HAUCHECORNITE*

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ABSTRACT

Study of a specimen (Harvard Mineralogical Museum, 89710) from the original locality, Friedrich mine, Hamm a. d. Sieg, Westphalia, confirms the individuality of hauchecornite. Tetragonal, $a : c = 1 : 0.7404$ (goniometric and x-ray), with $c(001)$, $a(010)$, $m(110)$, $q(011)$, $p(021)$, $e(111)$; tabular on c and bipyramidal. Laue symmetry $4/mmm$; $a = 7.28$, $c = 5.39$ kX (λ Cu$K\alpha_1 = 1.5374$ kX); allowable space groups, $P\bar{4}2m$, $P42$, $P4/mmm$ (not $P4_22$). Unit cell content, $Ni_9(Bi, Sb)_2S_8$ (not $Ni_8(Bi, Sb)_2S_8$). $G = 6.36$ (on crystal weighing 17 mg.). Strongest x-ray powder lines for identification: 2.79 kX (10), 2.39 (6), 2.30 (6), 4.34 (5), 1.861 (5). Associated with millerite, ullmannite (or kallilite), and gersdorffite (or corynite), with quartz.

Our continuing Toronto studies of rare and doubtful ore minerals often show that a substance originally thought to be a new mineral consists in fact of one or more already known species; and in this event we can do a service to mineralogy by striking the worthless name from the nomenclature. Occasionally, however, we find that a substance in question is composed, wholly or in part, of a mineral with clearly distinctive properties; and in such circumstance we have the pleasanter task of confirming the individuality of a mineral which was hitherto in disrepute, owing perhaps to an inadequate original description, or to later unfavourable but superficial observations or suggestions, or merely to lack of the eventual substantiating work by which the validity of most good mineral species is finally placed beyond all doubt.

Hauchecornite is a mineral of the second sort. Originally described in detail, with full goniometric, physical, and chemical information, and a careful account of associations and paragenesis, hauchecornite was never examined again except in polished sections of massive ore showing an intergrowth of several minerals. Thus the mineral has been condemned as "a mixture," a verdict by which many supposed new ore minerals and a few good species have been hustled to oblivion.

Since many may have access only to brief note in Dana (1944, p. 242) a more detailed summary of the work on hauchecornite will be useful. The mineral was first mentioned by Scheibe (1888) and later named after W. Hauchecorne (Director of the Geological Survey and the Mining Academy, Berlin) and fully described by Scheibe (1893). Crystals tetragonal, $a:c = 1:1.05215$ (8 crystals), with $c(001)$, $a(100)$, $m(110)$, $e(101)$, $s(112)$, $o(111)$, and vicinals, mostly tabular on c, also bipyramidal to short prismatic (14 figures). No cleavage; fracture flat conchoidal; $H = 5$; $G = 6.4$; light bronze-yellow, tarnishing darker; lively metallic lustre on a

fresh break; streak grey-black. Four generally concordant analyses (quoted later) by three chemists, interpreted as $(Ni, Co, Fe)_7(S, Bi, Sb, As)_8$ or $Ni_{14}SbBi_2S_{13}$. Found in a pocket opened in 1884, containing about 5 tons of ore in siderite gangue, in the Friedrich mine, near Wissen a. d. Sieg. The upper part of the pocket carried mainly millerite (NiS) and hauchecornite, the lower part kallilite (bismuthian ullmannite, $Ni(Sb, Bi)S$). Some specimens showed siegenite $(Co, Ni)_3S_4$ and zincblende and in cavities bismuthinite and quartz. Small crystals of hauchecornite perched on idiomorphic millerite proved the order of deposition of these minerals.

Polished sections of ore specimens containing hauchecornite from the original and only proved locality have been described by Schneiderhöhn & Ramdohr (1931, p. 372), Short (1940, p. 140), and Harcourt (1942, p. 105). Although differing in some details these notes describe hauchecornite as similar to pyrrhotite in colour, moderately to strongly anisotropic; hardness E; contains Ni, Bi, S; etch tests: HNO_3 brown, HCl, KOH, $FeCl_3$, KCN, $HgCl_2$, negative; associated with millerite and ullmannite. Harcourt obtained a distinctive x-ray powder pattern from hauchecornite. Short also noted a second unknown mineral, containing Ni, As, Sb, S; grey with yellow tinge; strongly anisotropic; hardness and etch-tests like those of hauchecornite. We have found nothing corresponding to this substance in our material.

Professor Clifford Frondel kindly provided a typical specimen and polished section of hauchecornite (Harvard Mineralogical Museum, 89710, Friedrich mine, Hamm a. d. Sieg, Westphalia) for the study of this mineral, and Professor R. M. Thompson (Vancouver, B. C.) assisted in the study of the polished section.

The hand specimen shows an open intergrowth of well crystallized, hauchecornite in bronze-colored squarish tables, up to 5 mm. wide and 3 mm. thick, showing good basal and truncating faces, and groups of brassy radiating prismatic crystals of millerite up to 5 mm. long, which sometimes penetrate the hauchecornite tables. These well crystallized minerals pass into massive tarnished ore with a little quartz gangue. The physical properties of hauchecornite agree well with the original description. A clean crystal (17 mg.) gave $G = 6.36$ on the Berman balance, as compared to $a = 6.35 - 6.47$ in Scheibe (1893).

The polished section from a piece of compact ore shows idiomorphic sections of tabular hauchecornite crystals, pinkish white, and distinctly anisotropic, giving parallel extinction and sometimes a blue polarization colour in the 45° position. Against the hauchecornite the millerite prisms are yellowish white and more anisotropic. Rounded blebs of a grey isotropic mineral occur with the hauchecornite. These give the ullmannite type of x-ray powder pattern, with $a = 5.91$ kX. The mineral could be

ordinary ullmannite ($a = 5.89 - 5.91$ A, Peacock & Berry, 1940) or the bismuthian ullmannite, kallilite ($a = 5.915$, Peacock & Berry, 1940) originally described from the Friedrich mine. In addition there are pinkish white isotropic subhedral grains in the gangue. These give the same type of x-ray powder pattern with $a = 5.71$ kX; this value compares with $a = 5.68 - 5.72$ for gersdorffite from German localities and it is near $a = 5.724$ for the antimonian variety, corynite (Peacock & Berry, 1940). By rough estimate the amount of millerite associated with hauchecornite is 10–30 per cent while the amount of ullmannite or kallilite might be 5–10 per cent.

Among the crumbs from the specimen of hauchecornite was found a small well-formed crystal which was suitable for reflection and x-ray goniometry as well as a measurement of specific gravity with the Berman balance. The crystal is 0.5 mm. in greatest dimension and it shows fair faces of all the common forms reported by Scheibe. The two-circle measurements obtained on this crystal are compared with calculated angles based on the tetragonal ratio:

$$a : c = 1 : 0.7404$$

which was derived from reflection and subsequent x-ray measurements. For comparison Scheibe's more numerous measurements of the angles cs, co, ce, are given (Table 1). The adopted setting corresponds to a tetragonal P-cell; it is related to Scheibe's setting by the transformation formulae:

Scheibe to Peacock: $\frac{1}{2}\bar{1}0/\frac{1}{2}\frac{1}{2}0/00\frac{1}{2}$
Peacock to Scheibe: $110/\bar{1}10/002$

In the absence of a general form (hkl) there is no direct morphological indication of the crystal class. But since the forms $s(011)$, $o(021)$, $e(111)$, are apparently tetragonal bipyramids, the class is probably $\bar{4}2m$, 422, or $4/mmm$.

TABLE 1. HAUCHECORNITE: MEASURED AND CALCULATED ANGLES
Tetragonal; $a:c = 1:0.7404$

Forms	Measured φ	ρ	No. of Faces	Calculated φ	ρ	Forms	Scheibe (1893) Measured $c:(hkl)$	No. of Faces
c (001)	—	0° 00′	1	—	0° 00′	c (001)		
a (010)	0° 00′	89 53	3	0° 00′	90 00	m (110)		
m (110)	45 02	90 28	1	45 00	90 00	a (010)		
s (011)	0 00	36 28	4	0 00	36 31	s (112)	35° 36′ —38°13′	13
o (021)	0 00	54 55	4	0 00	55 58	o (111)	54 57½—56 29	13
e (111)	45 02	46 24	2	45 00	46 19	e (011)	45 25½—46 46	31

The crystal of hauchecornite gave sharp rotation and Weissenberg photographs with [001] and [100] as rotation axes, leading to the cell dimensions:

$$a = 7.28, c = 5.39 \text{ kX}$$

using $CuK\alpha_1$ with $\lambda = 1.5374$ kX. The Laue symmetry is $4/mmm$ (classes $\bar{4}2m$, $4mm$, 422, $4/mmm$), but the bipyramidal crystal forms exclude $4mm$. Strictly, there are no systematically missing spectra and the probable space-groups are thus $P\bar{4}2m$, $P42$, $P4/mmm$. The space group $P4_22$ mentioned in an abstract of this paper (1950) was later found to be excluded by an exception, (003) vvw, to the condition $(00l)$ present only with l even.

The x-ray powder pattern (Table 2) is distinctive and unlike any other in our collection. The observed intensities and spacings agree well with those given by Harcourt (1942).

For the determination of the unit cell content of hauchecornite we have the four original analyses, given in the upper part of Table 3 with explanatory notes taken from Scheibe (1893).

In view of the care which was evidently given to the preparation and analysis of the samples, especially 2 and 3, it seems proper first to calculate the empirical cell contents form each analysis, using the given measured specific gravities (6.36, M.A.P., for analysis 4) and the appropriate mass factor, 1.650. In this calculation it is assumed that all the elements—except the trifling amounts of Zn, Pb, and Cu, which have been removed as the common sulphides—are contained in hauchecornite. This is in keeping with the composition of the ullmannite group in which the same elements, Ni, Co, Fe, Bi, Sb, As, S, are all found in various amounts in varieties from Siegen (Dana, 1944, p. 301). In the lower part of Table 3, especially under column A which gives the averages for the two most reliable analyses, 2 and 3, it is clear that (Bi, Sb, As) amounts to 2 atoms per unit cell while S evidently tends to 8 atoms. On the other hand, (Ni, Co, Fe) persistently and considerably exceeds 8 atoms, which was the number assumed in the cell content $Ni_8(Bi, Sb)_2S_8$ proposed in the abstract (1950), to suit the supposed space group $P4_22$ in which there are only 2-fold, 4-fold, and 8-fold positions.

A reconsideration of the problem of the cell content of hauchecornite now suggests $Ni_9(Bi, Sb)_2S_8$ as the ideal formula. This formula gives the calculated composition (column B) which agrees well with the analyses, and the best average cell content (column A) gives $(Ni, Co, Fe)_{8.98}$ $(Bi, Sb, As)_{2.01}S_{8.00}$ when increased by 1.7 per cent. This corresponds to an increase of density from 6.47 to 6.58. Such a difference between measured and calculated densities is not uncommon; for ullmannite, for

TABLE 2. HAUCHECORNITE—$Ni_9(Bi, Sb)_2S_8$: X-Ray Powder Pattern

Tetragonal, $P4/mmm$; $a=7.28$, $c=5.39$; $Z=1$

I	θ(Cu)	d(meas.)	(hkl)	d(calc.)	I	θ(Cu)	d(meas.)	(hkl)	d(calc.)
1	8.5°	5.20	(110)	5.148	½	28.5°	1.611	(232)	1.616
5	10.2	4.34	[(011)	4.332				(023)	1.611
½	10.65	4.16	—	—	2	29.25	1.573	(123)	1.573
4	12.2	3.64	(020)	3.640	1	30.7	1.506	(042)	1.508
4	13.7	3.25	(120)	3.256	½	32.0	1.451	(332)	1.447
1	14.7	3.03	(021)	3.017	½	33.1	1.408	(051)	1.406
10	16.0	2.79	(121)	2.787				(341)	1.406
1	17.6	2.54	(012)	2.527	1	33.5	1.393	(242)	1.393
6	18.75	2.39	(112)	2.388	2	34.7	1.350	(004)	1.348
6	19.5	2.30	(221)	2.323	2	35.8	1.314	(251)	1.311
			(130)	2.302	1	36.9	1.280	(052)	1.281
½	20.4	2.21	(031)	2.213				(342)	1.281
½	20.8	2.16	(022)	2.166				(043)	1.279
1	21.7	2.08	(122)	2.076	3	37.5	1.263	(024)	1.264
5	24.4	1.861	(222)	1.861				(152)	1.262
3	25.0	1.819	(040)	1.819	½	38.0	1.249	(350)	1.249
3	25.3	1.799	(032)	1.803				(124)	1.245
1	26.0	1.754	(132)	1.751	1	39.3	1.214	(351)	1.216
			(013)	1.744				(060)	1.213
2	26.6	1.717	(330)	1.716	2	41.3	1.165	(161)	1.168
1	27.25	1.679	(141)	1.678				(442)	1.161

I	θ(Cu)	d(meas.)	I	θ(Cu)	d(meas.)	I	θ(Cu)	d(meas.)
½	41.8°	1.153	1	52.9°	0.964	½	59.5°	0.892
1	42.7	1.134	1	53.4	0.958	½	61.2	0.877
2	45.3	1.082	½	55.7	0.931	1	65.5	0.845
2	46.45	1.061	1	56.7	0.920	1	71.7	0.810
1	48.2	1.031	2	58.4	0.903	2	79.6	0.782
1	49.7	1.008						

example, Dana (1944, p. 301) gives $G = 6.65 \pm 0.04$ (measured), 6.793 (calculated). Also, there is now no structural objection to 9 Ni atoms in the unit cell, since the probable space groups, $P\overline{4}2m$, $P42$, $P4/mmm$, all have 1-fold positions as well as positions with 2, 4, and 8 equipoints. And finally, metallic sulphides, especially those of Fe, Co, and Ni, are prone to give defective or complex compositions: one recalls pyrrhotite $Fe_{1-x}S$, smaltite $NiAs_{3-x}$, maucherite $Ni_{11}As_8$ or $4Ni_{3-x}As_2$, and most cogently, pentlandite, for which the composition $(Fe, Ni)_9S_8$ is established not only by chemical analyses but by successful synthesis and determination of the atomic arrangement.

The cell formula $Ni_9(Bi, Sb)_2S_8$ was not adopted for hauchecornite

TABLE 3. HAUCHECORNITE: ANALYSES AND CELL CONTENTS

	1	2	3	4	A	B
Ni	41.08	45.054	45.883	45.26	45.47	46.17
Co	2.83	0.704	0.82	—	0.76	—
Fe	0.89	0.271	0.17	trace	0.22	—
Zn	0.12	—	—	—	—	—
Pb	0.64	0.03	—	—	—	—
Cu	—	—	—	0.09	—	—
Bi	24.06	24.508	23.72	24.74	24.11	24.36
Sb	5.69	6.738	6.226	3.14	6.48	7.10
As	1.96	0.895	0.45	3.04	0.67	—
S	22.71	22.879	22.625	22.71	22.75	22.37
	99.98	101.079	99.894	98.98	100.46	100.00
Ni	7.77	8.51	8.77	8.59	8.64	9
Co	0.53	0.13	0.16	—	0.15	—
Fe	0.18	0.05	0.03	—	0.04	—
	8.48	8.69	8.96	8.59	8.83	9
Bi	1.28	1.30	1.27	1.32	1.29	4/3
Sb	0.52	0.61	0.57	0.29	0.59	2/3
As	0.29	0.13	0.07	0.45	0.10	—
	2.09	2.04	1.91	2.06	1.98	2
S	7.80	7.91	7.82	7.88	7.87	8

1. Anal. Fischer, after withdrawing 1.59 per cent quartz. G=6.35 after withdrawing quartz; made on carefully picked crystals and massive ore.

2, 3. Anal. Hesse, on material composed wholly of crystal fragments with bright fracture surfaces and no trace of impurities or alteration. G=6.47.

4. Anal. Fraatz, on a small sample of material carefully picked in Clausthal.

A. Average composition and cell content from analyses 2 and 3.

B. Composition calculated for the ideal cell content $Ni_9(Bi, Sb)_2S_8$, with Bi : Sb=2 : 1.

without searching for a simpler formula on the assumption that the analyzed samples did contain significant amounts of the observed associated minerals, millerite NiS, and kallilite $Ni(Sb,Bi,)S$. Since Ni and S are present in equal or nearly equal proportions in these minerals, and in the analyses of hauchecornite, the assumption that either millerite or kallilite was present even in considerable amounts in the analysed samples has mainly the effect of raising or lowering the proportion of (Bi, Sb) relation to Ni and S. Trial quickly shows that (Bi,Sb) is thus displaced away from the reasonable value of 2 atoms toward 1 or 3, and that even

improbably large admixtures give no satisfactory alternative cell content.

On the other hand, since the inferred composition of hauchecornite is roughly $3NiS + Ni(Sb, Bi)S$, admixture of 3 parts of millerite and 1 part of kallilite produces practically no change of composition. In the polished section the proportions of millerite and kallilite were estimated at 10–30 per cent and 5–10 per cent respectively. Even if such amounts were actually included in the analyzed hauchecornite, which can hardly be admitted in view of Hesse's statement regarding the preparation of his samples, the inferred composition of hauchecornite would be almost unchanged. From the appearance of the hand specimen and the polished section I am inclined to believe that, despite all reasonable care in picking, some smaller amounts of millerite and kallilite were inevitably included in analysed samples; but that, for the reasons just given, these admixtures have practically no effect on the inferred composition and cell content. The cell formula $Ni_9(Bi, Sb)_2S_8$ is therefore retained for hauchecornite. It will be interesting if this cell content should be confirmed by synthesis and structural analysis; so far these have not been attempted.

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