writers obtained an x-ray powder pattern and a specimen of the Utah tungstenite from the University of Manitoba (Number 2.9.6.2-1). Patterns were produced at the Royal Ontario Museum from Professor Ferguson's specimen as well as from specimens (M 16615 and M 11795) in our collections. Most of these patterns were similar to Professor Ferguson's pattern and showed only broad bands at the pertinent d-spacings. One pattern, however, showed discrete doubling and it must be concluded that the Utah tungstenite is the $3R$-polytype. In fact, it probably is a mixture of the $2H$- and $3R$-polytypes.

The limits of the broad bands given in Berry & Thompson (1962) correspond to the calculated d-spacings for tungstenite-$3R$, as shown in Table 1.

It is virtually impossible to distinguish the x-ray powder pattern of a given polytype of molybdenite from the same polytype of tungstenite, because of the almost identical unit cell parameters. Consequently it is quite possible that tungstenite is more widespread than the literature indicates and that some "molybdenite" may be in fact tungstenite.

The writers gratefully acknowledge Professor Ferguson's assistance.

REFERENCES

BERRY, L. G. & THOMPSON, R. M. (1962): X-ray powder data for ore minerals: The Peacock Atlas. *Geol. Soc. Am., Memoir*, **85**.

GRAESER, STEFAN (1963): Über Funde der neuen rhombohedrischen MoS_2-Modifikation (Molybdänit-$3R$) und von Tungstenit in den Alpen. *Schweiz. Min. Petr. Mitt.*, B.**44**, 121–128.

Manuscript received December 10, 1969

NEW DATA ON TYRRELLITE

D. C. HARRIS*

A new cobalt–nickel–copper selenide, at first unnamed was described by Robinson & Brooker (1952) from the Beaverlodge area (previously referred to as the Goldfields District), northern Saskatchewan. Subsequently, the name tyrrellite was given to the mineral by the authors in honour of Dr. J. B. Tyrrell, one of the first geologists of the Geological Survey of Canada to enter the now famous Beaverlodge area and whose report in 1896 first aroused the interest in the mining potentialities of the

---

*Research Scientist, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Sulphide Research Contribution No. 22, Mineral Sciences Division.

Lake Athabasca region (priv. comm.). The name is incorrectly referred to G. W. Tyrrell in *Mineral. Abs.* **15**, 361, but correctly in Hey's Mineral list (*Mineral. Mag.* **32**, 984) and Hey's 1963 Appendix to *Chemical Index of Minerals*. The name was also used on ASTM card 8-1, by Berry & Thompson (1962) and by Sindeeva (1964), but until now there was no record of the reason for the name.

More recently, Kvaček (1967) reported the second occurrence of tyrrellite from Bukov (Moravia), Czechoslovakia. Due to insufficient quantities of the mineral from either locality, some properties of tyrrellite have not been properly established, heretofore, in particular the composition. Although Robinson & Brooker derived a formula of $Co_{3.9}Ni_{2.0}Cu_{3.5}Se_{9.5}$ on the basis of an *x*-ray spectrographic analysis, Machatschki & Stradner (1952) pointed out that since the *x*-ray powder pattern resembles those of the spinel and linnaeite groups of minerals, tyrrellite should have a formula of $(Co, Cu, Ni)_3Se_4$. Machatschki & Stradner obtained good agreement between observed and calculated intensities of tyrrellite, on this assumption.

During a study of the copper selenide minerals, in which a new species, athabascaite has been characterized (Harris *et al.* 1969), specimens containing tyrrellite from the Beaverlodge area of Saskatchewan and Bukov in Czechoslovakia were examined. The purpose of this paper is to report electron microprobe analysis, reflectivity and microhardness measurements.

General Description

H. R. Steacy, Curator of the Systematic Mineral Collection, Geological Survey of Canada, Ottawa, kindly supplied specimens containing tyrrellite, collected in 1963 by S. C. Robinson at a locality 1/4 mile west of Eagle Shaft, Eldorado Mining and Refining, Beaverlodge area; and a specimen labelled as berzelianite from Bukov, near Dolni, Rozinka, W. Moravia, Czechoslovakia.

Tyrrellite from the Beaverlodge area occurs as large irregular to subhedral grains, up to 0.2 mm in diameter in umangite (Fig. 1). In polished section, it is isotropic and its colour is light brassy bronze. In comparison, tyrrellite from Bukov, occurs as subhedral to euhedral grains, up to 0.2 mm in diameter, in berzelianite (Fig. 2). In polished section, it is isotropic and its colour is light bronze with a distinct pinkish shade. As pointed out by Kvaček, the colour is particularly distinctive when associated with clausthalite.

For further information on the descriptive properties of tyrrellite, the reader is referred to the papers by Robinson & Brooker (1952), and Kvaček (1967).

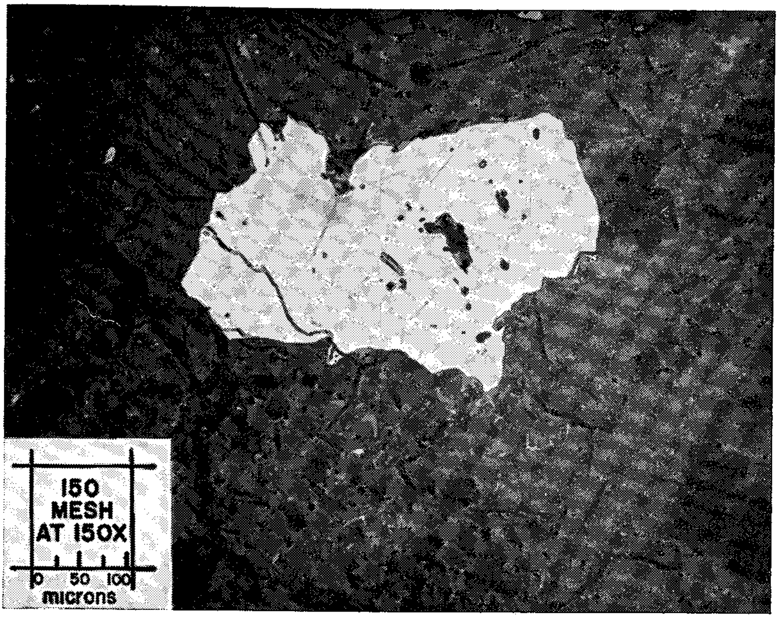

FIG. 1. Large irregular grains of tyrrellite (white) in a matrix of umangite (dark grey). The small inclusions (white) surrounding the tyrrellite are eucairite. The black areas are gangue.

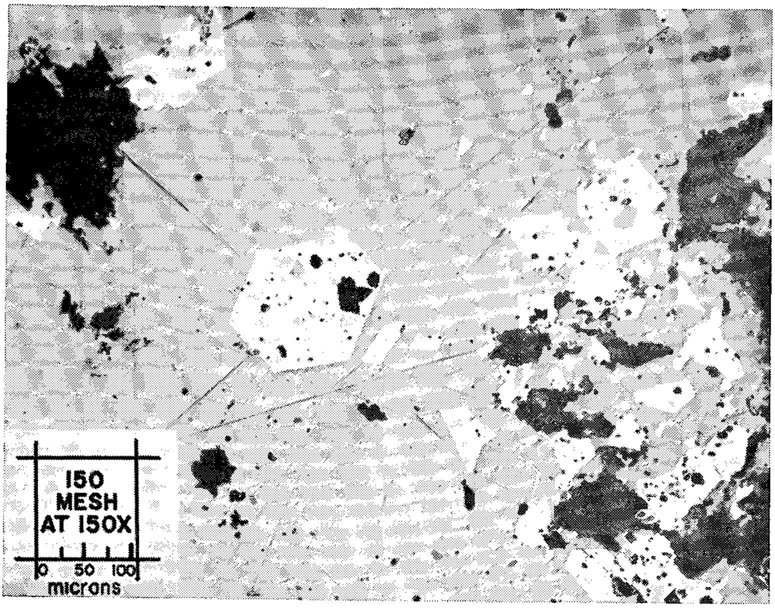

FIG. 2. Euhedral grains of tyrrellite (white) in berzelianite (light grey). The black areas are gangue.

ELECTRON MICROPROBE ANALYSIS

The analyses were performed on a Materials Analysis Company (MAC) electron microprobe, and the data processed by a computer program (Rucklidge 1967) which applied corrections for drift, dead time, background, absorption, fluorescence and atomic number. A synthetic CuSe, pure Ni and pure Co were used as standards. At least ten analyses were obtained from several grains in each section; the results are given in Table 1.

TABLE 1. ELECTRON MICROPROBE ANALYSIS OF TYRRELLITE

Locality	Elements	Wt. Percent	At. Prop.	
	Co	17.42	1.49	3.16
Beaverlodge Area	Cu	12.35	0.98	
Saskatchewan	Ni	8.05	0.69	
	Se	62.70	4.0	
		100.52		
Bukov	Co	13.51	1.17	3.31
CSSR	Ni	14.31	1.25	
	Cu	11.14	0.89	
	Se	61.80	4.0	
		100.76		

The electron microprobe analysis shows that the composition of the two tyrrellites are slightly different. The Beaverlodge material has Co > Cu > Ni (atomic proportions) while the Bukov material has Ni > Co > Cu. The *M*:Se ratios in the two analyses are 3.16:4 and 3.31:4, which are substantially in excess of the ideal 3.0:4 ratio in spinel-type minerals. This suggests that tyrrellite may contain some extra metal atoms, or a selenium deficiency, in a spinel-type lattice. This non-stoichiometry is certainly not unusual for sulphides with the spinel-type lattice as a recent publication by Vokes (1967) tabulates 40 linnaeite analyses, and shows that the number of S atoms occurring with three metal atoms varies from about 3.70 to 4.25. Deficiency in S is more usual than excess.

REFLECTIVITY AND MICROHARDNESS

The apparatus used for measuring the reflectivity was a Leitz Ortholux-Pol microscope, a Leitz MPE microscope photometer equipped with Dumont, type 6467 photomultiplier tube, two six-volt storage batteries connected in parallel, and a Veril B200 continuous-band interference filter. A 50:1 objective with a numerical aperture of 0.65 was used. The

TABLE 2. REFLECTIVITY AND MICROHARDNESS OF TYRRELLITE

	Reflectivity				Microhardness
Tyrrellite	470 nm	546 nm	589 nm	650 nm	VHN (in Kg/mm^2)
CSSR	32.3–37.8	36.9–40.5	38.9–42.0	41.3–44.6	336–398
2 grains	34.8	38.8	40.6	42.9	367
Sask.	40.8–41.6	43.0–43.6	43.9–44.4	45.7	404–469
5 grains	41.1	43.4	44.1	45.7	436

reflectivity values for the four standard wavelengths, using silicon as a standard, are given in Table 2 along with the microhardness values which were determined with a Leitz Durimet Vickers hardness tester. Reflectivity and microhardness values for the two minerals are significantly different.

X-RAY CRYSTALLOGRAPHY

Machatschki & Stradner (1952) pointed out that the *x*-ray powder pattern of tyrrellite resembles those of the spinel and linnaeite groups of minerals, and that the calculated intensities, assuming a spinel-type structure, agree very well with the probable formula of $(Co, Cu, Ni)_3Se_4$. However, on direct comparison of the tyrrellite powder pattern with those of the spinel and linnaeite minerals, tyrrellite is seen to have two strong reflections, namely the (222) (7) and (226)(5), which are either absent or very weak for the other minerals.

In an attempt to confirm the structure of tyrrellite, E. J. Gabe and S. R. Hall of the Crystal Structure Group, Mines Branch, examined several grains using the four-circle diffractometer. For this study, the original material separated by S. C. Robinson in the initial study was examined, but all the fragments were found to be unsuitable due to split reflections. Assuming that tyrrellite has a spinel structure, structure factor calculations were made using the =FC= computer program in the XRAY-67 crystallographic program system. Results of these calculations tend to confirm the work of Machatschki & Stradner that tyrrellite could have a spinel-type structure.

Kvaček (1967), noted from *x*-ray powder-data studies, somewhat lower *d*-values for tyrrellite from Bukov, Czechoslovakia, as compared to the *d*-values published by Robinson & Brooker for the Beaverlodge material. To explain this variation, he suggested a possible difference in the ratio of cations in the crystal lattice. *X*-ray powder patterns obtained in this study confirm Kvaček's observations, and the microprobe analyses support his suggestion that the differences are caused by a variation in the ratios of cations in the mineral.

DISCUSSION

Electron microprobe analyses of tyrrellite, from the two known occurrences, show that the ratio of cations in the crystal lattice is variable, and this may therefore account for the observed differences in reflectivity, microhardness, and unit-cell dimensions. In general, the reflectivity and microhardness appear to increase with increasing cobalt content. Although it seems unlikely that one element would be entirely responsible for these variations, it does appear that the Co:Ni ratio is responsible for these variations. Similar variations have been observed for the langisite-niccolite isomorphous series in which an increase in cobalt results in an increase of microhardness and change in the shape of the reflectivity spectrum (Petruk *et al.* 1969); also, Nickel *et al.* (1969) recently pointed out an increase in microhardness between NiS_2 and CoS_2.

ACKNOWLEDGMENTS

The author wishes to thank H. R. Steacy and R. J. Traill of the Geological Survey of Canada, who supplied the material for study and offered many helpful suggestions in the course of the study. My thanks also, to E. J. Gabe, S. R. Hall and J. M. Stewart of the Crystal Structure Group who provided the crystallographic data, and to D. R. Owens for the photomicrographs.

REFERENCES

BERRY, L. G. & THOMPSON, R. M. (1962): *X*-ray powder data for ore minerals. The Peacock Atlas. *Geol. Soc. Amer., Mem.*, **85**.

HARRIS, D. C., CABRI, L. J. & KAIMAN, S. (1969): Athabascaite, a new copper selenide mineral from Martin Lake, Saskatchwan. *Can. Mineral.*, **10**.

KVAČEK, M. (1967): A new selenide from Bukov (Moravia), *Casopis Narodnihomurea, Odd. prir.*, **136**, 10–12.

MACHATSCHKI, F. & STRADNER, E. (1952): Ein Selenid-Mineral vom Spinelltype. *Anzerg. Osterr. Akad. Wiss., Math.—Nat. Kl., Jahrg.*, **89**, Nr. 113, 211–213. Wien.

NICKEL, E. H., GILLIESON, A. H. & RIPLEY, L. G. (1969): Microhardness, infrared absorption and band energies of FeS_2, CoS_2 and NiS_2. (For presentation at the *Annual Meeting of the Min. Soc. Amer., Atlantic City, N.J.*, Nov. 12.)

PETRUK, W., HARRIS, D. C. & STEWART, J. M. (1969): Langisite, a new mineral, and the rare minerals cobalt pentlandite, siegenite, parkerite and bravoite from the Langis Mine, Cobalt-Gowganda Area, Ontario. *Can. Mineral.*, **9**, 597–616.

ROBINSON, S. C. & BROOKER, E. J. (1952): A cobalt-nickel-copper selenide from the Goldfields District, Saskatchewan. Amer. Mineral., **37**, 542–544.

RUCKLIDGE, J. (1967): A computer program for processing microprobe data. *Jour. Geol.* **75**, 126.

SINDEEVA, N. D. (1964): *Mineralogy and types of deposits of selenium and tellurium.* John Wiley and Sons, New York.

VOKES, F. M. (1967): Linnaeite from the Precambrian Raipas Group of Finnmark, Norway. *Mineralium Deposita* **2**, 11–25.

Manuscript received January 19, 1970