

# STUDIES OF MINERAL SULPHOSALTS: XXI—NUFFIELDITE, A NEW SPECIES

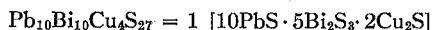
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## ABSTRACT

Nuffieldite occurs as prismatic to acicular crystals, up to 3 mm in length, in vugs in narrow quartz veins in the Lime Creek quartz diorite stock near Alice Arm, British Columbia on the property of B.C. Molybdenum Corporation. The mineral is orthorhombic, *Pnam* or *Pna2<sub>1</sub>*, with  $a = 14.61 \text{ \AA}$ ,  $b = 21.38 \text{ \AA}$ ,  $c = 4.03 \text{ \AA}$  (axis of elongation).

Qualitative analysis revealed the presence of the metals lead, bismuth, and copper. Quantitative analyses of these elements by x-ray spectroscopy, electron microprobe analysis, and atomic absorption spectroscopy are in close agreement. Because of the very small size of the sample (34 mg) a colorimetric analytical method was developed for sulphur analysis of samples weighing less than one milligram. The composition is Pb = 40.27%, Bi = 37.55%, Cu = 5.88%, S = 16.30% which gives the molecular formula:  $\text{Pb}_{10.0}(\text{Bi}_{9.45}, \text{Pb}_{0.22}, \text{Cu}_{0.87})\text{Cu}_{4.0}\text{S}_{20.73}$ . The calculated density is 7.006, and the measured density is 7.01. The ideal cell contents:



give the calculated density of 7.04.

The name is for Professor E. W. Nuffield of the University of Toronto.

## INTRODUCTION

Sulphosalt minerals at Alice Arm, British Columbia, were first recognized by A. D. Drummond in drill core from a molybdenum deposit of Kennco Exploration (Western) Limited, in 1960. They occur in vugs in quartz veins in quartz diorite. Similar sulphosalts are also found in quartz veins in the same quartz diorite exposed in the bed of Patsy Creek. In the course of the description of the principal new sulphosalt mineral<sup>1</sup> by Drummond, Trotter & Thompson (1962) a second new sulphosalt mineral was discovered by R. M. Thompson. Through the kindness of R. M. Thompson and E. W. Nuffield, the writer obtained the original x-ray powder photographs and entire sample (34.1 mg) of this second new mineral. In 1965 J. D. Scott visited the molybdenum property for the author and collected more material from eight of the quartz veins which outcrop in the bed of Patsy Creek. Only one of the veins contained the new sulphosalt, and from this an additional 20 milligrams were obtained. The new species is named nuffieldite<sup>2</sup> in honour of E. W.

\*Present address, Queen's University, Kingston, Ontario.

<sup>1</sup>This mineral, as yet unnamed, has the formula  $7\text{PbS} \cdot 3\text{Bi}_2\text{S}_8 \cdot (\text{Cu}, \text{Ag})_2\text{S}$ .

<sup>2</sup>The name has been approved by the Commission of New Mineral Names of the International Mineralogical Association.

Nuffield, who has made outstanding contributions to the understanding of many of the less well-known sulphosalt minerals.

#### *General geology of nuffieldite locality*

The Lime Creek stock is located six miles southeast of the town of Alice Arm on the northern coast of British Columbia. The stock is composite, and consists of granodiorite, quartz diorite, alaskite, granodiorite porphyry, and related breccia. The intrusion is intimately veined by a quartz stockwork in which molybdenite is the most important economic mineral.

The metallic minerals common to most of the quartz veins are: molybdenite, pyrite, galena, sphalerite, chalcopyrite, pyrrhotite, tetrahedrite, cosalite, aikinite, and Thompson's first new sulphosalt. The vein containing the nuffieldite differs from the others in that it lacks chalcopyrite, pyrrhotite, and tetrahedrite.

The quartz vein in which nuffieldite is found is  $\frac{1}{2}$  inch wide and contains small (1 mm) pyrite cubes and molybdenite flakes along the edges; the sulphosalt crystals are in 1–3 mm diameter vugs. Only two of the vugs were found to contain nuffieldite. The other vugs contained cosalite, aikinite, and the first new sulphosalt mineral. The only metallic mineral observed in contact with nuffieldite is aikinite.

#### PHYSICAL PROPERTIES

Nuffieldite has two distinct habits. The crystals from the vein in the bed of Patsy Creek are prismatic to acicular and are deeply striated and channelled parallel to [001]. The crystals frequently occur as bundles of parallel unterminated needles in the vugs. Some needles reach a length of 3 mm, although, typically, they are 1 mm long and 0.01 mm to 0.03 mm in diameter. The sample from the drill core consists of three small grains which are compact sub-parallel aggregates of stubby unterminated and deeply striated prisms; the individual crystals average 0.5 mm long and 0.2 mm in diameter.

The mineral is very brittle; the fracture is uneven to flat conchoidal. Cleavage is indistinct  $\perp$  [001], and excellent  $\parallel$  [001] (this may not be cleavage but rather the easy separation of parallel needles that have grown together). Long needles are quite elastic; a 2 mm crystal may be bent 15 degrees before breaking.

Measurements of the reflectivity and hardness of aikinite from Alice Arm and of two crystals of nuffieldite were kindly made by Professor W. Uytendogaardt at the Free University in Amsterdam.

Measurements were made on both crystals before and after repolish-

ing. Crystal A was oriented with the polished surface  $\perp$  [001] and crystal B was oriented with the  $c$  axis at  $30^\circ$  from the plane of the polished section. The following information is taken from Dr. Uytenbogaardt's report:

"The apparatus used for reflectivity measurements is a combination of a LEITZ' Ortholux and a LEITZ' MPE-photomultiplier equipment. The objective used is a dry P 16/0.40 objective.

"The Vickers hardness has been determined with a LEITZ' Durimet-Pol equipment. The load used for aikinite as well as for nuffieldite was 15 g. Because of the very small grains not more than 4 indentations could be made in each grain. However, these indentations did not show a variation of more than 0.2 microns, and can be accepted as satisfactory for the circumstances.

TABLE 1. REFLECTIVITY VALUES (IN %) OF TWO CRYSTALS OF NUFFIELDITE, (A) AND (B), AND OF AIKINITE

Wave Length in $m\mu$	Si-standard NPL No. 2538.40	Nuffieldite		(B)	Aikinite
		(A)			
		before	after		
		re-polishing			
470	40.4	39.0-43.0	<i>39.8-43.9</i>	42.9-45.6	38.0-44.0
546	36.9	38.2-42.3	<i>39.0-43.1</i>	42.2-44.9	39.2-45.7
589	35.7	37.9-42.0	<i>38.6-42.8</i>	41.8-44.5	39.5-46.0
		<i>Vickers hardness of nuffieldite and aikinite (load 15 g.)</i>			
		nuffieldite	149-178		
		aikinite	201-218		

"From Table 1 it appears that crystal (B) still shows a higher reflectivity than the re-polished crystal (A). This is caused by the differing crystallographic orientations of the grains. The maximum and minimum reflectivity values of nuffieldite, therefore, are the italicized values in the table. A comparison of the results for both minerals shows a distinct difference between the two spectral curves. (The values for red light are not given since the photomultiplier is not sensitive enough in this part of the spectrum.) The measurements are given with an error of  $\pm 0.1\%$ .

"It must be stated here, that a still better polish may give slightly higher values for both minerals, but will not change the character of the spectral curves."

The density was measured on three grains:

Weight of Fragment mg	Density
19.37	7.012
18.39	7.077
13.77	6.928
Arithmetic average:	7.006

The measured density is therefore  $7.01 \pm 0.07$ . The accuracy of the

equipment was verified both before and after the measurements were made by determining the density (to within  $\pm 0.01$ ) of a small quartz crystal whose density has been established with great accuracy over a period of years. A Berman density balance was used for all the measurements; toluene was employed as the immersion liquid.

The mineral has a bright metallic lustre and is shiny lead-grey to steel-grey in colour on the freshly broken surface. Over a period of time the surface tarnishes pale iridescent greyish-green to reddish-brown. The streak is dark greenish-grey to black. The mineral is opaque even in thin splinters in oil.

In polished section the mineral has no perceptible reflection pleochroism and has very weak anisotropism with polarization colours: bluish-grey to greyish-red. The mineral is pale creamy-white in colour. No evidence of twinning was seen in the polished section study.

TABLE 2. NUFFIELDITE: X-RAY POWDER DATA

CuK $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ); Ni Filter, 114.59 mm diameter camera.  
 $a = 14.61 \text{ \AA}$ ,  $b = 21.38 \text{ \AA}$ ,  $c = 4.03 \text{ \AA}$

<i>I</i>	<i>d</i> (meas.)	<i>d</i> (calc.)	<i>hkl</i>	<i>I</i>	<i>d</i> (meas.)	<i>d</i> (calc.)	<i>hkl</i>
1	7.30	7.30	200	3	2.31	2.31	521, 271
$\frac{1}{2}$ *	5.38	5.34	040	1	2.22	2.22	640
$\frac{1}{2}$	5.09	5.10	230	1	2.16	2.16	541
$\frac{1}{2}$	4.75	4.75	310	1	2.13	2.13	281
1	4.29	4.28	050	3	2.04	2.04	091, 621
9	4.00	4.02	330	3	2.02	2.02	471, 381
10	3.66	3.65	400	2	1.967	1.969	561, 291
10	3.54	3.53	201	2	1.940	1.941	641, 202
$\frac{1}{2}$	3.44	3.46	420	6	1.871	1.872	651, 232
$\frac{1}{2}$	3.35	3.35	221	1	1.821	1.819	810
8	3.16	3.16	231	$\frac{1}{2}$	1.796	1.798	661
3	2.98	2.98	170, 321	$\frac{1}{2}$ *	1.765	1.767	252
2	2.94	2.94	241	1*	1.751	1.750	062, 741
3	2.87	2.87	360, 151	1	1.697	1.699	690, 751
1	2.81	2.82	520, 270	1	1.631	1.629	452
2	2.76	2.78	450	1	1.581	1.582	930, 462
2	2.72	2.71	251	1	1.549	1.549	851
$\frac{1}{2}$	2.67	2.67	080	1	1.515	1.516	632
$\frac{1}{2}$	2.62	2.62	161, 421	2	1.400	1.400	7.10.1
7	2.54	2.55	460	2	1.374	1.373	2.11.2, 10.0.1
2	2.40	2.40	171	4	1.349	1.349	971, 812
2	2.34	2.34	470, 380	3	1.280	1.280	5.15.0, 053

\*diffuse line plus 18 other very diffuse lines with *d* less than 1.28

Nuffieldite alters to a buff to light tan-coloured powder that is probably a bismuth ochre; greenish grains in the bismuth ochre may be admixed malachite.

#### X-RAY CRYSTALLOGRAPHY

Both the compact and the acicular varieties of nuffieldite yielded

unterminated crystal fragments suitable for rotation and Weissenberg x-ray photographs, with the needle axis (*c* axis) as the axis of rotation. The acicular variety gave the smaller and more sharply defined reflection spots because the crystals are smaller and more nearly cylindrical in shape. The positions of the reflection spots from the two crystals are very nearly identical; the relative intensities of the spots match exactly. Weissenberg photographs resolving the zero, first, second, and third layers (*/hk0/* to */hk3/*) were made.

The photographs indicate orthorhombic symmetry; the reflections in */hk0/* and */hkl/* conform to the conditions:

- (*hkl*) present in all orders . . . . . (*P*)
- (*0kl*) present only with (*k + l*) = 2*n* . . . . . (*n*)
- (*h0l*) present only with *h* = 2*n* . . . . . (*a*)
- (*hk0*) present in all orders . . . . . (*m* or 2*1*)

These criteria for non-extinction give the space group:  $D_{2h}^6 = Pnam$  or  $C_{2v}^9 = Pna2_1$  if the point group is *mm2*. The measured cell constants and the errors of replication are:

	Compact Variety	Acicular Variety
<i>a</i>	14.605 ± 0.01 Å	14.59 ± 0.02 Å
<i>b</i>	21.375 ± 0.01 Å	21.21 ± 0.02 Å
<i>c</i>	4.025 ± 0.005 Å	4.025 ± 0.005 Å

In both cases *a* and *b* are the extrapolated values obtained using the numerical values for the extrapolation function of Taylor, Sinclair, Nelson, and Riley given in Azaroff & Buerger (1958). The difference in the *b* dimensions of the two varieties appears to be real but proof must await the use of precision instruments. The cell dimensions of nuffieldite (compact variety) were refined at Queen's University using the 360 computer and a program developed at the United States Geological Survey. The refined cell edges based on 53 indexed *d*-spacings are: *a* = 14.602 ± 0.006 Å; *b* = 21.344 ± 0.011 Å; *c* = 4.026 ± 0.002 Å. Morphological measurements could not be made because of the deep striations and channels on all the prism faces of the crystals, and because of the complete absence of terminal faces.

A number of precession photographs were taken of the same acicular crystal used for the Weissenberg photographs in order to verify the symmetry and the slightly different cell dimensions. These films gave identical cell constants within the limits of measurement error.

CHEMICAL COMPOSITION

*Introduction*

Recently D. C. Harris (Nuffield & Harris 1966, Harris & Brooker 1966)

developed *x*-ray spectroscopic methods for analyzing less-than-one-milligram mineral samples. More recently the Department of Geology at the University of Toronto acquired an electron microprobe analyzer and also established a laboratory, under the supervision of Professor J. C. Van Loon, for analyzing minerals. It seemed an excellent opportunity for comparing the various analytical methods as applied to the analysis of very small samples of ore minerals.

*Part I: X-ray Spectroscopic Analysis*

Harris' method virtually eliminates effects due to matrix, particle size, and sample size by the use of the relation between spectral intensity ratios and atomic ratios of pairs of elements.

Results of the analyses of three separate samples of nuffieldite are given in Table 3.

TABLE 3. NUFFIELDITE: X-RAY FLUORESCENCE  
INTENSITY RATIOS

Sample	Atomic Ratio	First Analysis	Second Analysis
C-1	Bi/Pb	0.892	0.9079
"	Pb/Cu	7.58	7.698
"	Bi/Cu	6.71	6.941
C-2	Bi/Pb	0.909	0.9650
"	Pb/Cu	7.94	7.328
"	Bi/Cu	7.17	7.026
C-3	Bi/Pb	0.858	0.8496
"	Pb/Cu	5.66	5.776
"	Bi/Cu	4.82	4.875

The ratios in Table 3 were recalculated to include the necessary sulphur, and to total 100.00. For each sample the two analyses were averaged:

Element	C-1	C-2	C-3
Pb	41.21	40.46	41.23
Bi	37.09	37.89	35.22
Cu	5.42	5.33	7.24
S	16.28	16.32	16.31
	100.00	100.00	100.00

Samples C-1, C-2, C-3, were finely ground single crystals extracted from the compact masses of nuffieldite.

*Part II: Electron Microprobe Analysis*

A number of electron microprobe analyses were made of selected

crystals of both the acicular and the compact varieties of nuffieldite. Crystals of aikinite, cosalite, the first new Alice Arm sulphosalt (Drummond *et al.* 1962), and galenobismutite were also analyzed as standards and as checks on the accuracy and the reproducibility of the analytical method.

The results of five point-analyses (recast to total 100.0) on each of two crystals of nuffieldite are given below. The analyses were done on an ARL EMX electron microprobe analyzer by Dr. J. C. Rucklidge. Analysis "A" is on a crystal of compact nuffieldite previously used for Weissenberg photographs; analysis "B" is on an acicular crystal.<sup>3</sup> Analyzed aikinite was used as a copper standard (11.0% Cu) and analyzed aikinite (16.7% S) and analyzed pyrite (53.5% S) were used as sulphur standards.

	A	B	Average
Pb	38.9	41.1	40.0
Bi	39.0	36.8	37.9
Cu	5.7	5.7	5.7
S	16.4	16.4	16.4
	100.0	100.0	100.0

There was no detectable difference in the copper and sulphur analyses between the two samples.

### *Part III: Colorimetric Analysis of Sulphur*

The small quantity of nuffieldite available precluded wet chemical analysis using established methods. Consequently a colorimetric method was developed capable of determining sulphur in sulphide minerals for samples in the 0.1–1.0 mg range. This method has been fully described elsewhere (Van Loon, Parissis, & Kingston 1968).

Two samples of the compact variety of nuffieldite were selected for analysis using this colorimetric technique.

Sample	Sample Weight	Weight of Sulphur Found	Percent Sulphur
C-1	0.580 mg	95.7 $\mu$ g	16.4
C-2	0.402 mg	65.7 $\mu$ g	16.3

The average sulphur content is 16.35%, a value which is in close agreement with that obtained by electron microprobe analysis (16.4% S).

<sup>3</sup>These crystals A and B are the same crystals used for reflectivity and hardness tests (p. 441).

*Part IV: Atomic Absorption Spectrophotometric Analysis of Lead, Bismuth, and Copper in Nuffieldite*

A Perkin-Elmer Model 303 atomic absorption spectrophotometer was used for all the following analyses. Hollow cathode tubes were used as sources of lead, bismuth, and copper radiations. The samples of nuffieldite used for atomic absorption analysis were the solutions from which the sulphur had been removed in the colorimetric sulphur analysis. These solutions contained dissolved nuffieldite, hydrochloric acid, dissolved tinfoil, and dissolved calcium carbonate. The tinfoil, calcium carbonate, and hydrochloric acid were carefully analyzed for lead, bismuth, and copper and were found to contain insignificant quantities of the metals.

Because the samples of the mineral contained lead, bismuth, copper, and tin, standard solutions were prepared containing all these elements in approximately the same proportions as they were present in the samples in order to eliminate problems arising from inter-element interference. The small size of the samples available for analysis made it impossible to determine all three metals (lead, bismuth, and copper) in each sample.

The resulting analysis for nuffieldite based on the atomic absorption data is given in Table 4.

TABLE 4. NUFFIELDITE: ATOMIC ABSORPTION ANALYSIS

Element	Samples		"Average" of C-1 and C-2	Recast to total 83.6	
	C-1	C-2			
Pb	40.3	nd	40.3	40.0	
Bi	nd*	37.5	37.5	37.2	
Cu	6.4	nd	6.4	6.4	
			84.2	83.6	
				+16.4% S	(from colorime- tric ana- lysis)
				100.0	

\*nd—not determined.

This is in good agreement with the analysis as determined by electron microprobe and fluorescence techniques.

*Part V: Summary of Analytical Results*

The analyses of nuffieldite obtained by various analytical methods cannot be averaged together as these methods have different limitations and varying degrees of accuracy. Preferred values for each element are chosen from the analytical results bearing these limitations in mind.

The amount of sulphur in nuffieldite was found to be 16.35% by colorimetric analysis, and 16.4% by electron microprobe analysis.



Greater weight is given to the colorimetric data and 16.35% sulphur is the adopted value.

The copper content of nuffieldite was found to be 5.7% by electron microprobe analysis, and 6.36% by fluorescence analysis. A value of 6.4% was determined by atomic absorption spectroscopy. Greater weight is given to the microprobe analysis and the fluorescence analysis with the microprobe data being the most reliable. The adopted copper value is 5.90%.

The lead and bismuth values determined by the various methods are:

Element	Fluorescence	Microprobe	Atomic Absorption
Pb	40.84%	40.0%	40.0%
Bi	37.49%	37.9%	37.2%

The fluorescence and microprobe analysis results are adopted as being the most reliable and accurate ones for the lead and bismuth contents of nuffieldite. The atomic absorption data confirm these results.

The final analysis of nuffieldite is found to be:

	Pb	Bi	Cu	S	Total
Nuffieldite analysis	40.42	37.67	5.90	16.35	100.36
Same recast to 100.00	40.27	37.55	5.88	16.30	100.00

### ANALYSES AND CELL CONTENT

The final analysis of nuffieldite as presented above is used to calculate the number of atoms in the unit cell. These data are given in Table 5.

TABLE 5. NUFFIELDITE: ANALYSIS AND CELL CONTENTS

	1	2	3	4	5	6
Pb	40.42	0.4027	0.001943	10.22	10	39.23
Bi	37.69	0.3755	0.001797	9.45	10	39.57
Cu	5.90	0.0588	0.000925	4.86	4	4.81
S	16.35	0.1630	0.005083	26.73	27	16.39
	100.36	1.0000				100.00

1 : Final (average) analysis.

2 : Analysis reduced to unity.

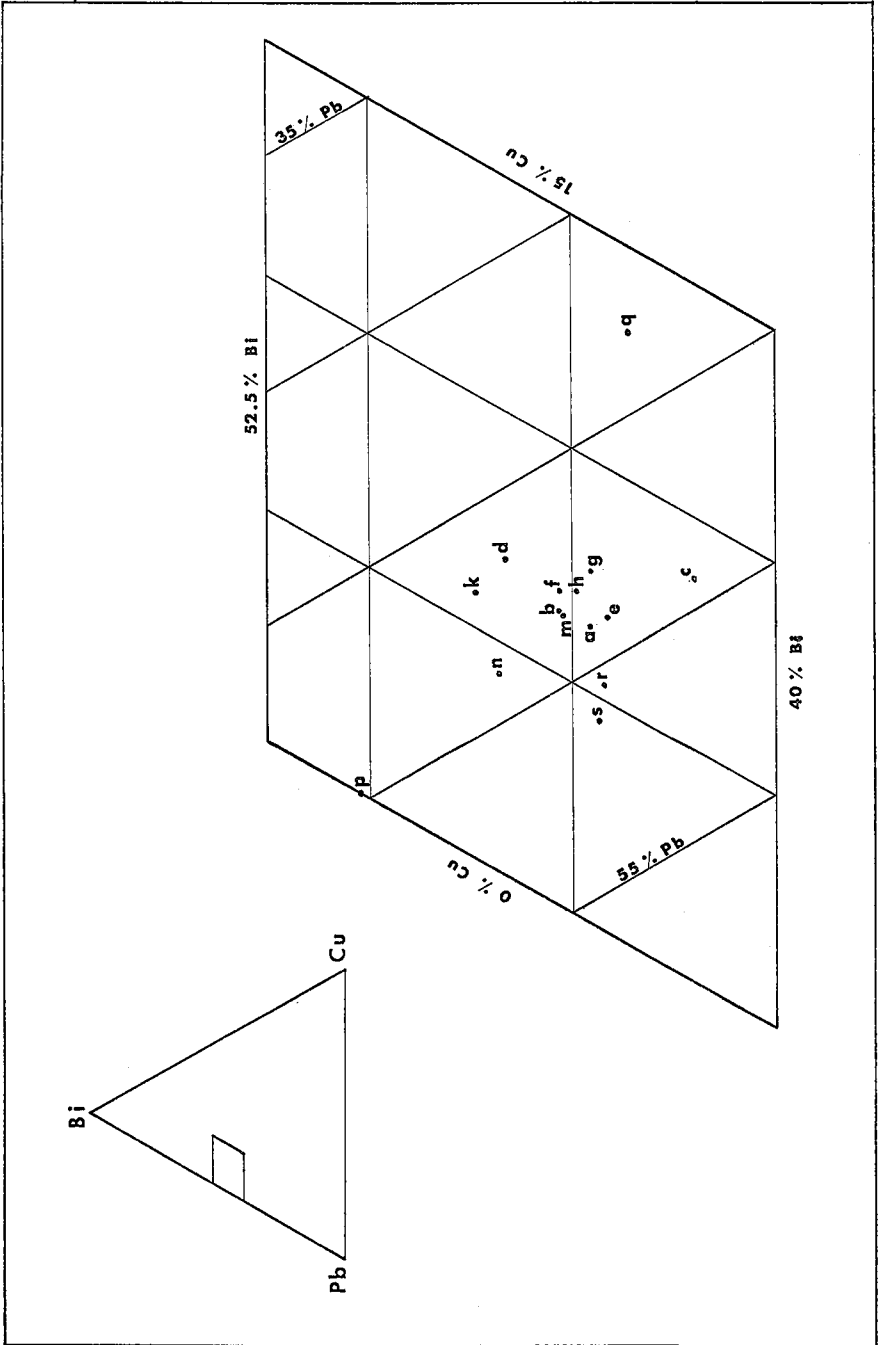
3 : Atomic proportions (values in column 2 divided by the appropriate atomic weights).

4 : Number of atoms in the unit cell obtained by multiplying the values in column 3 by the molecular weight.

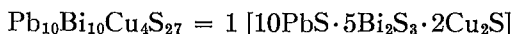
$$MW = (V \times D)/1.66 = (1245.6 \times 7.01)/1.66 = 5259.4$$

5 : Ideal cell contents.

6 : Analysis calculated for  $Pb_{10}Bi_{10}Cu_4S_{27}$ .



The indicated cell content is:



which gives the calculated density 7.04. At first glance it would seem that there should be 5 atoms of copper in the unit cell (columns 4 and 5, Table 5). A cell content of  $\text{Pb}_{10}\text{Bi}_{10}\text{Cu}_5\text{S}_{27}$  is impossible because 5 atoms of copper combine with sulphur as  $2\text{Cu}_2\text{S} \cdot \text{CuS}$ ; this necessitates an additional sulphur atom and a cell content of  $\text{Pb}_{10}\text{Bi}_{10}\text{Cu}_5\text{S}_{28}$ . This formula is not correct because the sulphur analysis is quite accurate enough to rule out the extra sulphur atom and  $\text{Pb}_{10}\text{Bi}_{10}\text{Cu}_5\text{S}_{28}$  gives a non-integer value of  $Z$  when related to the cell volume and density. The rest of this section is concerned with explaining the small, though real, difference between the composition as analyzed and the calculated ideal composition.

In the investigations of minerals and mineral systems it is desirable to rapidly process physical, chemical, and  $x$ -ray data in order to eliminate incompatible observations. The author has developed a computer program that relates cell parameters, density,  $Z$  (number of formula weights per unit cell), and chemical elements present in the mineral, and calculates the resulting possible molecular formulas. If the chemical composition of the mineral is approximately known it is possible to reduce the number of possible molecular formulae to a small number, and in some instances to only one possible answer. The program, UNRAVL, has been developed to handle data for sulphosalt minerals.

The basis of the calculations performed by the program is the following relation:

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FIG. 1. Chemical Analyses of Nuffieldite and related Sulphosalts recalculated to  $\text{Pb} + \text{Bi} + \text{Cu} = 100$ .

- a. Nuffieldite fluorescence analysis C-1.
- b. Nuffieldite fluorescence analysis C-2.
- c. Nuffieldite fluorescence analysis C-3.
- d. Nuffieldite electron microprobe analysis A.
- e. Nuffieldite electron microprobe analysis B.
- f. Nuffieldite average of electron microprobe analyses A and B.
- g. Nuffieldite atomic absorption analysis.
- h. Nuffieldite final analysis:  $\text{Pb}_{10.0}(\text{Bi}_{9.45}\text{Pb}_{0.22}\text{Cu}_{0.87})\text{Cu}_{4.0}\text{S}_{26.73}$ .
- k. Nuffieldite ideal composition:  $\text{Pb}_{10}\text{Bi}_{10}\text{Cu}_4\text{S}_{27}$ .
- m. Nuffieldite ideal composition ( $\text{Pb}_{10}\text{Bi}_{10}\text{Cu}_4\text{S}_{27}$ ) with calculated substitution:  
 $\text{Pb}^{++} + \text{Cu}^+ \rightarrow \text{Bi}^{+++}$ ;  $\text{Pb}_{10.0}(\text{Bi}_{9.585}\text{Pb}_{0.41}\text{Cu}_{0.42})\text{Cu}_{4.0}\text{S}_{27.0}$ .
- n. Cosalite of Warren, 1939.
- p. "Ideal" cosalite:  $\text{Pb}_2\text{Bi}_2\text{S}_5$ .
- q. Ideal aikinite:  $\text{PbBiCuS}_3$ .
- r. Thompson's (1962) new sulphosalt as analysed ( $\% \text{Cu} + \% \text{Ag}$  plotted as  $\% \text{Cu}$ ).
- s. Thompson's (1962) new sulphosalt ideal:  $\text{Pb}_7\text{Bi}_6\text{Cu}_2\text{S}_{17}$ .

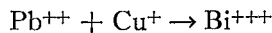
$$(1) \quad MW \times Z = \frac{V \times D}{1.66}$$

$MW$  = molecular weight (of mineral)  
 $Z$  = number of formula weights per unit cell  
 $V$  = volume of unit cell (cubic angstroms)  
 $D$  = density

Cell volume is known or can be evaluated and the density is known or can be estimated.  $Z$  is always an integer and 1.66 is a constant derived from Avogadro's number. A quantitative (or semi-quantitative) analysis of the mineral in question reveals what elements are present and approximately in what amounts.

Thus it is possible to solve equation (1) for a number of values of  $Z$  and  $MW$ . The value  $MW$  is dependent on the numbers of atoms of the different elements in the mineral, and their atomic weights. In the program, the number of atoms of each element is varied over a range of values. A large number of possible molecular formulae is generated but only a small number of these will have a molecular weight close to  $(V \times D)/(Z \times 1.66)$ . For nuffieldite the calculated ideal molecular formula that fell closest to the chemical analysis was  $10\text{PbS} \cdot 5\text{Bi}_2\text{S}_3 \cdot 2\text{Cu}_2\text{S}$ . All other calculated possible ideal molecular formulae were greatly different from the chemical analysis.

The apparent discrepancy between the final analysis and the calculated composition (Table 5) is readily explained by the following atomic substitution:



Thus 207.21 gm Pb + 63.54 gm Cu substitute for 209.00 gm Bi. In nuffieldite (Table 6) 1.53 gm Pb + 0.47 gm Cu substitute for 1.55 gm Bi.

The calculated molecular formula (from column 5, Table 6) for nuffieldite, after the above substitution is made, is

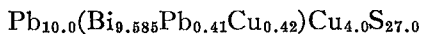
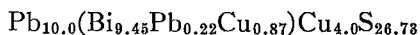


TABLE 6. NUFFIELDITE: DERIVATION OF CALCULATED MOLECULAR FORMULA FROM IDEAL FORMULA BY ATOMIC SUBSTITUTION

1	2	3	4	5	6
Element	Ideal Composition	Calculated Substitution	Ideal With Calculated Substitution	Same Recast to 100.00%	Final Analysis of Natural Nuffieldite
Pb	39.23	+1.53	40.76	40.58	40.27
Bi	39.57	-1.55	38.02	37.84	37.55
Cu	4.81	+0.47	5.28	5.26	5.88
S	16.39		16.39	16.32	16.30
	100.00		100.45	100.00	100.00

and the molecular formula derived from the analysis of the natural material (column 6, Table 6) is



The calculated density is 7.006 (based on data in column 5, Table 6) and the measured density of the natural mineral is  $7.01 \pm 0.07$ . The ideal molecular formula for nuffieldite is  $\text{Pb}_{10}\text{Bi}_{10}\text{Cu}_4\text{S}_{27}$ , and the ideal cell content is  $1[10\text{PbS} \cdot 5\text{Bi}_2\text{S}_3 \cdot 2\text{Cu}_2\text{S}]$  which gives the ideal calculated density = 7.041.

Recently Welin (1966) has published a revision of Johansson's original study (1924) of the Gladhammer bismuth sulphosalt minerals in which he gives powder data for most of these minerals, and single crystal data for three of them. Welin discovered that "single crystal data show that unit cells of various size occur, each corresponding to a particular composition and possessing a common sub-structure. Consequently, no continuous solid solution series exists" (Welin 1966, pp. 383-384). The copper-lead ratio in this bismuthinite-aikinite "series" is 1:1 while the copper-lead ratio in nuffieldite is 2:5, indicating that nuffieldite does not belong to this "series". Furthermore the powder pattern of nuffieldite bears only superficial resemblance to the patterns of the members of the bismuthinite-aikinite "series."

Nuffieldite lies midway between cosalite and aikinite in composition but the cell dimensions, particularly  $a$  (Table 7) preclude the possibility that a solid solution series exist between cosalite and aikinite.

Warren (1939) described cosalite from British Columbia with a composition very close to that of nuffieldite. Warren's "cosalite" may well be nuffieldite but as he gives no powder data or density measurement this cannot be confirmed.

It is thus evident that nuffieldite is a mineral characterized by a unique chemical composition and by unit cell parameters unlike those of any other known mineral.

TABLE 7: CELL CONSTANTS FOR COSALITE, NUFFIELDITE, AND AIKINITE

	Cosalite*	Nuffieldite	Aikinite*
$a$	19.09 Å	14.61 Å	11.32 Å
$b$	23.87	21.38	11.66
$c$	4.05	4.03	4.01
$Z$	8	1	2
$D$	6.86 (calc)	7.01	7.22 (calc)

\*Berry and Thompson (1962).

TABLE 8: COSALITE OF WARREN (1939), AND NUFFIELDITE COMPARED

Element	Cosalite (Warren, 1939)		Nuffieldite
Pb	41.20	40.97	40.27
Bi	39.35	39.13	37.55
Cu	3.60	3.58	5.88
S	16.40	16.32	16.30
	100.55	100.00	100.00

## ACKNOWLEDGMENTS

The author extends his warmest thanks to Professor E. W. Nuffield for his advice and guidance during the research, and to Cominco who awarded the author a Graduate Research Fellowship for the duration of the study.

Special thanks are due Professor J. C. Van Loon for his assistance with the colourimetric sulphur analysis and to the late Professor R. M. Thompson of the University of British Columbia who suggested the problem and supplied the specimens.

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*Manuscript received January 1968, emended March 18, 1968*