

## KAWAZULITE $\text{Bi}_2\text{Te}_2\text{Se}$ , RELATED BISMUTH MINERALS AND SELENIAN COVELLITE FROM THE NORTHWEST TERRITORIES

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### ABSTRACT

Kawazulite, tellurobismuthite and selenian *blau-bleibend* covellite are associated with pitchblende and hematite in a breccia pipe that cuts Aphebian dacitic ignimbrites at Mazenod Lake, Northwest Territories. Electron-microprobe analyses of kawazulite give  $\text{Bi}_{2.13}\text{Te}_{1.98}\text{Se}_{1.04}$  and  $\text{Bi}_{2.13}\text{Te}_{2.01}\text{Se}_{0.99}$ , with minor Cu and Fe. Three unidentified bismuth minerals (*A*, *B*, *C*), with the general formula  $\text{Bi}_2(\text{S}, \text{Se}, \text{Te})_3$ , were also found. Anisotropy for kawazulite is distinct, with polarization colors bluish grey to brownish grey; its measured reflectivity is 60.0 to 61.6% (547-591 nm). Tellurobismuthite and mineral *A* have measured reflectivities of 61.6 to 62.0% and 51.1 to 51.6%, and micro-indentation hardness values ( $VHN_{50}$ ) of 155 to 180 and 199 to 205, respectively. This is not only the first reported Canadian occurrence, but also the first recorded occurrence of kawazulite outside Japan. The covellite, which exhibits weak anisotropy, contains up to 15 wt. % Se. Associated digenite and chalcopyrite have normal compositions and optical properties.

**Keywords:** kawazulite, tellurobismuthite, guanajuatite, covellite, Se, Te, Bi, Mazenod Lake, Bear Province, Northwest Territories, hardness, reflectivity, microprobe.

### SOMMAIRE

Kawazulite, tellurobismuthite et covelline *blau-bleibend* sélénifère sont associées à la pitchblende et à l'hématite dans une brèche en pipe qui recoupe des ignimbrites dacitiques d'âge Aphébien au lac Mazenod (Territoires du Nord-Ouest). La kawazulite possède la composition  $\text{Bi}_{2.13}\text{Te}_{1.98}\text{Se}_{1.04}$  et  $\text{Bi}_{2.13}\text{Te}_{2.01}\text{Se}_{0.99}$  avec un peu de Cu et de Fe (déterminations par microsonde électronique). Trois minéraux de bismuth, non-identifiés (*A*, *B* et *C*); de formule idéalisée  $\text{Bi}_2(\text{S}, \text{Se}, \text{Te})_3$ , sont aussi présents. La kawazulite est grise, anisotrope de bleuâtre à brunâtre entre nicols croisés. On mesure une réflectivité de 60.0 à 61.6% (de 547 à 591 nm). Pour la tellurobismuthite et l'espèce *A*, la réflectivité a les valeurs 61.6-62.0% et 51.1-51.6% et la dureté (par micro-indentation,  $VHN_{50}$ ), 155-180 et 199-205, respectivement. C'est la première fois qu'on trouve la kawazulite ailleurs qu'au Japon. La covelline, légèrement anisotrope, contient jusqu'à 15% de Se (en poids). Les cristaux de digénite et de

chalcopyrite associés ont des propriétés optiques et des compositions normales.

(Traduit par la Rédaction)

**Mots-clés:** kawazulite, tellurobismuthite, guanajuatite, covelline, Se, Te, Bi, lac Mazenod, province de l'Ours, Territoires du Nord-Ouest, dureté, réflectivité, microsonde.

### INTRODUCTION

A small U-Cu deposit occurs at Mazenod Lake, Northwest Territories, on the so-called Dianne mineral claims of the Noranda Exploration Company Limited (Long.  $116^{\circ}55'W$ , Lat.  $63^{\circ}45'30''N$ ). A breccia pipe several hundred metres in diameter, defined by tourmaline veinlets and a large aeromagnetic anomaly, cuts dacitic ignimbrites of the Great Bear plutonic-volcanic suite. These intensely hematized host rocks are occasionally cut by small (1 to 2 mm across) veinlets of hematite-pitchblende that also host the Bi-Cu-Pb-S-Se-Te mineralization. Primary and secondary hematite can be distinguished in the veinlets; primary hematite has a platy habit, whereas secondary hematite, produced by the oxidation of magnetite, is present as equidimensional grains with relict magnetite cores. The pipe exhibits extensive superficial copper-rich oxidation products.

### METHODOLOGY

Reflectivity measurements were made with a photometer calibrated to a tungsten carbide standard (Carl Zeiss no. 47 42 53). Reflectivity is 46.1% at 546 nm and 45.7% at 589 nm, with an accuracy of  $\pm 1.5\%$ . Monochromatic filters were used to obtain the wavelengths required. The reflectivity values given are the highest of four or more measurements. Freshly polished material was always used, since mineral *A* and tellurobismuthite both showed significant brown tarnishing after a period of a month.

Micro-indentation hardness was measured with a Vickers diamond indenter. The  $VHN$  numbers so obtained have been corrected by

reference to a calibration curve, constructed by comparing the measured and actual hardnesses of a range of six standard minerals. This led to a corrected value about 15% lower than the apparent value at  $VHN_{50} = 100$ .

The electron-microprobe analyses all involve the energy-dispersion technique and were made on an ARL EMX instrument fitted with an ORTEC energy-dispersion analyzer. The data were processed by the program EDATA2 (Smith & Gold 1979). Count times were 400 seconds for both the standards and the samples, with full-spectrum total counts of 1.5 to 2.5 million. The accelerating voltage was 15 kV in all cases.

Two sets of standards were used on different runs. One set comprised silver-bismuth selenide, cobalt telluride, chalcopyrite, pitchblende and lead-silica glass. The second set comprised a gold-silver alloy, Bi, Se and Te metals, chalcopyrite, pitchblende and lead-silica glass. As and Sb might be expected to be present, but a check by wavelength-dispersion techniques did not reveal them.

EDATA2 calculates the background continuum radiation for the average atomic number of the specimen; experience to date confirms that this procedure is entirely satisfactory (Smith & Gold 1979). Computer plots of the spectra after removal of the calculated background showed no significant residuals. The background calculation is based upon a "normative background", derived from a diamond sample, which models precisely the efficiency characteristics of the particular detector.

The program is set to reject concentrations of less than 0.03% as being below detection limits. In practice, elements analyzed on high-energy lines (*i.e.*, 5 kV and up) under these conditions have lower detection limits than this. In the suite of elements sought, major overlaps occur between the spectra of S, Pb and Bi, ranging from 26 to  $\approx 100\%$ . Overlap coefficients were calculated from the standards; the close approach to 100% totals (with the exception of analyses 7-9) indicates that these coefficients are correct. However, the detectability of these elements is no longer of the order of 0.03%. For example, analysis 1, on tellurobismuthite, had 301,134 counts in the Bi  $M\beta$  region of analysis. Of these counts, 26%, or 78,294, fall in the S region of analysis. The statistical variation of these counts, *i.e.*, the square root (at the 1  $\sigma$  level), is 280 counts. At the 2.58  $\sigma$  or 99% confidence level, a peak of 722 counts could therefore register in the S region, owing to Bi, which sets the limit on S detectability in the presence of this amount of

Bi. A comparison with the analysis of digenite suggests that this represents about 0.05% S, although its different atomic weight makes direct comparison uncertain. I suggest that a detection limit of 0.1% is reasonable for S in a matrix of 50-60% Bi, with an analytical accuracy of  $\pm 0.2$  wt. %. Similar logic gives slightly higher values for Pb in a Bi- or S-rich matrix. Se, Te, Fe and Cu are not subject to interference in this suite, and a detection limit of perhaps 0.05% with an accuracy of  $\pm 0.1\%$  is reasonable. The situation for S deteriorates further in the Pb-bearing phase, mineral *A*. The analytical X-ray lines were  $K\alpha$  for S, Fe and Cu;  $L\alpha$  for Se, Ag and Te;  $M\beta$  for Pb and Bi.

#### MINERALOGY

The bismuth minerals found in this study all have the general formula  $Bi_2(S,Se,Te)_3$  and similar optical properties. They were identified during routine electron-microprobe studies and cannot be distinguished optically except by reflectivity measurements. Kawazulite was first reported and described by Kato (1970), whose type material came from the Kawazu mine, Japan. It has not apparently been reported in the literature since then.

The Canadian kawazulite occurs in trace amounts, intimately associated with selenian covellite. The anhedral grains do not exceed 25 micrometres in diameter, so that X-ray-diffraction analyses and micro-indentation-hardness measurements are not practicable. Trace amounts of a similar phase occur nearby and form a very fine intergrowth with pitchblende and primary hematite. These grains are of the order of one micrometre in size and may be a different bismuth mineral. Kawazulite is also found as myrmekitic, submicrometre inclusions within the covellite; it has either exsolved from covellite or coprecipitated with it.

Tellurobismuthite has coprecipitated with about 50% pitchblende and is associated with some primary hematite. It is anhedral, forming grains generally less than 20  $\mu\text{m}$  in diameter. It is also found as interstitial blebs, up to 100  $\mu\text{m}$  in diameter, between grains of secondary hematite. There are trace amounts of chalcopyrite, bornite and, rarely, covellite, but these are not closely associated with the tellurobismuthite.

Mineral *A* was found in one veinlet as blebs up to 100  $\mu\text{m}$  or more in diameter, interstitial to primary hematite. Although these blebs are large enough for microprobe analysis, they nearly all contain exsolved rods of covellite, up to 10  $\mu\text{m}$  long and 0.3  $\mu\text{m}$  in diameter. Oc-

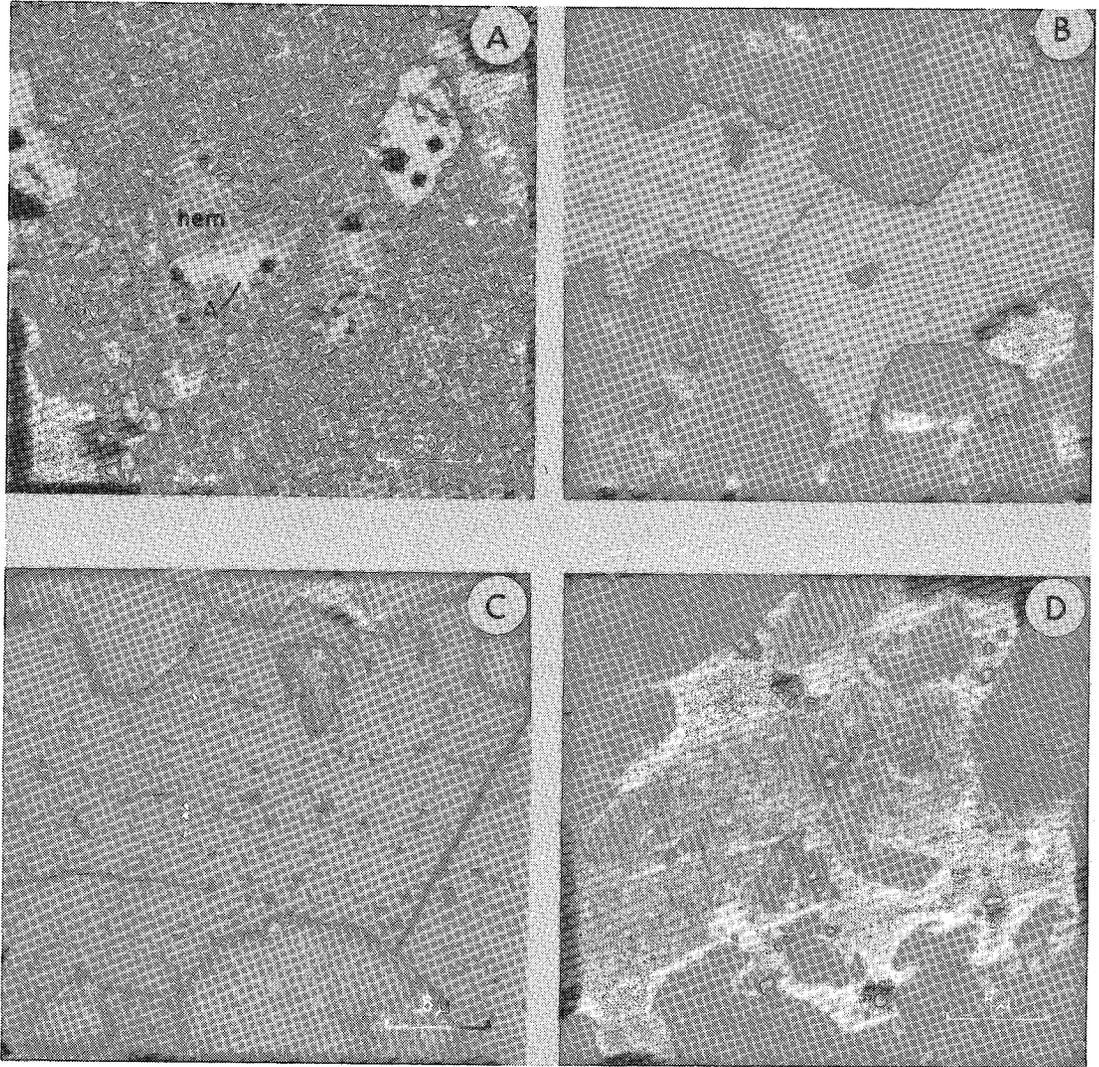


FIG. 1. A. Mineral *A* (white) and minor covellite (medium grey) in hematite (light grey) and silicate (black); x8 objective, photographed under oil immersion (as B, C and D). B. Central grain of mineral *A* in Figure 1A, x40 objective; exsolution rods of covellite are barely resolved at left, and three exsolution lamellae of mineral *B* (white) are at top. C. Left-hand section of grain of mineral *A* in Figure 1B, x100 objective; exsolution rods of covellite, in long and cross sections. D. Covellite grain, same scale as Figure 1C, 100  $\mu\text{m}$  from the grain of mineral *A*, shows myrmekitic exsolution of mineral *A*.

asionally, the reverse relationship can also be seen. Like the kawazulite, mineral *A* was precipitated simultaneously with covellite, and the exsolution that resulted indicates a high-temperature solid solution between covellite and  $\text{Bi}_2(\text{Se}, \text{Te})_3$ . It is possible that this covellite is the selenian analogue, klockmannite, which has similar optical properties (Uytenbogaardt &

Burke 1971). Figure 1 illustrates the distribution of this phase.

Mineral *B* occurs as a few exsolution blebs in mineral *A*. These blebs are about  $2 \times 10 \mu\text{m}$  on average and have a rather higher reflectivity than the host.

Mineral *C* occurs as a few single grains up to  $4 \mu\text{m}$  in diameter, intergrown with pitchblende

or primary hematite. The veinlet in which it was found adjoins the one containing kawazulite.

The selenian *blaubleibend* covellite commonly occurs as grains up to 100  $\mu\text{m}$  across; it is a primary mineral. A little secondary covellite forms alteration rims around chalcopyrite and bornite, which both occur as such smaller grains. Chalcopyrite exsolution lamellae occur within the bornite, which was not analyzed. Digenite was identified optically, but Goble & Smith (1973) studied very similar material and concluded that it was perhaps anilite that had been converted to a digenite-like material by the polishing process; the same may also be true in this case.

The first of these minerals to be deposited at Mazenod Lake was magnetite, although nothing indicates the stage at which it was subsequently oxidized. Some primary hematite followed, before the main period of hematite formation and U-Cu-Bi-Pb-S-Se-Te mineralization. Isotopic analyses by the author give an age of  $460 \pm 30 \text{ Ma}$  for the veins. A general age of 1800  $\text{Ma}$  is assigned to the igneous rocks of the Great Bear batholith.

## RESULTS

### Kawazulite

Analyses 2 and 3 (Tables 1, 2) are essentially

TABLE 1. COMPOSITION OF BISMUTH MINERALS

	Bi	Cu	Pb	Fe	Ag	S	Se	Te	Total*	Mineral
1)	52.6	(ND)	(ND)	0.45	(ND)	(ND)	0.26	46.3	99.95	Tellurobismuthite (this study)
2)	56.4	1.38	(ND)	0.48	(ND)	(ND)	10.4	31.8	100.99	Kawazulite (this study)
3)	56.3	(ND)	(ND)	0.37	(ND)	(ND)	9.92	32.4	99.33	Kawazulite (this study)
4)	48.8	6.35	10.7	1.02	(ND)	(ND)	32.9	0.90	101.08	Mineral A (this study)
5)	46.7	6.40	10.4	0.90	0.10	(ND)	33.6	0.79	99.19	Mineral A (this study)
6)	47.1	6.14	10.2	2.01	0.23	(ND)	33.5	0.93	100.34	Mineral A (this study)
7)	56.2	0.30	(ND)	2.24	(ND)	(ND)	20.1	17.6	96.57	Mineral B (this study)
8)	52.5	5.53	(ND)	0.37	(ND)	(ND)	1.47	18.8	96.26	Mineral B (this study)
9)	55.1	0.69	(ND)	1.63	(ND)	(ND)	14.6	25.1	97.25	Mineral C (this study)

Compositions are expressed in weight %; ND: not detected. \* Minor deviations from listed totals are due to minor Si (less than 0.2%) or U (less than 0.4%). The first may be due to an error in background fitting, the second to a halo effect from surrounding pitchblende.

TABLE 2. COMPOSITION OF  $\text{Bi}_2(\text{S,Se,Te})_3$  MINERALS

	Bi	Cu	Pb	Fe	Ag	S	Se	Te	Mineral
1)	2.06	(ND)	(ND)	0.07	(ND)	(ND)	0.03	2.97	Tellurobismuthite (this study)
2)	2.13	0.17	(ND)	0.07	(ND)	(ND)	1.04	1.96	Kawazulite (this study)
3)	2.13	(ND)	(ND)	0.05	(ND)	(ND)	0.99	2.01	Kawazulite (this study)
4)	1.65	0.71	0.37	0.13	(ND)	(ND)	2.95	0.05	Mineral A (this study)
5)	1.55	0.70	0.35	0.11	0.01	(ND)	2.96	0.04	Mineral A (this study)
6)	1.56	0.67	0.34	0.25	0.02	(ND)	2.95	0.05	Mineral A (this study)
7)	2.06	0.04	(ND)	0.31	(ND)	(ND)	1.94	1.06	Mineral B (this study)
8)	1.80	0.62	(ND)	0.05	(ND)	0.33	1.70	0.97	Mineral B (this study)
9)	2.07	0.09	(ND)	0.23	(ND)	(ND)	1.45	1.55	Mineral C (this study)
10)	2.18#	-	-	-	-	3.00	-	tr	Bismuthinite (Durembergová & Kratochvíl 1977)
11)	2.22#	-	0.10	-	-	1.30	-	1.70	Tetradymite (Durembergová & Kratochvíl 1977)
12)	1.73	-	-	0.05	-	1.13	tr	1.86	Tetradymite (Timofeevskii 1972)
13)	1.77	-	-	0.05	-	1.04	tr	1.95	Tetradymite (Timofeevskii 1972)
14)	1.82	-	-	-	-	1.14	0.22	1.64	Tetradymite (Guha & Darling 1972)
15)	1.73	-	-	-	-	1.26	0.48	1.27	Tetradymite (Guha & Darling 1972)
16)	2.17	-	-	-	-	1.14	0.46	1.40	Tetradymite (Sarkar & Deb 1969)
17)	2.03	-	-	-	-	1.00	-	2.00	Tetradymite (Kashkaï et al. 1974)
18)	2.30	(ND)	(ND)	(ND)	-	1.10	(ND)	1.90	Tetradymite (Harada et al. 1972)
19)	1.88	-	-	-	-	0.93	0.18	1.89	Tetradymite (Palache et al. 1944, p.162 analysis 8)
20)	1.79	-	0.03	-	-	1.16	-	1.84	Tetradymite (Plimer 1977)
21)	1.60	-	0.40	-	-	1.61	-	1.38	Plumbian tetradymite (Plimer 1977)
22)	1.92#	0.02	0.01	0.12	-	2.98	0.02	(ND)	Bismuthinite (Harada et al. 1972)
23)	2.00	-	-	-	-	2.40	0.60	-	Bismuthinite (Palache et al. 1944, p.276 analysis 7)
24)	1.96	0.05	-	0.02	-	2.96	-	0.04	Bismuthinite (Palache et al. 1944, p.276 analysis 4)
25)	2.01	-	-	-	-	0.18	-	2.82	Tellurobismuthite (Palache et al. 1944, p.160 analysis 4)
26)	2.01	-	-	-	-	0.03	0.02	2.94	Tellurobismuthite (Palache et al. 1944, p.160 analysis 6)
27)	1.83	-	0.17	-	-	2.47	-	0.53	Plumbian csiklovaite (Plimer 1977)
28)	2.05	-	-	-	-	0.14	2.86	-	Guanaquatite (Palache et al. 1944, p.278 analysis 2)
29)	1.89	-	-	-	-	1.21	1.79	-	Guanaquatite (Palache et al. 1944, p.278 analysis 4)

# These values are (Bi+Sb). Atomic proportions, S+Se+Te = 3. ND not detected, - no data.

identical, except for a little Cu in the former. This may be due to copper in the kawazulite lattice rather than to exsolved covellite, since sulfur was not detected. If the exsolution product is klockmannite rather than covellite, however, this could produce copper contamination without sulfur.

The optical properties of the kawazulite are: reflectivity = 60.0% at 547 nm and 61.6% at 591 nm [*cf.*, type material: 45 to 50% (Kato 1970)]; color white; bireflectance, twinning and internal reflections not observed; anisotropy strong, with colors bluish grey to brownish grey (*cf.*, type material: grey to reddish brown-grey); *VHN* not obtainable, but the material is markedly softer than covellite; one good cleavage locally visible.

The reflectivity and reddish anisotropy reported for type kawazulite (Kato 1970) are consistent with a poor-quality polish, reducing the reflectivity and giving false anisotropy colors. Although X-ray-diffraction data exist for synthetic  $\text{Bi}_2\text{Te}_2\text{Se}$  (PDF 29-247), it has not been possible to confirm that the mineral from Mazenod Lake is structurally identical to kawazulite. However, the electron-microprobe analyses, coupled with the generally strong physical resemblance to the other minerals of the group, support the identification.

#### *Tellurobismuthite*

The tellurobismuthite (analysis 1) is interesting only because of the absence of Se from the analysis, despite the Se-bearing minerals elsewhere. This suggests that there is no solid solution between tellurobismuthite and kawazulite.

The measured reflectivity of the tellurobismuthite is 61.6% at 547 nm and 62.0% at 591 nm, both marginally below previously reported values;  $VHN_{50} = 155-180$ , compared with reported values of  $VHN_{10-20} = 32-93$  (Uytendogaardt & Burke 1971).

#### *Mineral A*

Analyses 4, 5 and 6 (Tables 1, 2) are essentially identical. The grains commonly have exsolved covellite (or klockmannite) rods in them; although visually clear areas were selected for analysis, similar rods may have been present below the sample surface but within the analyzed volume. However, the consistent Cu and Pb contents suggest that both of these elements are contained within the mineral lattice.

The best-fitting formula from the analyses is

$\text{Bi}_9\text{Cu}_4\text{Pb}_2\text{Se}_{18}$ , with minor Te substituting for Se. Alternatively, the mineral may have a paraganajuatite structure, presumed to be analogous to the tetradymite and tellurobismuthite structures (Harker 1934, Brown & Lewis 1962), in which Bi has been replaced by  $0.75(\text{Pb}+2\text{Cu})$ . However, these structures comprise hexagonal layers of close-packed, identical atoms in a five-layer sandwich; for paraganajuatite this is (Se-Bi-Se-Bi-Se), with metallic bonding within layers and van der Waals bonds between adjacent Se layers. There is no space in the structure for the extra atoms required for the suggested substitution, unless voids are created in the Se layers or unless Bi, Cu or Pb can substitute for Se.

Brown & Lewis (1962) have shown that a high degree of solid solution can occur in the Bi-Te system. The extra atoms are probably accommodated by the addition of extra layers to the structure, such as those shown by Strunz (1963) in the system Bi-Se. Until more data are obtained, this mineral should perhaps be regarded as a Cu-Pb-bearing variety of guanajuatite or paraganajuatite. "Mineral S" (Cech & Vavřin 1978),  $\text{PbCuBi}(\text{S},\text{Se},\text{Te})_3$ , is the closest published analogue found by the author. It has the same property of being derivable from a  $\text{Bi}_2(\text{S},\text{Se},\text{Te})_3$  formula by the substitution of  $\text{Pb}+\text{Cu}$  for Bi, so that ionic charges would be balanced.

The measured reflectivity of mineral A is 51.1% at 547 nm and 51.6% at 591 nm;  $VHN_{50} = 199-205$ .

#### *Mineral B*

Analyses 7 and 8 (Tables 1, 2) are less reliable than others in Table 1 because mineral B, which exists as exsolved patches in mineral A, is too small to avoid significant contamination during analysis by radiation from mineral A as well as from adjacent hematite (analysis 7) and covellite (analysis 8). These patches or lamellae were also visibly affected by the electron beam: they turned brown. The other bismuth phases were not markedly affected.

Both analyses of mineral B give low totals (96.6 and 96.3%). A grain was checked qualitatively by wavelength-dispersion methods to look for As or Sb, which could be hidden by the Se and Te X-ray peaks, respectively; none was found. The low analyses could be due to oxidation of the mineral surface during analysis or to slight volatilization and crater formation under the beam. Mineral B is a relatively minor product of exsolution; it possibly has the

formula  $\text{Bi}_2\text{Se}_2\text{Te}$ , which would make it a previously unrecorded member of this mineral group.

### Mineral C

Analysis 9 (Tables 1, 2) represents the composition  $\text{Bi}_4\text{Se}_3\text{Te}_3$ , a previously unrecorded species. As the grain analyzed is small, confirmation of the composition would be desirable. It may be a member of a solid solution whose observed Se:Te ratio of 1:1 is a matter of coincidence, but this ratio also suggests an ordered phase. If we fit the formula to Harker's (1934) structural model as discussed, the logical possibilities are that each Te or S layer of Harker is filled with an ordered mixture of Se and Te, or that there are alternating layers of (Te-Bi-Se-Bi-Te) and (Se-Bi-Te-Bi-Se), or that there are alternating five-layer sandwiches of  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$ .

### Selenian covellite

Selenian *blaubleibend* covellite occurs closely associated with the bismuth minerals and as exsolution bodies within them. There is evidently a solid solution between covellite and  $\text{Bi}_2(\text{Se},\text{Te})_3$ . As discussed, some of the smaller exsolution bodies may in fact be klockmannite, but are far too small to analyze. It is notable that the digenite has comparatively little Se, and that the chalcopyrite has no detectable Se at all. Te is probably incapable of entering these lattices by virtue of its greater ionic size.

Ramdohr (1969) has attributed the *blaubleibend* effect to solid solution with  $\text{Cu}_2\text{S}$ , which is borne out by the excess Cu in the structural formulae (Tables 3, 4). Goble & Smith (1973)

analyzed suites of anilite and *blaubleibend* covellite and concluded that there are two varieties of the covellite, with the formulae  $\text{Cu}_{1.12 \pm 0.03}\text{S}$  and  $\text{Cu}_{1.32 \pm 0.04}\text{S}$  [yarrowite and spionkopite, respectively, of Goble (1980)]. The present study duplicates the yarrowite data, with the formula  $\text{Cu}_{1.12 \pm 0.07}(\text{S},\text{Se})$ . The digenite-like altered anilite of Goble & Smith (1973) gave an average composition of  $\text{Cu}_{1.76 \pm 0.06}\text{S}$ ; the digenite of this study may well be similar, with the composition  $\text{Cu}_{1.73}(\text{S},\text{Se})$ .

The covellite is notable for its subdued birefractance, whereas its anisotropy under crossed nicols is much reduced, or even absent in a number of grains. Under oil, it remains blue in unpolarized or plane-polarized light. The adjacent digenite, bornite and chalcopyrite have normal optical properties.

### DISCUSSION

Solid solution is known to exist in the series  $\text{Bi}_2\text{S}_3$ - $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_2\text{S}_3$ - $\text{Bi}_2\text{Se}_3$ , despite the different crystal structures involved in the latter series. Named minerals in these series are bismuthinite  $\text{Bi}_2\text{S}_3$ , orthorhombic; csiklovaite  $\text{Bi}_2\text{S}_2\text{Te}$ , "undetermined" (Roberts *et al.* 1974); tetradymite  $\text{Bi}_2\text{Te}_2\text{S}$ , rhombohedral (Harker 1934); tellurobismuthite  $\text{Bi}_2\text{Te}_3$ , hexagonal or rhombohedral (Kato 1970); guanajuatite/paraguanajuatite  $\text{Bi}_2\text{Se}_3$  (Palache *et al.* 1944), orthorhombic/hexagonal [but note that Strunz (1963) gave paraguanajuatite as  $\text{Bi}_4(\text{Se},\text{S})_3$ ; Henley *et al.* (1975) gave guanajuatite as  $\text{Bi}_2\text{Se}_2\text{S}$ ; Roberts *et al.* (1974) and others gave  $\text{Bi}_2(\text{Se},\text{S})_3$  for both)]; kawazulite  $\text{Bi}_2\text{Te}_2\text{Se}$ , rhombohedral (Bland & Basinski 1961). Bland & Basinski showed that synthetic  $\text{Bi}_2\text{Te}_2\text{Se}$  is isostructural with tetradymite, whose structure was determined by Harker (1934).

Although solid solutions occur between the S and Se, and S and Te end-members (Fig. 2), apparently no analyses have been reported along the Se-Te tieline apart from kawazulite. This study suggests the existence of two other minerals along this line,  $\text{Bi}_2\text{Se}_2\text{Te}$  (mineral B) and  $\text{Bi}_4\text{Se}_3\text{Te}_3$  (mineral C). Of the five bismuth minerals found in this study, tellurobismuthite was found in one veinlet, kawazulite and mineral C coexist in a second, and mineral A and exsolved mineral B occur in a third. This suggests that there is no solid solution between kawazulite and mineral C, nor between mineral B and mineral A (possibly guanajuatite). It is also likely that there is no solid solution between tellurobismuthite and kawazulite, nor between mineral B and mineral C. Although these pairs were

TABLE 3. COMPOSITION OF SELENIAN COVELLITE

	Cu	Fe	Pb	S	Se	Te	Total*	Mineral
30)	61.2	1.06	0.87	25.7	9.4	0.07	98.46	Covellite (this study)
31)	58.0	3.57	1.28	21.5	15.7	0.05	100.45	Covellite (this study)
32)	60.4	3.98	2.57	20.5	12.4	0.13	100.00	Covellite (this study)
33)	60.3	1.83	1.77	21.7	13.7	(ND)	99.49	Covellite (this study)
34)	61.3	2.65	2.23	22.0	12.5	(ND)	100.79	Covellite (this study)
35)	74.1	1.13	1.60	20.2	3.3	(ND)	99.69	Digenite (this study)
36)	33.3	31.6	0.78	34.7	(ND)	(ND)	100.44	Chalcopyrite (this study)

Expressed in weight %. \* Minor deviations from the listed totals are due to traces of S1 (less than 0.2%) or U (less than 0.4%). The first may be due to an error in background fitting, the second may be a halo effect from adjacent pitchblende.

TABLE 4. COMPOSITION OF SELENIAN COVELLITE

	Cu	Fe	Pb	S	Se	Te	Mineral
30)	1.05	0.02	tr	0.87	0.13	tr	Covellite (this study)
31)	1.05	0.07	0.01	0.77	0.23	tr	Covellite (this study)
32)	1.19	0.09	0.02	0.80	0.20	tr	Covellite (this study)
33)	1.11	0.04	0.01	0.80	0.20	(ND)	Covellite (this study)
34)	1.14	0.06	0.01	0.81	0.19	(ND)	Covellite (this study)
35)	1.73	0.03	0.01	0.94	0.06	(ND)	Digenite (this study)
36)	0.97	1.05	0.01	2.00	(ND)	(ND)	Chalcopyrite (this study)

Expressed in atomic proportions, S+Se+Te = 1.

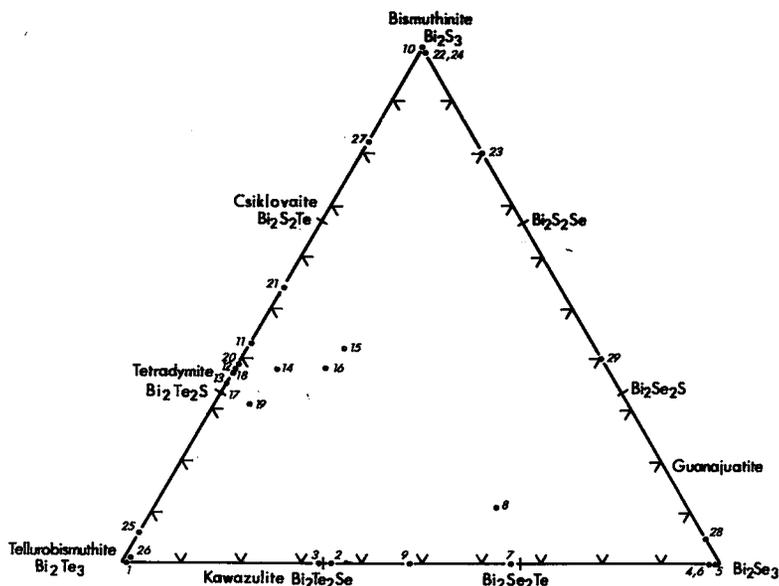


FIG. 2. Reported analyses of  $\text{Bi}_2(\text{S,Se,Te})_3$  minerals; for key to individual analyses, see Table 2.

not found coexisting, the common origin and proximity of the veinlets, coupled with the almost perfect ratios of Se to Te, support this view.

Despite the presence of sulfur in the veinlets, as shown by the copper sulfides, there is virtually no sulfur in the bismuth minerals. This does not necessarily indicate a miscibility gap between minerals along the  $\text{Bi}_2\text{Te}_3$ – $\text{Bi}_2\text{S}_3$  tieline and  $\text{Bi}_2\text{S}_3$ , but rather that chalcopyrite and digenite are intolerant of Se, whereas covellite is more tolerant and the bismuth minerals are more tolerant still. Under conditions of higher sulfur availability, sulfur may well enter the lattice of kawazulite and the unidentified minerals.

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