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ELECTRON MICROPROBE ANALYSIS OF HODRUSHITE

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ABSTRACT

Electron microprobe analysis of hodrushite, a new sulphosalt mineral from Hodrusa, Czechoslovakia, gave Cu 13.88 ± 0.88, Bi 64.92 ± 0.55, Fe 0.44 ± 0.01 and S 18.98 ± 0.89 (wt. %; error = 1 standard deviation). Mn, Co, Ni, Zn, Sb, Pb and Ag were not detected. The compositional formula based on 22 sulphur atoms is

$$Cu_{8.12\pm0.06}\ Bi_{11.54\pm0.12}\ Fe_{0.29\pm0.01}\ S_{22.00\pm1.04}$$

in good agreement with the formula, $Cu_8Bi_{10}Me_2S_{22}$, derived from *x*-ray crystal structure analysis.

Because of uncertainty in some of the matrix correction procedures the *x*-ray intensity data was processed using the Ziebold-Ogilvie empirical procedure and by two theoretical procedures involving absorption, fluorescence and atomic number corrections. All three procedures gave very close results when emplectite was used as a standard, but differed significantly when only elements and binary sulphides were used in the theoretical procedures.

ELECTRON MICROPROBE ANALYSIS OF HODRUSHITE

Hodrushite, a new sulphosalt mineral of copper and bismuth, was described from copper-bearing ore veins of volcanic origin in the region of Banska Hodruša, Czechoslovakia (Kodĕra *et al.* 1970). It occurs in small amounts as needle-shaped crystals, irregular grains of fine-grained aggregates, and multiple crystal intergrowths, associated with quartz, hematite, and locally chalcopyrite and wittichenite (?).

Because of the difficulties encountered in obtaining a clean sample for wet-chemical analysis, a typical hodrushite specimen was polished for chemical analysis by an electron microprobe. Procedures available for correcting microprobe *x*-ray intensities for matrix effects to obtain element concentrations were carefully chosen and the results compared in order to provide a reliable analysis of hodrushite.

The analysis was performed on an ACTON-CAMECA MS-64 electron microprobe. Fixed-time counts of *x*-ray intensities were made on hodrushite and standards, comprising copper and bismuth metals, synthetic compounds and minerals. This data was treated in two fundamentally different ways to

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obtain the hodrushite composition. In the first method *x*-ray intensity data was corrected for matrix effects using the empirical procedures of Ziebold & Ogilvie (1964). In the second, or theoretical, method, matrix effects were corrected using a number of well-known absorption, fluorescence and atomic number procedures.

STANDARDS

Copper (99.99%), bismuth (99.99%), Cu_2S (melted with Cu in slight excess), Bi_2S_3, emplectite, $CuBiS_2$ were used as standards. Available chemical analyses of emplectite[1] (given in Dana's System of Mineralogy, 7th ed., vol. 1, p. 436) from this area are very close to ideal, hence the mineral is taken as stoichiometric. The sample used was identified as emplectite from an *x*-ray diffraction powder pattern which was identical to those published for this mineral from the same locality (PDF Card #10-474).

DATA PROCESSING

Multiple readings of peak and background intensities taken for Cu, Bi and S on hodrushite and standards were averaged, their ratios calculated and standard deviations, σ, obtained (Table 1). No deadtime correction was applied (except where noted) because of relatively low count rates and a deadtime correction for each spectrometer of less than one microsecond. Count rates for all elements in hodrushite were corrected for drift by periodically repeating readings on standards and interpolating these values against time using a 2 to 4 term Lagrange formula.

There are a number of procedures for changing *x*-ray intensity data into chemical compositions but the relative merits of any one procedure over another is still a matter of debate. A particular correction procedure may give reasonable results when used on elements relatively close to one another in atomic number, but when they differ widely in atomic number these procedures are less accurate. In the present case there are large atomic number differences between sulphur, copper and bismuth wherein absorption, fluorescence and atomic number corrections are imperfectly known. In such cases analyses should be made using standards as close in composition to the unknown as possible. In our analysis we used the mineral standard emplectite and computed the composition of hodrushite using the Ziebold-Ogilvie (1964) empirical procedure, and the Ruberol-Tong-Conty (1966) and MAGIC (Colby 1967) theoretical procedures.

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[1] From the Tannenbaum Mine, Schwartzenberg, Saxony; obtained from the Redpath Museum, McGill University, Cat. No. 734.

A. *Ziebold-Ogilvie empirical correction procedure*

1) Concentrations of Cu and Bi were obtained using the form of the Ziebold-Ogilvie (1964) equation

$$\frac{1 - K_A}{K_A} = \alpha_{AB}\frac{1 - C_A}{C_A} \qquad \ldots\ldots\ldots\ldots (1)$$

where K_A and C_A are the measured count ratio and concentration of element A in compound AB. When compounds are used on the binary join, such as $AS - BS$, the measured count ratio K_A and the concentration C_A relate to the binary end member AS. Hence using a simplified formula

$$\mathrm{var}\ (y) = \sum_i \left(\frac{\delta y}{\delta x_i}\right)^2 \mathrm{var}\ (x_i) \qquad \ldots\ldots\ldots\ldots (2)$$

TABLE 1. DATA ON MICROPROBE MEASUREMENTS MADE ON HODRUSHITE AND EMPLECTITE.

Measurement # 1 — 15kv

		Hodrushite			Emplectite		
Radiation	Standard	n	$K\ \frac{\text{hd}}{\text{std}}$	σ	n	$K\ \frac{\text{emp}}{\text{std}}$	σ
Cu$K\alpha_1$	Cu	27	0.14996	0.00124	21	0.21077	0.00162
Bi$L\alpha_1$	Bi	27	0.63780	0.01260	21	0.58920	0.01268
Fe$K\alpha_1$	Fe	20	0.00504	0.00019	10	0.00000	0.00013
	py	27	0.01054	0.00060	21	0.00000	0.00052
			Measurement # 2 — 15kv				
Cu$K\alpha_1$	Cu	13	0.14742	0.00117			
	Cu_2S	13	0.19830	0.00165			
Bi$L\alpha_1$	Bi	13	0.61016	0.00912			
	Bi_2S_3	13	0.73314	0.01289			
			Measurement # 3 — 20kv				
Cu$K\alpha_1$	Cu	28	0.14066	0.00067	20	0.19080	0.00079
	Cu_2S	28	0.18797	0.00067	20	0.19080	0.00079
Bi$L\alpha_1$	Bi	28	0.56163	0.00287	20	0.53469	0.00256
	Bi_2S_3	28	0.75673	0.00403	20	0.70243	0.00361
S$K\alpha_1$	Cu_2S	28	1.40180	0.00725	20	1.37791	0.00872
	Bi_2S_3	28	0.95011	0.00461	20	0.94401	0.00725
	py	25	0.35492	0.00269	20	0.34776	0.00234
Fe$K\alpha_1$	Fe	25	0.00465	0.00007	7	0.00000	0.00003
	py	25	0.01078	0.00017	7	0.00000	0.00008

the variance of C_A becomes :

$$\mathrm{var}\,(C_A) = \frac{(K_A - K_A{}^2)^2}{(1 + \alpha_{AB}K_A - K_A)^4}\,\mathrm{var}\,(\alpha_{AB}) + \frac{\alpha^2{}_{AB}}{(1 + \alpha_{AB}K_A - K_A)^4}\,\mathrm{var}\,(K_A) \qquad \ldots\ldots\ldots\ldots(3)$$

In addition to the end members of the Cu_2S — Bi_2S_3 binary, or the pure metal standards Cu and Bi, only one intermediate member, emplectite, was used, but its closeness in composition to hodrushite assured satisfactory results. Both methods of treatment of data, using binary sulphides or metals as standards, gave very similar results (Table 2). Hodrushite was treated as a member of the Cu_2S — Bi_2S_3 system, disregarding its small content of iron.

TABLE 2. REPRESENTATIVE RESULTS OF HODRUSHITE ANALYSES FROM VARIOUS CORRECTION PROCEDURES (IN WEIGHT PERCENT). THE ERROR IS ONE STANDARD DEVIAITION.

	Cu	Bi	Fe	S	Standards and remarks
A.	*Ziebold-Ogilvie procedure :* 3rd measurement.				
1)	13.82 ± 0.08	64.75 ± 0.29	0.47 ± 0.01	18.98 ± 0.89*	Sulphides
2)	13.90 ± 0.09	64.63 ± 0.30	0.47 ± 0.01	18.98 ± 0.89*	Elements
	Combined 1, 2 and 3 measurements from Table 1.				
3)	13.82 ± 0.08	64.85 ± 0.46	0.47 ± 0.01	18.98 ± 0.89*	Sulphides
4)	13.92 ± 0.08	65.25 ± 0.55	0.47 ± 0.01	18.98 ± 0.89*	Elements
B.	*Ruberol-Tong-Conty procedure :* 3rd measurement.				
5)	13.50 ± 0.06	61.35 ± 0.16	0.45 ± 0.01		Elements
6)	13.87 ± 0.09	64.67 ± 0.25	0.47 ± 0.01		5) recalculated using $H_{\mathrm{emp.}}$ and H_s.
C.	*MAGIC :* 3rd measurement.				
7)	11.79 ± 0.11	64.56 ± 0.40	0.41 ± 0.01	13.73 ± 0.28	Elements, and sulphur from FeS_2.
8)	11.95 ± 0.14	65.28 ± 0.42	0.38 ± 0.01	15.50 ± 0.25	Sulphides, and sulphur from Cu_2S.
9)	13.87 ± 0.15	64.58 ± 0.61	0.41 ± 0.01	18.87 ± 0.45	7) recalculated using $H_{\mathrm{emp.}}$; sulphur from FeS_2.
10)	14.00 ± 0.16	64.70 ± 0.64	0.41 ± 0.01	18.99 ± 0.40	7) recalculated using $H_{\mathrm{emp.}}$ and H_s; sulphur from Cu_2S.

* Sulphur by modified Ziebold-Ogilvie procedure and data only from measurement 3.

2) Sulphur was measured using a modification of the Ziebold-Ogilvie formula. A new sulphur "count ratio" K^* may be computed in a binary system AS — BS as follows :

$$K^* = \frac{K^U_{AS} - K^{AS}_{AS}}{K^{BS}_{AS} - K^{AS}_{AS}} = \frac{K^U_{AS} - 1}{K^{BS}_{AS} - 1} \qquad (4)$$

where K^U_{AS} is the ratio of sulphur counts in an unknown compared to that in the end member AS ; K^{BS}_{AS} and K^{AS}_{AS} are similar terms, the latter being equal to 1. The variance of K^* is then

$$\mathrm{var}\ (K^*) = \left(\frac{1}{K^{BS}_{AS} - 1}\right)^2 \mathrm{var}\ (K^U_{AS}) + \left(\frac{1 - K^U_{AS}}{(K^{BS}_{AS} - 1)^2}\right) \mathrm{var}\ (K^{BS}_{AS}) \qquad (5)$$

Having calculated K^*, the concentration of the first binary compound C_{AS} in the unknown can be calculated from sulphur count rates using a modified expression of equation 3,

$$\frac{1 - K^*}{K^*} = \alpha \frac{C_{AS}}{1 - C_{AS}} \qquad (6)$$

where α was evaluated in the present analysis using emplectite. The variance of C_{AS} can be computed from the same type of expression (eqn. 3) as was the variance of C_A. The amount of sulphur is obtained by computing C_{AS} or C_{BS} and reducing them to sulphur percentages. It must be stressed that this is a direct measurement and calculation for sulphur and not a "sulphur by difference" analysis.

B. Theoretical correction procedures

The count rate data for Cu, Bi and S used in part A were also converted to weight percentages using theoretical matrix corrections for *x*-ray absorption, fluorescence and atomic number effects.

1) The Ruberol-Tong-Conty (1966) absorption and atomic number correction and Reed-Long (1963) fluorescence correction were used assuming hodrushite to be in the Cu_2S — Bi_2S_3 binary system and using elements as standards. Standard deviations of concentrations were calculated for arrays of precalculated count ratios using a 4-point Lagrange interpolation procedure for this purpose.

2) MAGIC, a computer program written by J. W. Colby (1968) was used. It includes the following corrections : dead-time, absorption (Duncumb & Shields 1966), characteristic fluorescence (Reed 1965), and atomic

number (Duncumb & Shields 1963, and Duncumb & de Casa 1967). This program processes all the elements and calculates standard deviations.

The element concentrations in hodrushite obtained from these procedures were again corrected by comparing theoretical and measured values for each element in Cu_2S, Bi_2S_3 and emplectite. The formula

$$C_{\text{hd}} \text{ (corrected)} = C_{\text{hd}} \text{ (measured)} \times H \quad \ldots\ldots\ldots\ldots (7)$$

was used where C_{hd} (measured) is a concentration of the *i*th element in hodrushite as measured and processed, and H is the correction coefficient. Two ways of finding H were chosen :

a) using data from emplectite only, hence

$$H = H_{\text{emp}} = \frac{C_{\text{emp}} \text{ (theoretical)}}{C_{\text{emp}} \text{ (measured)}} \quad \ldots\ldots\ldots\ldots (8)$$

where C_{emp} denotes concentrations of a given element in emplectite; and

b) using linear interpolation between data for emplectite and one of the end member standards in the $Cu_2S - Bi_2S_3$ system. Thus

$$H = \frac{H_s (C_{\text{hd}} - C_{\text{emp}}) + H_{\text{emp}} (C_s - C_{\text{hd}})}{C_s - C_{\text{emp}}} \quad \ldots\ldots\ldots\ldots (9)$$

the subscript *s* denoting the end-member sulphide used. As the theoretical C_{emp} and C_s were used the final value for the composition of hodrushite was obtained by re-iterating the expression

$$C_{\text{hd}\,(n+1)} = C_{\text{hd}\,(n)} H_{(n)} \quad \ldots\ldots\ldots\ldots (10)$$

until a desired precision of corrected C_{hd} was reached.

Minor and trace elements in hodrushite and emplectite were calculated from *x*-ray intensities, minus backgrounds, using the calculated composition of hodrushite and the stoichiometric composition of emplectite in all correction procedures. Iron was the only minor element detected in hodrushite. The Ruberol-Tong-Conty (1966) absorption and atomic number correction, along with the Reed & Long (1963) fluorescence correction, were used to process the *x*-ray intensities of these elements. The elements checked are listed in Table 3.

DISCUSSION OF RESULTS

A summary of count rates, weight percentages and standard deviations is given in Tables 1, 2 and 3. Three independent sets of measurements for Cu and Bi gave mutually similar results. However when these measurements were processed by different correction procedures to yield element concentrations it was found that these computed concentrations differed significantly from one correction procedure to another. When the additional "*H*" correction procedure was applied to analyses obtained by the theoretical procedures in part B, page 509, they correlated more closely with those obtained using the Ziebold-Ogilvie empirical procedure.

All correction procedures yielded standard deviations for element concentrations based only on those calculated for count rates. As there are no precision limits available for the physical constants used in the theoretical procedures in part B, the apparent standard deviations of concentrations do not represent true estimates. The Ziebold-Ogilvie empirical procedure in which all corrections were made directly from standards, and where the bias is minimal due to the closeness in composition of emplectite and hodrushite, is believed to yield the best standard deviation of concentration estimates. These estimates were used to give precision limits to the accepted hodrushite analysis.

Table 3. Trace Element Analysis of Hodrushite and Emplectite.

Mineral	Radiation	n	K	σ_K	C wt. %	σ_C	Remarks
hd	$\mathrm{Mn}K\alpha$	20	0.00006	0.00015	0.006	0.015	n.d.
emp	″	10	0.00019	0.00015	0.019	0.015	n.d.
hd	$\mathrm{Zn}K\alpha$	20	0.00008	0.00028	0.007	0.025	n.d.
emp	″	20	0.00000*	0.00023	0.000*	0.021	n.d.
hd	$\mathrm{Pb}M\alpha$	25	0.00439	0.00222	0.47	0.24	n.d.
emp	″	15	0.0032	0.0028	0.31	0.53	n.d.
hd	$\mathrm{Ag}L\alpha$	25	0.00044	0.00044	0.08	0.07	n.d.
emp	″	15	0.00000*	0.00061	0.00*	0.10	n.d.
hd	$\mathrm{Sb}L\alpha$	15	0.00030	0.00035	0.04	0.05	n.d.
emp	″	15	0.00078	0.00067	0.11	0.10	n.d.
hd	$\mathrm{Co}K\alpha$	20	0.00000*	0.00012	0.00*	0.011	n.d.
emp	″	20	0.00018	0.00022	0.017	0.020	n.d.
hd	$\mathrm{Ni}K\alpha$	20	0.00000*	0.00024	0.000*	0.022	n.d.
emp	″	20	0.00000*	0.00032	0.000*	0.029	n.d.

n.d. = Not detectable.
* Peak-backgroud value zero or slightly negative.
$K = \dfrac{\text{Counts on unknown.}}{\text{Counts on pure element.}}$
n = Number of fixed-time readings.
hd = Hodrushite.
emp = Emplectite.
σ_K and σ_C are standard deviations.

The sulphur content calculated by the MAGIC program gave 13.73, 15.50 and 19.45 per cent S when FeS_2, Cu_2S and Bi_2S_3, respectively, were used as standards. After a recalculation which took into account the H_{emp} and H_s factors the sulphur analysis based on FeS_2 changed to 18.87 ($\sigma =$ 0.45), and that based on Cu_2S and Bi_2S_3 changed both to 18.99 ($\sigma = 0.40$) per cent S. These values are in excellent agreement with the 18.95 ($\sigma =$ 1.16) and 19.01 ($\sigma = 0.89$) obtained from the modified Ziebold-Ogilvie procedure when Cu_2S and Bi_2S_3 were in the *AS* position of equation 4. Sulphur analyses are the least accurate of all because the modified Ziebold-Ogilvie procedure depends directly on the difference in sulphur content, in this case very small, in the end members of the binary system.

The iron analysis was obtained from two independent measurements. The first measurement, processed in the trace element program (page 508), gave 0.48 ($\sigma = 0.02$) per cent Fe using the iron standard, and 0.43 ($\sigma = 0.02$) per cent Fe using the pyrite standard. In the second measurement the same correction program gave 0.47 ($\sigma = 0.007$) per cent Fe with the iron standard, whereas the MAGIC program gave 0.41 ($\sigma = 0.01$) with the iron standard and 0.38 ($\sigma = 0.01$) per cent Fe with the pyrite standard. As there is no available criterion for assessing the reliability of these results, a simple averaging was used.

From the minor and trace elements checked (Table 3), only *x*-ray counts on iron exceeded the detectability limits used, which were that detection is assumed when count rate exceeds that of background plus 3σ of background. Lead, reported in the classical chemical analysis by Kodera *et al.* (1970), is just below its detectable limit. As the sensitivity of the analysis for lead was low ($\sigma = 0.24$ per cent Pb), its detectability limits are high (about 0.5 per cent Pb). If the probable systematic errors of the measurements are taken into account they favor the decision to omit any appreciable amount of lead from the formula of hodrushite. Net counts for Mn, Zn, Ag, Sb, Co, Ni and As in hodrushite were statistically insignificant. In emplectite these elements, along with Pb and Fe, were also all below the detection limits.

Count rates for Cu, Bi and S in emplectite (Table 1) served as intermediate-standard values for the calculations on hodrushite. These data were used directly in the Ziebold-Ogilvie empirical procedure for the hodrushite analysis. However, in order to compute "*H*" factors, analyses of emplectite were obtained from the theoretical correction procedures. In the Ruberol-Tong-Conty procedure the copper analysis of emplectite was close to that expected in $CuBiS_2$, whereas that for bismuth was significantly lower. The results from MAGIC differed in the opposite way: copper was significantly low but bismuth was acceptable. Sulphur processed on MAGIC yielded low values which also differed significantly according to the standard used. The closest sulphur analysis was obtained using $\mathrm{Bi_2S_3}$ as a standard, indicating that Bi has most effect on SK_α radiation and that corrections for this effect are not well established. Thus we must assume that theoretical correction constants for Cu, Fe and S in the presence of Bi are not yet well known ; these procedures appear only to be usable in this and similar cases when standards close in composition to the unknown are available.

The homogeneity of hodrushite was checked using count rates taken on Cu, Bi and Fe simultaneously on three spectrometers from individual analyzed spots on the polished surface. When analyzed, the count rates revealed no mutual correlation nor was there a correlation with respect to location of analyzed spots on the specimen surface. All the deviations were small and when correlated with time they could be attributed to measurement errors. The pooled results of count rates from different areas of the sample showed no significant differences.

For a best estimate of the composition of hodrushite the results obtained from the empirical Ziebold-Ogilvie procedure, using all three measurements, were averaged with those obtained from the theoretical procedures, the latter with the additional "*H*" correction described on page 6 (Table 4). The possible biases of the individual measurements, and of individual correction procedures, are thus most probably diminished or mutually cancelled.

The structural formula of hodrushite based on the *x*-ray crystal structure analysis is $\mathrm{Cu_8Bi_{10}}Me_2\mathrm{S_{22}}$, where *Me* is mainly Bi with partial substitution of other metals (Kupčík & Makovicky 1968). The compositional formula may then be based on the assumption that sulphur positions are fully occupied, or that there are 20 metal atoms in the formula unit. Both these assumptions give practically the same compositional formula

TABLE 4. CHEMICAL COMPOSITION (WEIGHT PERCENT) AND FORMULAE OF HODRUSHITE.

1) Chemical composition :					
	13.88 ± 0.08	64.92 ± 0.55	0.44 ± 0.01	18.98 ± 0.89	98.23 ± 1.05
2) #1 normalized :					
	14.13 ± 0.17	66.09 ± 0.90	0.45 ± 0.02	19.33 ± 0.93	100.00 ± 1.30
3) Formula of hodrushite based on 20 metal atoms :					
	8.14 ± 0.06	11.57 ± 0.12	0.29 ± 0.01	22.05 ± 1.04	
4) Formula of hodrushite based on 22 sulphur atoms :					
	8.12 ± 0.38	11.54 ± 0.55	0.29 ± 0.22	22.00 ± 1.46	

(Table 4) which allows us to assume that all atomic positions in the structure are fully occupied.

The chemical formula of hodrushite based on the best estimates is then

$$Cu_{8.12\pm0.06}Bi_{11.54\pm0.12}Fe_{0.29\pm0.01}S_{22.00\pm1.04}$$

where the error estimate is the standard deviation of the number of atoms in the formula unit.

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