HAUCHECORNITE — ANTIMONIAN, ARSENIAN AND TELLURIAN VARIETIES

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Abstract

Three varieties of hauchecornite, each from a different locality, are described : arsenian hauchecornite from the Vermilion mine, Sudbury District, Ontario ; antimonian hauchecornite from the Friedrich mine, Westphalia ; and tellurian hauchecornite from the Strathcona mine, Sudbury District, Ontario. The electron microprobe analyses yielded the following formulae : Vermilion — Ni₉(Bi,As)₂S₈ ; Westphalia — Ni₉(Bi,Sb)₂S₈ and Strathcona — Ni₉(Bi,Te)₂S₈. Small amounts of Co and Fe may substitute for Ni. The cell dimensions vary slightly for each variety ; the ranges are : a = 14.52 to 14.64Å and c = 10.80 to 10.87Å, Z = 8. S.G. (calc.) vary from 6.50 to 6.56, S.G. (meas.) 6.35. The space group is either P42m, P422 or P4/mmm. Reflectance values for each variety were measured, and for wavelengths betwen 470 and 650 nm the ranges are : Vermilion (max.) 43.0 to 51.6, (min.) 41.6 to 50.8; for Westphalian hauchecornite (max.) 44.8 to 51.9, (min.) 41.2 to 48.2, VHN₅₀(kg/mm²) for Vermilion hauchecornite are 516-655, for Westphalian material 447-655, and for Strathcona 182-825. In 1950, Peacock (1950a & b) reinstated hauchecornite (Westphalia) as a valid species. Our data for arsenian and tellurian hauchecornite are similar to Peacock's for antimonian hauchecornite.

INTRODUCTION

In 1969, a mineral collector from the Sudbury area, Mr. R. C. Butler, sent three specimens of hauchecornite from the Vermilion mine, Lot 6, Conc. IV, Denison township, Sudbury district, Ontario, to the Royal Ontario Museum for identification. X-ray powder patterns obtained from these specimens matched the *d*-spacings given for hauchecornite from Westphalia (Peacock 1950b; Berry & Thompson 1962). Electron microprobe analyses confirmed these identifications. The only other known reference to Sudbury hauchecornite is given in Berry & Thompson (1962) who state under their entry #152, referring to Westphalian hauchecornite : "Same pattern given by material from the Vermilion mine, Sudbury, Ontario (GSC, 8941)". Unfortunately this specimen cannot be located. In 1971, after the main study on Vermilion hauchecornite was completed, a new locality for this mineral was found — Strathcona mine, Sudbury, Ontario.

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This paper compares chemical analyses, x-ray diffraction data, reflectance and microhardness data for hauchecornite from the three localities. The electron microprobe analyses, reflectance and microhardness measurements were performed by DCH.

OCCURRENCE

Hauchecornite from the Friedrich mine, Hamm a.d. Sieg, Westphalia, is described in detail by Peacock (1950b) who reinstated the mineral as a valid species. At this locality tetragonal, tabular, euhedral hauchecornite crystals, up to 4 mm on an edge, occur on millerite crystals. The studies on Westphalian antimonian hauchecornite were performed on HMM 89710, kindly loaned to us by the Harvard Mineralogical Museum. The electron microprobe study of Westphalian hauchecornite revealed inclusions of other minerals — millerite, bismuthinite, galena, gold, bismuthianarsenian ullmannite and antimonian gersdorffite.

Hauchecornite from the Vermilion mine occurs mostly as irregular masses up to 10 mm across, occasionally as tabular crystals up to 2×20 mm embedded in chalcopyrite and, rarely, as subhedral crystals exhibiting crystal faces several millimetres across. The mineral is brassy-coloured, resembles pyrrhotite but is slightly darker. It possesses a bright metallic lustre on fresh surfaces and exhibits conchoidal fracture. Hauchecornite is associated most commonly with chalcopyrite. Other minerals in the ore are millerite, pyrrhotite, gersdorffite, pyrite, gold, niccolite, galena, native copper and sperrylite. Michenerite and froodite also have been identified (Cabri, *et al.* 1972). Three specimens of arsenian hauchecornite from the Vermilion mine were presented to the Royal Ontario Museum by Mr. R. C. Butler and are registered as M 29206, M 29207 and M 29208; other specimens have since been acquired. Hauchecornite from the Vermilion mine appears to be free of inclusions.

Hauchecornite from the Strathcona mine, Lot 4, Conc. IV, Levack township, Sudbury district, Ontario, occurs as irregular grains up to 150 microns, associated with chalcopyrite and millerite. The optical properties are similar to pyrrhotite for which it was mistaken originally. A polished section of tellurian hauchecornite from the Strathcona mine has been deposited at the Royal Ontario Museum and is registered as M 30942.

CHEMISTRY

The electron microprobe analyses and atomic proportions of hauchecornite from Westphalia, the Vermilion mine and the Strathcona mine are given in Table 1. All the analyses were performed on a Materials Analysis Company (MAC) electron microprobe and these data were processed by a computer program (Rucklidge 1967) which applied corrections for drift, dead time, background, absorption, fluorescence and atomic number. Synthetic (Co,Fe)As, tellurium metal and antimony metal, as well as the minerals niccolite (NiAs) and bismuthinite (Bi_2S_3) were used as standards. The analyses quoted in Table 1 represent the average of 3 analyses on material from each of the three localities.

Table 1 shows that in hauchecornite from Westphalia antimony is the main element substituting for bismuth; in hauchecornite from the Vermilion mine, arsenic is the main element substituting for bismuth;

Specimen Number and Locality	Wt. %		Wt. % (Recalc. to 100%) Atm. Wt.	Atm. Props. (Recalc. to 8 Sulphur Atoms)	
HMM 89710 Antimonian hauchecornite, Westphalia. Ideal formula : $Ni_9(Bi,Sb)_2S_8$	Ni Co Bi Sb As S	$\begin{array}{c} 46.8 \pm 0.5 \\ 0.3 \pm 0.1 \\ 22.3 \pm 1.0 \\ 7.8 \pm 0.5 \\ 0.2 \pm 0.1 \\ 22.6 \pm 1.0 \end{array}$	7971 8021 0050 1067 0641 1733 0027 7048	$ \begin{array}{c} 9.1\\ 0.1\\ 1.2\\ 0.7\\ \hline (8.0) \end{array} \right\} 9.2 $ 1.9	
	Total	100.0	_		
	Pb, Cu, Zn not detected		Empirical formula : (Ni	.1,Co _{0.1}) (Bi _{1.2} ,Sb _{0.7}) S ₈	
$\begin{array}{c} \operatorname{ROM} \ \# \operatorname{M} 29207\\ \operatorname{Arsenian}\\ \operatorname{hauchecornite},\\ \operatorname{Vermilion} \operatorname{Mine}.\\ \operatorname{Ideal} \ \operatorname{formula}:\\ \operatorname{Ni}_9(\operatorname{Bi},\operatorname{As})_2 S_8 \end{array}$	Ni Fe Co Bi As Sb S S	$\begin{array}{c} 44.9 \pm 0.5 \\ 1.4 \pm 0.1 \\ 0.3 \pm 0.1 \\ 26.5 \pm 1.0 \\ 4.4 \pm 0.5 \\ 0.1 \pm 0.1 \\ 22.0 \pm 1.0 \end{array}$	$ \begin{array}{c} 7682\\0250\\0051\\1273\\0587\\0008\\6892 \end{array} \\ \end{array} \begin{array}{c} 7983\\7983\\7983\\7983\\7983\\7983\\7983\\7983\\$	$ \begin{array}{c} 8.9\\ 0.3\\ 0.1\\ 1.5\\ 0.7\\ \hline 0.7\\ \hline 8.0 \end{array} \right\} 9.3 $ 2.2 (8.0)	
	Total	99.6	- · ·		
	Ph not	, Cu, Zn t detected	Empirical formula: (Ni _{8.9} ,	Fe _{0.8} ,Co _{0.1}) (Bi _{1.5} ,As _{0.7})S ₈	
$\begin{array}{c} \operatorname{ROM} \ \# \operatorname{M} \ 30942 \\ \operatorname{Tellurian} \\ \operatorname{hauchecornite}, \\ \operatorname{Strathcona} \ \operatorname{Mine}. \\ \operatorname{Ideal} \ \operatorname{formula}: \\ \operatorname{Ni}_9(\operatorname{Bi},\operatorname{Te})_2 S_8 \end{array}$	Ni Co Fe Bi Te S	$\begin{array}{c} 44.1 \pm 0.5 \\ 0.9 \pm 0.1 \\ 0.9 \pm 0.1 \\ 22.4 \pm 1.0 \\ 8.5 \pm 0.5 \\ 21.9 \pm 1.0 \end{array}$	$ \begin{array}{c c} 7614 \\ 0153 \\ 0161 \\ 1086 \\ 0674 \\ 6924 \end{array} 7928 \\ 1760 \\$	$\begin{array}{c} 8.8\\ 0.2\\ 0.2\\ 1.2\\ 0.8\\ 8.0 \end{array} \right\} \begin{array}{c} 9.2\\ 2.0\\ (8.0) \end{array}$	
	Total	98.7	<u>.</u>		
	Pb, C no	u, Zn, Sb, As t detected	Empirical formula: (Ni _{8.8} ,	Co _{0.2} Fe _{0.2}) (Bi _{1.2} , Te _{0.8})S ₈	

TABLE 1. ELECTRON MICROPROBE ANALYSES OF HAUCHECORNITE

and in hauchecornite from the Strathcona mine, it is tellurium which substitutes for bismuth. Thus three varieties of this mineral have been recognized — antimonian, arsenian and tellurian hauchecornite. Westphalian hauchecornite shows minor Co and no Fe substituting for Ni, but hauchecornite from both the Vermilion and the Strathcona mines has minor amounts of Fe and Co substituting for Ni.

Peacock (1950a) originally suggested $Ni_8(Bi,Sb)_2S_8$ as the ideal formula for Westphalian hauchecornite; but later (1950b), on the basis of a revised space group, he proposed $Ni_9(Bi,Sb)_2S_8$ for the same material. In Table 1 the numbers of atoms were calculated on the basis of 8 sulphur atoms as per the formulae of Peacock (1950a & b); in all three the $\Sigma(Ni,$ Co,Fe) is close to 9 and $\Sigma(Bi,Sb,As,Te)$ is close to 2. Thus the general formula $Ni_9(Bi,X)_2S_8$ is suggested, where X is either Sb, As or Te. This is in agreement with the formula of Peacock (1950b) — $Ni_9(Bi,Sb)_2S_8$ for Westphalian hauchecornite. Either Sb, As or Te substitutes for Bi, and in any one variety the other two elements either do not exist or may be present only in very small amounts.

Specific gravity calculations on these three varieties of hauchecornite, using the proportions from Table I, are considerably greater than those measured; however, the measured values probably are not reliable and the margin of error, certainly for the Vermilion mine hauchecornite, likely exceeds the discrepancy shown in Table 2.

X-RAY DIFFRACTION DATA

An x-ray diffraction study of hauchecornite from the Vermilion mine by both powder and precession methods showed similarity with the data for Westphalian hauchecornite (Peacock 1950b). However, Mr. J. D. Grice (pers. comm.) determined that the cell parameters for Vermilion hauchecornite are double those given by Peacock (1950b) for Westphalian material. Similar evidence for the larger cell is given by the x-ray powder pattern for tellurian hauchecornite from the Strathcona mine. This pattern

Locality	S.G. (meas.)	S.G. (calc.)
Vermilion	6,35	6.52
Westphalia	6.36 *	6.56
Strathcona	no data	6.50

TABLE 2. SPECIFIC GRAVITY OF HAUCHECORNITE

* Peacock (1950b).

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contains several weak reflections which can be indexed only on the larger cell. The x-ray powder diffraction data (obtained from a Debye-Scherrer, 114.7 mm diameter camera, with Ni filtered Cu radiation) for tellurian hauchecornite, are given in Table 3.

TABLE	3.	X-Ray	Powder	DIFF	RACTION	DATA	FOR	Tellur	IAN	HAUCHECORNE	ГЕ
		FROM	(Strath	CONA	Mine,	SUDBU	ry D	ISTRICT,	On	TARIO	

d(meas.)Å	hkl	d(calc.)Å	I(est.)	d(meas.)Å	hkl	d(calc.)Å
5.20	220	5.176	1	1.899	462	1.902
4.80	112	4.813	4	1.868	444	1.874
4.35	022	4.364	1	1.833	080	1.830
3.66	040	3 660	3	1811	064	1.816
3.00	040	3.000	J	1.011	006	1.812
3.53	132	3.525	1/2	1.776	280	1.775
3.28	240	3 974	2	1 758	264	1.762
	210	3,217	4	1.100	026	1.759
3.04	042	3.036	3	1.725	660	1.725
2.80	242	2.8 04	2	1.686	282	1.688
2.71	004	2.718	$\frac{1}{2}$	1.611	046	1.624
2.53	024	2.548	3	1.577	246	1.585
2.405	224	2.406	1/2	1.573	482	1.567
2.314	260	2.315	2	1.515	084	1.518
2.228	062	2.226	1/2	1.448 {	664	1.457
0 171	044	0.100	0	1 (10	066	1.457
2.171	044	2.182	2	1.412	682	1.414
2.083	244	2.091	2	1.401	484	1.402
d(meas.)Å	I(est.)	d(meas.)Å	I(est.)	d(meas.)Å	I(est.)	d(meas.)Å
1.359	2	1.220	¹ /2	1.109	2	.9662
1,320	1/2	1.205	2	1.086	1	.9593
1.292	2	1.167	2	1.064	1/2	.9215
1.269	1	1.156	1	1.026	2	.9051
1.254	1	1.136	2	1.013	1	.8953
	d(meas.)Å 5.20 4.80 4.35 3.66 3.53 3.28 3.04 2.80 2.71 2.53 2.405 2.314 2.228 2.171 2.083 d(meas.)Å 1.359 1.320 1.292 1.269 1.254	d(meas.)Å hkl 5.20 220 4.80 112 4.35 022 3.66 040 3.53 132 3.28 240 3.04 042 2.80 242 2.71 004 2.53 024 2.405 224 2.314 260 2.228 062 2.171 044 2.083 244 2.083 244 2.171 044 2.083 242 2.171 044 2.083 244 2.171 044 2.083 244 2.171 044 2.083 2 1.359 2 1.320 1/2 1.292 2 1.269 1 1.254 1	d(meas.)Å hkl d (calc.)Å 5.20 220 5.176 4.80 112 4.813 4.35 022 4.364 3.66 040 3.660 3.53 132 3.525 3.28 240 3.274 3.04 042 3.036 2.80 242 2.804 2.71 004 2.718 2.53 024 2.406 2.314 260 2.315 2.228 062 2.226 2.171 044 2.182 2.083 244 2.091 d (meas.)Å d (meas.)Å 1.359 2 1.205 1.292 2 1.167 1.269 1 1.136	d(meas.)Å hkl $d(calc.)$ Å $I(est.)$ 5.20 220 5.176 1 4.80 112 4.813 4 4.35 022 4.364 1 3.66 040 3.660 3 3.53 132 3.525 $1/2$ 3.28 240 3.274 2 2.304 042 3.036 3 2.80 242 2.804 2 2.71 004 2.718 $1/2$ 2.53 024 2.548 3 2.405 224 2.406 $1/2$ 2.314 260 2.315 2 2.228 062 2.226 $1/2$ 2.083 244 2.091 2 1.359 2 1.220 $1/2$ 1.320 $1/2$ 1.167 2 1.269 1 1.136 1	$d(\text{meas.})$ Å hkl $d(\text{calc.})$ Å $I(\text{est.})$ $d(\text{meas.})$ Å 5.20 220 5.176 1 1.899 4.80 112 4.813 4 1.868 4.35 022 4.364 1 1.833 3.66 040 3.660 3 1.811 $\left\{ \begin{array}{c} 3.53 \\ 3.28 \\ 240 \\ 3.28 \\ 240 \\ 2.80 \\ 242 \\ 2.804 \\ 2.804 \\ 2.804 \\ 2.804 \\ 2.171 \\ 004 \\ 2.718 \\ 1.611 \\ 2.53 \\ 024 \\ 2.548 \\ 3 \\ 1.577 \\ 2.405 \\ 224 \\ 2.406 \\ 1.251 \\ 2.228 \\ 062 \\ 2.226 \\ 1.412 \\ 2.083 \\ 244 \\ 2.091 \\ 2 \\ 1.401 \\ 2.083 \\ 244 \\ 2.091 \\ 2 \\ 1.09 \\ 1.320 \\ \frac{1}{2} \\ 1.254 \\ 1 \\ 1.156 \\ 1 \\ 1.026 \\ 1.254 \\ 1 \\ 1.136 \\ 2 \\ 1.013 \\ 1.01$	$d(meas.)$ Å hkl $d(calc.)$ Å $I(est.)$ $d(meas.)$ Å hkl 520 220 5.176 1 1.899 462 4.80 112 4.813 4 1.868 444 4.35 022 4.364 1 1.833 080 3.66 040 3.660 3 1.811 $\begin{pmatrix} 064\\ 006 \end{pmatrix}$ 3.53 132 3.525 $\frac{1}{2}$ 1.776 280 3.28 240 3.274 2 1.758 $\begin{cases} 264\\ 026 \end{pmatrix}$ 3.04 042 3.036 3 1.725 660 2.80 242 2.804 2 1.686 282 2.71 004 2.718 $\frac{1}{2}$ 1.611 046 2.53 024 2.548 3 1.577 246 2.405 224 2.406 $\frac{1}{2}$ 1.573 482 2.314 260 2.315 2 1.412 682 2.083 244 2.091 2 1.412 682 2.083 244 2.091 2 1.401 484 $d(meas.)$ Å $I(est.)$ $d(meas.)$ Å $I(est.)$ $I(est.)$ 1.359 2 1.205 2 1.086 1 1.292 2 1.167 2 1.064 $\frac{1}{2}$ 1.269 1 1.136 2 1.013 1

(114.6 mm. diameter camera with Ni filtered Cu radiation) Tetragonal : a = 14.64Å. c = 10.87Å.

The space group, either $P\overline{4}2m$ or P422 or P4/mmm, determined by Peacock (1950b), is confirmed. Cell parameters and contents are given in Table 4 for hauchecornite from the three localities.

Reflectance and Microhardness

The apparatus for measuring the reflectance 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 16.5:1 objective with a numerical aperture of 0.40 was used. The reflectance

Locality	a(Å)	c(Å)	Z
Westphalia	7.29 **	5.40 **	1
-	(14.58)	(10.80)	(8)
Vermilion	14.517 *	10.803 *	8
Strathcona	14.64 ± 0.01	10.87 ± 0.01	8

TABLE 4. CELL PARAMETERS OF HAUCHECORNITE

* J. D. Grice (pers. comm.) Accuracy within 0.005%.

** Peacock (1950b).

Wavelength	(nm)	470	546	589	650	VHN ₅₀ (kg/mm²)
<i>n</i>	Max.	40.4-44.4	44.6-48.1	47.1-50.3	49.7-52.5	
		43.0	47.1	49.2	51.6	
Vermilion						516-655
	Min.	40.0-43.4	44.6-48.0	46.8-49.9	49.1-52.4	
		41.6	46.2	48.2	50.8	
	Max.	41.1-42.7	44.4-45.3	45.8-47.1	47.0-49.8	
		42.1	44.9	46.1	48.5	
Wesphalia	L					447-655
*	Min.	40.6-41.9	43.4-44.8	45.9-46.1	46.7-48.5	
		41.3	44.1	46.0	47.9	
	Max.	44.6-45.2	47.2-48.1	48.6-49.8	50.6-54.1	
		44.8	47.7	49.4	51.9	
Strathcona	1					182-825
	Min.	40.7-41.5	43.3-44.4	44.9-46.4	47.6-49.0	
		41.2	43,9	45.6	48.2	

TABLE 5. REFLECTANCE AND MICROHARDNESS OF HAUCHECORNITE

values for the four standard wave-lengths, using silicon as a standard, are given in Table 5 for the three varieties of hauchecornite.

The microhardness measurements for hauchecornite from the Vermilion mine, Westphalia and the Strathcona mine, are given in Table 5. The microhardness was determined using a Leitz Durimet Vickers hardness tester equipped with polarizing filters and rotating stage. An indentation time of 20 seconds and a load of 50 grams was used for all measurements.

Conclusion

The formula for hauchecornite may be written $Ni_9(Bi,X)_2S_8$, where X is either As, Sb or Te. The arsenian, antimonian and tellurian varieties are characterized by the substitution of the appropriate element for Bi, but not in excess of Bi. These varieties may be designated arsenian, antimonian and tellurian hauchecornite.

A crystal structure determination on hauchecornite currently is being undertaken by Mr. J. D. Grice at the University of Manitoba, Department of Earth Sciences.

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