR | where twinned, bright reddish/purplish grey to pale light blue to fawn. More sombre where untwinned | slightly greenish light grey to greenish mid-grey to brownish dark grey | |
| OIL | the same tints as in air but slightly darker | bright light grey to purplish pale grey to mid-grey to reddish brown to rich reddish brown | |

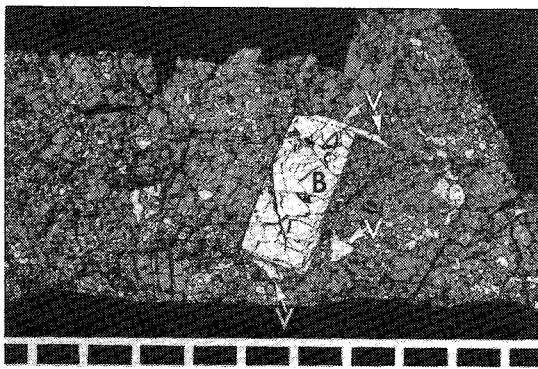


FIG. 1. Photomacrograph of a polished section from Stillwater. The braggite B prism is characteristically fractured. At both ends of the prism and to one side are compositionally homogeneous areas of vysotskite V. A color filter was used to exaggerate the difference between the groundmass (dark grey) of yellower pyrrhotine, pentlandite and chalcopyrite, and the whiter Pt, Pd sulfides. As a result, pyrite dispersed throughout the groundmass also appears white. The bar scale is in millimetres.

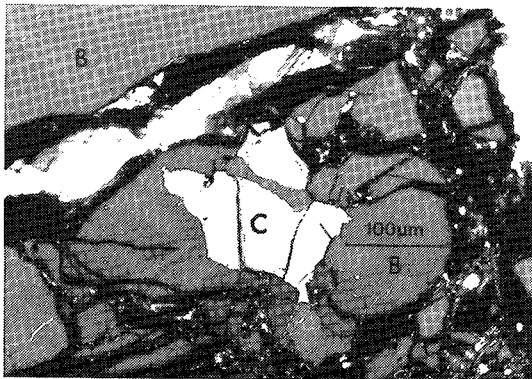


FIG. 2. Oil-immersion photomicrograph of cooperite C showing simple twinning and strong anisotropy included in darker, polysynthetically twinned braggite B. Polars slightly uncrossed.

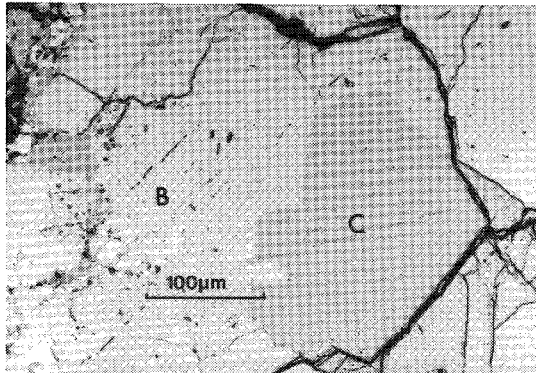


FIG. 3. Oil-immersion photomicrograph of cooperite C and braggite B. The section is oriented for R_0 cooperite. Plane-polarized light.

cooperite from BM 1932, 1301 were polished in mount E.700. In plane section all are anhedral, with angular outlines and curved and angular embayments. They vary in size from 1 to 1.5 mm. In plane-polarized light in air they appear pleochroic from white or creamy white to bluish white. They do not appear to be bireflectant (*cf.* quantitative properties). In immersion oil, under otherwise the same conditions, they are *apparently* pleochroic and bireflectant from white (higher R) to bluish white. Between crossed polars their anisotropy in both media is strong. Their rotation tints between crossed and slightly uncrossed polars are summarized in Table 1. None of the grains is twinned.

Three roughly equant grains of *braggite* from BM 1932, 1304 were polished in E.701. They are all slightly less than 1 mm across and have rounded outlines (one has small angular embayments). In plane-polarized light, in air and in oil, braggite is white and very slightly bireflectant; it lacks reflectance pleochroism. Its moderately high reflectance is similar to that of *cooperite*. Between crossed polars, its anisotropy is distinct in air and is reduced, to weak to distinct, in oil (Table 1). Like *cooperite*, all of the grains are untwinned.

Thus, the features that enable the two minerals to be distinguished where isolated in separate grain-mounts, are 1) the absence in braggite of the apparent reflectance-pleochroism of *cooperite* and 2) the much more strongly anisotropic character of *cooperite*. In our grain mounts we did not have any pyrrhotine for comparison but this was remedied in the Stillwater samples.

Qualitative optical data for the minerals from Stillwater

The Stillwater samples offer an ideal opportunity to compare the optical properties of the three Pt-Pd-Ni-S minerals with pyrrhotine and with many of the other minerals with which they are commonly associated. Details of the mineral association and paragenesis of the Minneapolis Adit samples are to be reported separately; however, insofar as they have a bearing on the diagnostic properties of the three PGM, the association will be outlined here.

The three sulfides occur in a pegmatitic gabbro in association with: major pentlandite, pyrrhotine, chalcopyrite and pyrite, minor cubanite and nickelian mackinawite, and accessory gold and the PGM, *e.g.*, moncheite, isoferroplatinum, kotulskite, keithconite, palladian tulameenite and a number of other unnamed minerals. Unusually large (by PGM standards) prismatic crystals of braggite, up to 8 mm long (Fig. 1), are not uncommon. All of them are fractured. They are compositionally homogeneous, except that a distinctive rim of slightly more highly reflecting vysotskite invariably occurs at the 'ends'

of the prisms. In addition, as is shown in Figure 1, vysotskite may be separated from, but is closely associated with, the braggite prisms. Cooperite was not found in association with these euhedra. It occurs as subhedral to anhedral inclusions, from 30 to 250 μm in size (Figs. 2,3), within large (up to 15 mm) irregular areas of braggite (Fig. 4). Vysotskite, which was not found in direct contact with cooperite, is invariably present as a selvage to braggite at its boundaries with the Fe, Ni and Cu sulfides (Fig. 5). Texturally, there is abundant evidence that vysotskite was the last of the three PG sulfides to form and that it replaced braggite: it forms thin selvages to fractures in braggite, 'healed' fractures, and finger-like projections, or penetration textures (Fig. 6). In this latter form, the vysotskite changes in composition, moving toward that of braggite the further it penetrates into the braggite from its boundaries with the other sulfides. In some instances the change appears to have been sequential and is detectable optically as a subtly stepped reduction in reflectance and intensity of rotation tints. Compositionally homogeneous vysotskite occurs as small and irregular areas near the larger areas of braggite. Here, and in the thicker selvages to braggite (Fig. 5), guided penetration and vermiform textures are common. The dominant interpenetrant minerals are pyrrhotine, pentlandite and chalcopyrite, although gold and the Pt-Pd tellurides are not uncommon in these veinlets, which are usually compound.

Our examination of the qualitative optical behavior of the three minerals from Stillwater illustrates how the assessment of brightness and the relative intensities of color and rotation tints of one mineral could be influenced by the presence of other minerals in the same field.

In plane-polarized light, *cooperite* from Stillwater, unlike that from Potgietersrus, is bireflectant and *apparently* pleochroic from white (higher R) to bluish white in both media. Braggite, which surrounds it, appears slightly lower reflecting, slightly greenish white against white cooperite, and slightly higher reflecting and pinkish white against the bluish white cooperite. The higher bireflectance and more pronounced pleochroism of the Stillwater samples are, however, more apparent than real, as will be demonstrated in the description of quantitative properties. In comparison with cooperite, pyrrhotine is significantly less bright and pale brown to pale milky brown in color. Between crossed polars, the anisotropy of cooperite is strong, apparently stronger than that of the type specimens, and as strong, or stronger than that of pyrrhotine. The rotation tints of cooperite from both localities are virtually identical and differ from those of pyrrhotine, a difference that is even more marked with the analyzer uncrossed by 3° (Table 1). Simple twinning was observed in only one small grain of cooperite (Fig.

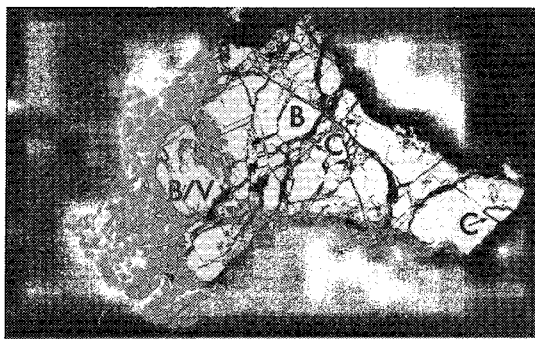


FIG. 4. Photomicrograph of an irregular area of intergrown braggite, vysotskite and cooperite from Stillwater. The central and smaller grain of cooperite is illustrated in Figure 2. The bar scale is in millimetres.

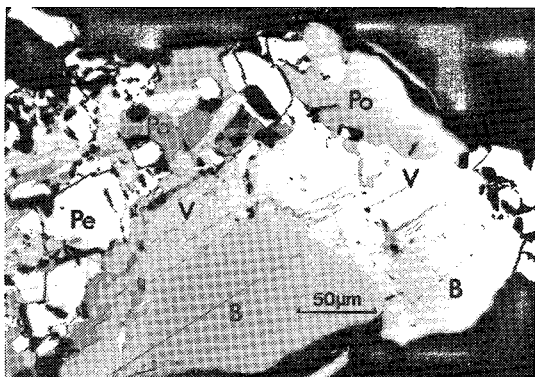


FIG. 5. Oil-immersion photomicrograph of vysotskite V selvage to braggite B with associated pentlandite Pe, pyrrhotine Po and minor chalcopyrite. Note the guided penetration textures of chalcopyrite, pyrrhotine and pentlandite in the vysotskite. Plane-polarized light.



FIG. 6. Oil-immersion photomicrograph of vysotskite V selvage to twinned braggite B. Note the optical behavior of the vysotskite as it penetrates the braggite. Slightly uncrossed polars.

2), and undulatory extinction, which may be due to deformation, in one of the larger grains.

In plane-polarized light, the single crystals of *braggite* are white and neither bireflectant nor pleochroic; none is twinned. A characteristic feature of the polycrystalline aggregates of grains that constitute the larger anhedral areas of *braggite* is polysynthetic and simple twinning and, to a lesser extent, kinkbanding [cf. Schneiderhöhn (1929a,b) on cooperite, and Kingston & El-Dosuky (1982) on *braggite*]. In these areas bireflectance is weakly perceptible. In fact, as will be demonstrated below, the bireflectance is minimal, 1 to 1.5% in both media, and lower than that of the Potgietersrus *braggite*. Nevertheless, this small difference in reflectance is within the visual threshold of the eye, and discrimination is helped by the small-scale twin lamellae where bright and less bright lamellae are juxtaposed. Between crossed polars, anisotropy is distinct in air for both the single crystals and the polycrystalline areas (Table 1). In oil, it is reduced to "weak" for the single crystals but remains distinct (again, probably because of the juxtaposition of lamellae with different hues and relative intensities) in the twinned areas. It should be clear from the above, from Table 1, and from our comparison of the appearance of cooperite and *braggite*, that there is little likelihood of confusing the two, and it is equally improbable that *braggite* could be confused with pyrrhotine.

It has been suggested recently that in the isomorphous solid-solution series from *braggite* (Pt,Pd)S to *vysotskite* PdS, the name *vysotskite* be restricted to minerals containing less than 10 mole % PtS (Cabri *et al.* 1978). This followed from the observation that, at the time, no members of the series containing between 10 and 30 mole % PtS were known. In our investigation, whereas most of the larger grains of *vysotskite* analyzed contain about 10 mole % PtS, a significant number of homogeneous and inhomogeneous areas and grains were found in the 10–30 mole % PtS range. In this account, we will limit ourselves to descriptions of those optical properties of *vysotskite* that are characteristic and to others that might cause confusion with *braggite*. The latter arise from a gradual change in these properties as the composition moves from that of one end-member toward that of the other. A more detailed account of the compositional variation in the series, together with textural relationships, will be reported separately.

In plane-polarized light, in air and in oil, *vysotskite* (containing 10 mole % or less PtS) has a slightly higher reflectance than *braggite* and is a slightly creamier white. Neither bireflectance nor reflectance pleochroism is detectable visually. In isolation, homogeneous *vysotskite* could be mistaken for *braggite* and *vice versa*. Similarly in intergrown areas, where the constituents are inhomogeneous, it is usually impossible to distinguish them by eye. Between crossed polars, *vysotskite* is appreciably less anisotropic than *braggite*, and its sombre rotation-tints in air are even more subdued in oil (Table 1). Even more distinctive are the tints that are seen when the analyzer is uncrossed by 3° (Table 1). In untwinned areas these tints are less bright than those of *braggite* but, when twinned, as is usually the case, they are much brighter. Other, more unusual phenomena were observed: a gradual 'bleaching' or desaturation of the tints away from a saturated centre, and a play of color resembling iridescence, or undulose extinction of randomly oriented aggregates of minute grains (no grain boundaries were detectable, however, in these areas). Possible explanations for these phenomena are compositional inhomogeneity and deformation.

To summarize, the qualitative optical properties of cooperite are sufficiently distinctive for it not to be confused with other minerals. Those of *braggite* and *vysotskite* similarly are distinctive, but they are difficult to distinguish from each other except where near end-member compositions occur together.

Quantitative optical data

Reflectance spectra are reported for five grains of cooperite from Potgietersrus and six from Stillwater, three grains of *braggite* from both localities, and four

TABLE 2. CHEMICAL COMPOSITION OF COOPERITE, BRAGGITE AND VYSOTSKITE*

| | wt. % | | | | TOTAL | Σ atoms = 2 | | | |
|----------------------|-------|------|-----|------|-------|-------------|------|------|------|
| | Pt | Pd | Ni | S | | Pt | Pd | Ni | S |
| Cooperite | | | | | | | | | |
| POTGIETERSRUS | | | | | | | | | |
| E.700,1 | 85.1 | 0.6 | 0.7 | 13.9 | 100.3 | .98 | .01 | .03 | .98 |
| E.700,3 | 84.2 | 0.5 | 0.7 | 13.7 | 99.1 | .99 | .01 | .03 | .98 |
| E.700,4 | 84.1 | 1.5 | 0.8 | 13.9 | 100.3 | .97 | .03 | .03 | .97 |
| E.700,5 | 84.5 | 0.6 | 0.8 | 13.6 | 99.5 | .99 | .01 | .03 | .97 |
| E.700,6 | 85.2 | 0.8 | 0.7 | 13.6 | 100.3 | .99 | .02 | .03 | .96 |
| STILLWATER | | | | | | | | | |
| E.389,1 | 78.6 | 6.5 | 0.2 | 14.9 | 100.2 | .86 | .13 | .008 | 1.00 |
| E.389,2 | 79.9 | 6.0 | 0.1 | 14.7 | 100.7 | .88 | .12 | .006 | .99 |
| E.392,1 | 79.0 | 6.9 | 0.2 | 14.4 | 100.5 | .88 | .14 | .008 | .97 |
| E.391,1 | 79.7 | 5.6 | 0.1 | 14.3 | 99.7 | .90 | .12 | .004 | .98 |
| E.391,2 | 78.3 | 5.7 | 0.2 | 14.6 | 98.8 | .88 | .12 | .008 | 1.00 |
| E.391,3 | 80.6 | 5.5 | 0.2 | 13.9 | 100.2 | .92 | .12 | .008 | .96 |
| Braggite | | | | | | | | | |
| POTGIETERSRUS | | | | | | | | | |
| E.701,1 | 62.7 | 14.8 | 4.8 | 17.3 | 99.6 | .60 | .26 | .15 | 1.00 |
| E.701,2 | 63.2 | 15.4 | 4.4 | 17.4 | 100.4 | .60 | .27 | .14 | 1.00 |
| E.701,3 | 61.2 | 16.6 | 4.2 | 17.5 | 99.5 | .58 | .29 | .13 | 1.00 |
| STILLWATER | | | | | | | | | |
| E.389 | 62.9 | 18.3 | 1.7 | 16.9 | 99.8 | .61 | .33 | .06 | 1.00 |
| E.395,5 | 62.1 | 19.0 | 2.0 | 16.9 | 100.0 | .60 | .34 | .06 | 1.00 |
| E.391 | 62.0 | 19.2 | 1.9 | 16.9 | 100.0 | .60 | .34 | .06 | 1.00 |
| Vysotskite | | | | | | | | | |
| STILLWATER | | | | | | | | | |
| E.392 | 13.5 | 60.8 | 4.1 | 22.1 | 100.5 | .10 | .82 | .10 | .98 |
| E.395,d | 15.5 | 59.2 | 4.0 | 21.8 | 100.5 | .11 | .80 | .10 | .98 |
| E.395,e | 14.6 | 59.4 | 3.9 | 22.1 | 100.0 | .11 | .80 | .10 | .99 |
| E.395,c-f | 5.3 | 66.9 | 5.8 | 23.4 | 101.4 | .04 | .85 | .13 | .98 |
| Pyrrhotine | | | | | | | | | |
| STILLWATER | | | | | | | | | |
| E.392 | 60.4 | 0.1 | 0.6 | 39.2 | 100.3 | .884 | .002 | .008 | 1.00 |

* electron-microprobe data.

position: the Stillwater samples have consistently higher Pd and lower Pt and Ni contents than those from Potgietersrus (Table 2).

One of the grains from the type locality is isotropic (E.700,6). The reflectances of this grain confirm the assignment of R_o to the spectral curves of lower reflectance. Hence, the sign of the bireflectance is positive. Earlier, we pointed out that cooperite from Potgietersrus is *apparently* pleochroic when immersed and cooperite from Stillwater is *apparently* pleochroic in both media. The reflectance curves and color values (Table 4) show that the dominant wavelengths λ_d (in subjective terms, the hues) of both R_o and R_e are nearly constant, and hence the mineral is, strictly speaking, not pleochroic. The

explanation for the perception of blue and white hues is that the higher reflecting component R_e is closer to the illuminant point and at most half as saturated (in quantitative terms, the excitation purity, $P_e\%$) as the R_o component. Thus, what is perceived as reflectance pleochroism is nothing more than a difference in brightness (quantitatively, the luminance, $Y\%$) and is properly a function of the mineral's bireflectance.

Several grains of *monoclinic pyrrhotine* from the same polished mounts were measured by N.S. Oldfield. From these measurements we selected representative spectra (Table 3) and plotted them with those of cooperite (Fig. 7). Inspection of these data should prove that there are no similarities between cooperite

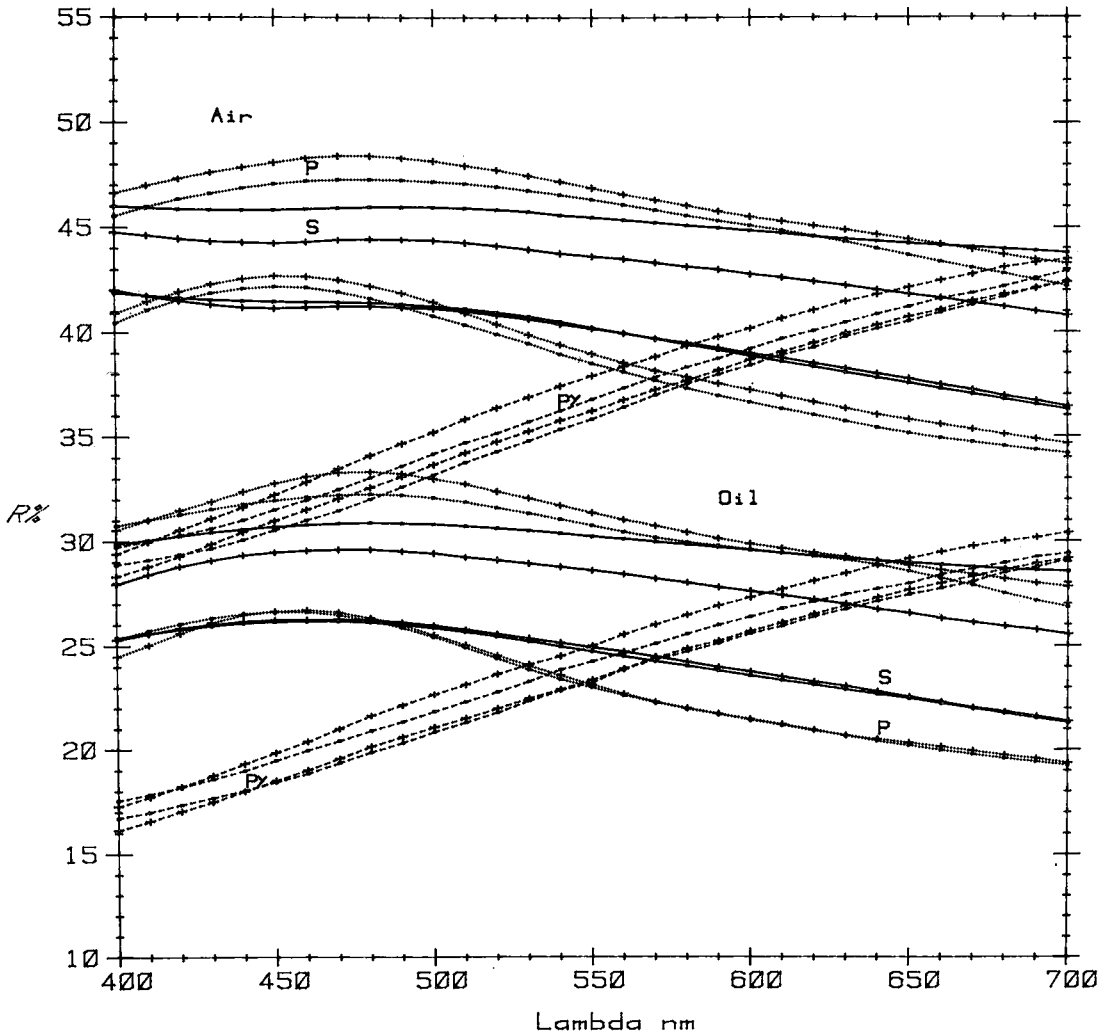


FIG. 7. R and imR spectra for cooperite from Potgietersrus (P, dotted) and Stillwater (S, continuous) compared with pyrrhotine (py, dashed) from Stillwater.

and pyrrhotine. That point is made even more convincing in Table 4; here the values are referred to the two illuminants recommended by the COM, *C* and *A*, with correlated color-temperatures of 6774 and 2856 K, respectively. It will be recalled that our qualitative observations were made with respect to a lamp run at about 3100 K. It follows that our descriptions will correspond most closely to the quantitative values for illuminant *A*. The brownish to brownish white color of pyrrhotine is explained by its fairly high saturation or excitation purity of about 14% in air, and its hue, or dominant wavelength, of about 588 nm. The fact that darker browns are seen in oil is a consequence of it being more saturated, with a P_e of 20%, and less strongly reflect-

ing (by about 13%) than in air. In contrast, cooperite has dominant wavelengths in the 490 nm range, and the reason that it does not appear more than slightly blue is due to its low excitation-purities of 1–4.8%. In terms of relative brightness or luminance, the bireflectance of cooperite immediately distinguishes it from pyrrhotine and, although $Y\% R_i$ for pyrrhotine is about the same as $Y\% R_o$ for cooperite, the two could not be confused because of the differences in hue and saturation.

The reflectance spectra of three grains of *braggite* from both localities (Fig. 8), plotted to the same scale as those of cooperite (Fig. 7), illustrate that the mineral is much less bireflectant than cooperite. They also show that, like cooperite, the Potgietersrus

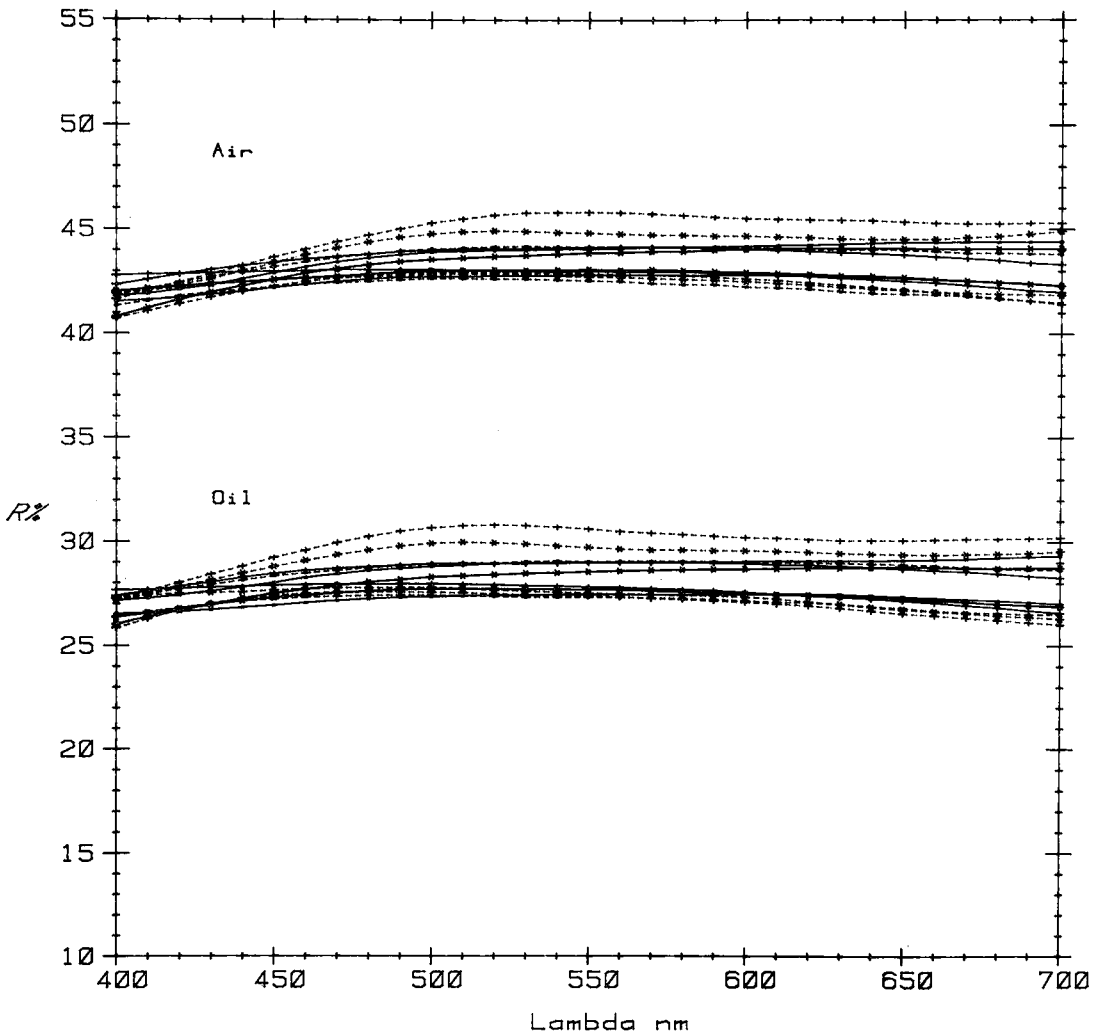


FIG. 8. R and imR spectra for 3 grains of braggite from Potgietersrus (dashed lines) and 3 grains from Stillwater (continuous lines).

braggite is slightly more bireflectant than its Stillwater counterpart. These slight differences can be attributed, in the same way as for cooperite, to compositional variation (Table 2): the Stillwater grains are more Pd- and less Ni-rich than the type specimens.

In terms of color, the undispersed R_o spectra indicate that the mineral will be white, lacking any noticeable hue, but that it will take on the color attributes of the light source, that is, it should appear white to bluish white with a *C* source and a creamier white with the *A* source. This fact is emphasized by the very low levels of excitation purity in Table 4. The scatter of the dominant wavelengths is insignificant since the chromaticity co-ordinates plot within less than 1% of those of the illuminants. The

levels of excitation purity for R_o are a little higher, with the result that more consistent and reliable dominant wavelengths of about 570–580 nm are obtained. The difference in the dispersion of the reflectance of the two vibration directions accounts for the detection by eye of the small measured bireflectance. One factor that is not readily explained in terms of color science is the presence of pinkish and greenish tints to the white braggite where it is in contact with cooperite. We can only speculate that as a result of differences in the polishing hardness of the two minerals, we were observing Kalb light-lines.

Vysotskite posed problems for reflectance measurements since, unlike the other two minerals, selection of compositionally homogeneous areas large

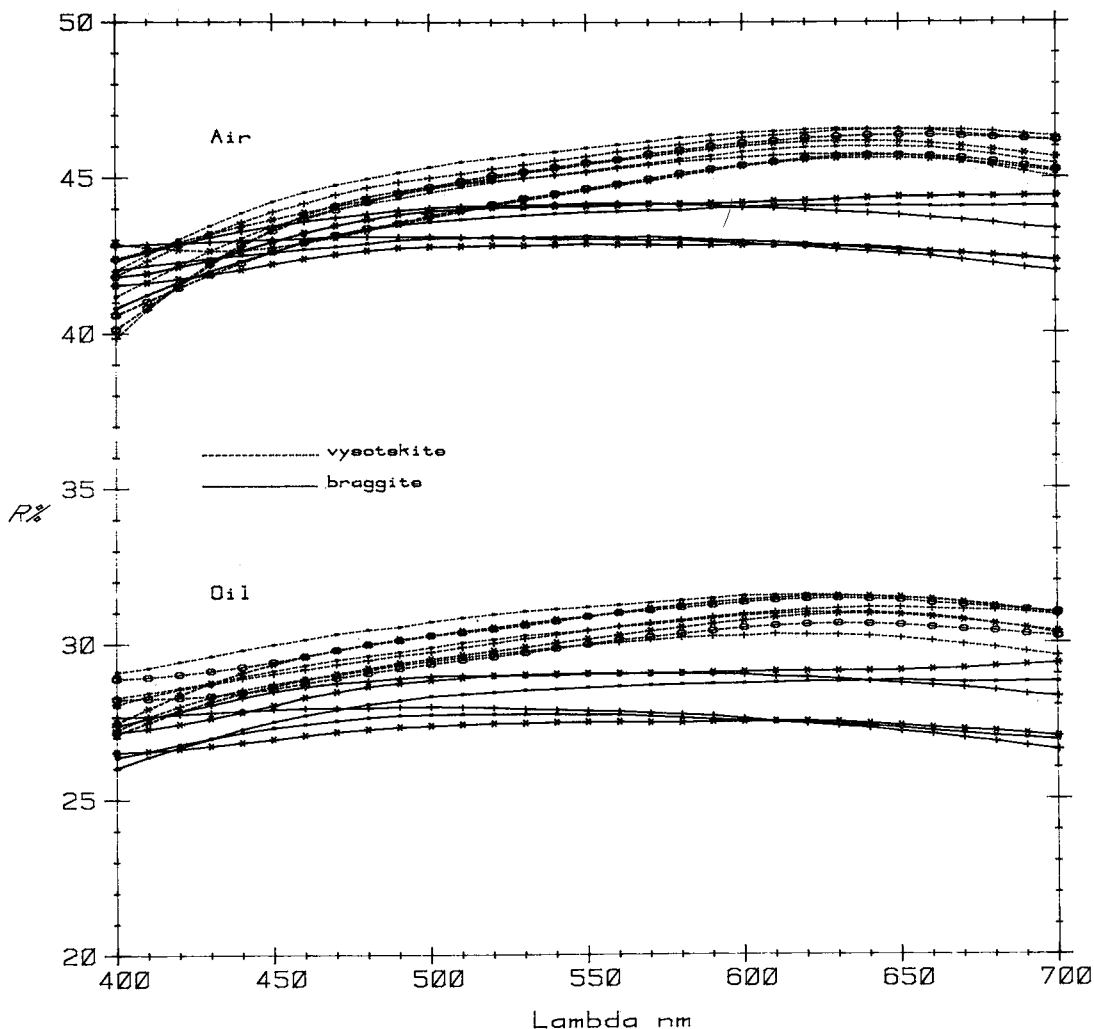


FIG. 9. Representative R and ^{im}R spectra for vysotskite and braggite from Stillwater. Note the lower bireflectance of vysotskite.

enough for photometry required that a large number of composite braggite-vysotskite grains be analyzed by electron microprobe. As we have mentioned, the series was discovered to be continuous; however, grains suitable for photometry are, with the exception of a near end-member vysotskite, all of similar composition, that is, they contain about 10 mole % PtS (Table 2). Also, owing to the extremely subdued rotation-tints and weak anisotropy, it was not possible to be certain of the extinction positions of any of these grains. For this reason, it was necessary to use the photometer to select reflectance maxima and minima for each grain. This was done at 560 nm.

The four grains measured have bireflectances of less than 1% throughout the visible spectrum, dis-

tinctly lower than that of braggite. The dispersion of their reflectance also differs from that of braggite, as can be seen in Figure 9. It was not possible, because of the low bireflectance, to determine which of the two vibration directions measured corresponds to R_o . This was assigned, by analogy with the R_o of braggite, to the spectra of lower luminance. It will be apparent from Figure 9 why vysotskite, when adjacent to braggite, appears a creamier white and slightly brighter; the reflectances of both vibration directions of all of the grains are higher than those of braggite above 520 nm. This is confirmed by the color values in Table 4; the luminances of vysotskite are 1-2% higher in air and 1-3% higher in oil than those of braggite; the dominant wavelengths for the A illuminant are nearly constant between 580 and

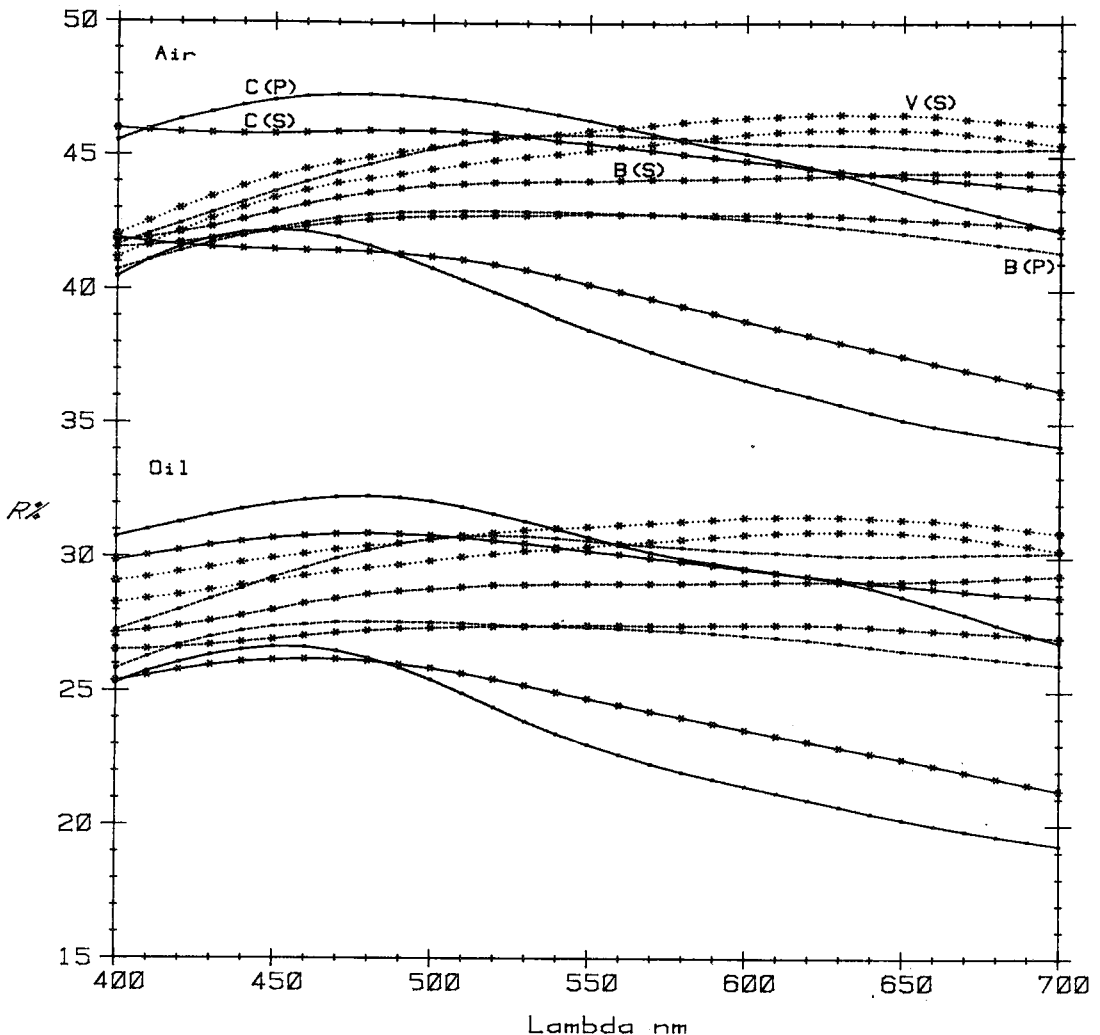


FIG. 10. Representative R and imR spectra for cooperite, braggite and vysotskite. The ornament is the same for each pair of curves and for both media. S and P for Stillwater and Potgietersrus, respectively.

590 nm and, perhaps more importantly, the excitation purities are 3–4% higher than those of braggite.

Thus there should be no difficulty in identifying the end members of the braggite–vysotskite series, but it seems likely that if grains intermediate in composition were measured, their reflectance spectra would fall between the extremes shown in Figure 9. This conclusion is supported by the qualitative observations of gradational and stepped reduction in the reflectance of vysotskite reported earlier.

To conclude this section, we have plotted representative spectra for the three minerals (Fig. 10), including examples from the type specimens as well as for material from Stillwater. These spectra are characteristic for the minerals. In our opinion, whereas the qualitative properties that we have described could suggest to the trained observer the possible identity of one or other of these minerals, reflectance spectra provide the only reliable means of confirming this identification optically.

Micro-indentation hardness

The published VHN values for cooperite and braggite are few and contradictory; there are none for vysotskite. All of our measurements were made with a Vickers indenter at a 100-gram force. Grains were selected for their compositional homogeneity, and the number of indentations made in each grain was governed by its size. Wherever possible, at least 10 indentations were made, but fewer in the case of the smaller grains of vysotskite and cooperite from Stillwater (the actual number is shown as a subscript to the mean VHN in Table 5). Our results are reproducible, similar for the same mineral from the two localities, and their precision is good (Table 5). In terms of micro-indentation hardness, cooperite is softer than braggite but in the same range as vysot-

skite. Pyrrhotine, by comparison, is softer than all three.

Of the published data, only those of Cabri (1981) agree with ours for braggite (his data for cooperite were made at a different loading and so are not comparable with ours). Compared with our results, Kingston & El-Dosuky (1982) obtained lower values for braggite (mean VHN₁₀₀ 864) and higher values for cooperite (mean VHN₁₀₀ 939). In fact, their braggite values match ours for cooperite except that the hardness anisotropy of their mineral is much lower and similar to our braggite. The only other data available are those of Rozhkov *et al.* (1962) for indentations at an unspecified load. For this reason their data cannot be regarded with any confidence.

We have no reason to doubt that our data are as accurate as the technique permits; whereas we do not consider the VHN to be useful as a 'primary' means of identification, we believe that it has some value as a support to identifications made on the basis of reflectance determinations.

DISCUSSION AND CONCLUSIONS

The main objectives of this study were 1) to complete the characterization of braggite and cooperite made by Bannister & Hey (1932), our predecessors at the BM(NH), 2) to provide characteristic optical data for vysotskite (accepting that the material at our disposal is not from the type locality at Noril'sk), 3) to dispel the extraordinary confusion that has surrounded braggite and cooperite and that was developing around vysotskite and, finally, 4) to attempt to explain how this occurred.

We have shown that the qualitative properties of cooperite are particularly distinctive and those of braggite and vysotskite are sufficiently distinctive for end members of the series to be identified with some confidence. Reflectance spectra for the three minerals provide even greater assurance of a positive identification, and have the added advantage of supplying the data necessary for deriving unambiguous color-values. In this, they remove the subjectivity of color description and the assessment of relative brightness which, even for the experienced microscopist, cause confusion through the eye's ability to modify impressions of color and brightness depending on the appearance of the associated minerals.

It only remains for us to try and explain why the original descriptions of cooperite were so misleading. When Schneiderhöhn described *cooperite* in 1929, it was considered to be a platinum sulfarsenide (Cooper 1928). This was revised by Cooper (1929) to PtS₂, and it was not until 1932 that Bannister & Hey, using X-ray diffraction to identify individual grains in the concentrates for wet-chemical analysis, proved it to be PtS. Schneiderhöhn's (1929a,b)

TABLE 5. VALUES OF MICRO-INDENTATION HARDNESS

| | Range VHN ₁₀₀ | Mean VHN ₁₀₀ | |
|-------------------|--------------------------|-------------------------|-------|
| Cooperite | | | |
| POTGIETERSRUSS | | | |
| E.700,4 | 762–920 | 835 ₍₁₀₎ | f-ssc |
| E.700,5 | 743–1018 | 878 ₍₁₀₎ | f-ssc |
| STILLWATER | | | |
| E.391,1 | 782–907 | 839 ₍₅₎ | f-ssc |
| Braggite | | | |
| POTGIETERSRUSS | | | |
| E.701,1 | 974–1033 | 1003 ₍₁₀₎ | f-ssc |
| E.701,3 | 946–1026 | 991 ₍₁₀₎ | f-ssc |
| STILLWATER | | | |
| E.389 | 946–1003 | 973 ₍₁₀₎ | f-ssc |
| E.395,5 | 981–1064 | 1015 ₍₁₀₎ | f-ssc |
| E.391 | 953–1048 | 1002 ₍₁₀₎ | f-ssc |
| Vysotskite | | | |
| STILLWATER | | | |
| E.395,d | 792–864 | 834 ₍₄₎ | sf-cc |
| E.395,e | 813–847 | 830 ₍₅₎ | sf-cc |
| E.395,c-f | 715–792 | 745 ₍₄₎ | f-cc |
| Pyrrhotine | | | |
| STILLWATER | | | |
| E.392 | 292–331 | 318 ₍₄₀₎ | sf-cc |

descriptions of his mineral as white with a distinct greyish yellow tint, with high reflectivity in air and in oil, distinct anisotropy with grey-pink and grey-green rotation tints, and characteristic polysynthetic twinning, would not fit our description of cooperite. This description of the appearance of his prismatic grains does, however, correspond to a mineral which, at that time, was unknown: braggite. In the same papers, Schneiderhöhn recorded the results of Frick's determinations with the reflection-photometer ocular of the 'absolute reflectivities' of *cooperite* in green, orange and red light. These values, 37, 37 and 36%, respectively, are exactly the same as those determined at the same time for pyrrhotine (and within 2% of those for chalcopyrite). In 1931 the description was changed by Schneiderhöhn & Ramdohr; the reflectance of cooperite was described as similar to that of chalcopyrite and pyrrhotine, and its anisotropy as weak. The reflectance values were also revised to 41, 34 and 34% (these were later attributed to Frick by Ramdohr 1969). Frick, himself, reported (1930) slightly different values again of 37.8, 37.8 and 36.4%. Subsequently, Ramdohr (1950), describing Schneiderhöhn's observations in 1929, stated that they were incorrect because 2 or 3 different minerals were considered as one. Obviously, fifty years after the event, we cannot be certain of what happened, but suggest that the most plausible explanation is:

1. Schneiderhöhn originally described braggite as cooperite (braggite, although found in concentrates from the same locality by Bannister & Hey in 1932, was unknown in 1929).

2. The concentrates examined by Schneiderhöhn contained pyrrhotine, and it was pyrrhotine and not braggite or cooperite that was measured by Frick (1930), leading to the apparent identity of cooperite and pyrrhotine. Frick's (1930) tables of reflectance for the opaque minerals, except for a consistent underestimate of the reflectance in green light, conform well with reflectances obtained with modern microscope-photometers. So the fact that he repeatedly obtained reflectances that match pyrrhotine more closely than cooperite-braggite tends to confirm this error.

3. Schneiderhöhn accepted these values, and he and Ramdohr in 1931 noted the similarity between cooperite and pyrrhotine. This was to remain firmly entrenched in the literature into the 1980s.

Kingston & El-Dosuky (1982) suggested that the original mistake made by Schneiderhöhn (1929) and repeated by Schneiderhöhn & Ramdohr (1931), Frick (1930) and Ramdohr (1969), was that of confusing braggite with cooperite and 'braggite-cooperite intergrowths' as braggite showing 'pleochroism'. Whereas we consider that Schneiderhöhn's original description was that of braggite, not cooperite, this was not a question of mistaken identity between two known

minerals. As we have shown, the optical properties of both minerals are distinctive.

The explanation for the continued misidentification of the minerals and the mistaken belief that they are rare followed naturally from the acceptance of the original mistake. It would, after all, be impossible to identify cooperite from the 1929 or 1931 descriptions. What is more difficult to understand is how the mistake was perpetuated when combined optical and electron-microprobe studies were made of the PGM in the 1970s.

The qualitative and quantitative data in the literature for vysotskite are few and contradictory. Near end-member vysotskite, we have shown, can be identified with some confidence. Its reflectance is not lower than that of chalcopyrite (Genkin 1968), it is slightly higher, but nowhere near as high as reported by Vyalsov (1973). The dispersion of his reflectance spectrum for vysotskite is similar to that of our spectra but is inexplicably 7-8% higher. Until such time as type material from Noril'sk is thoroughly re-examined, our data for vysotskite can be taken as characteristic, as they are for cooperite and braggite.

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