

## BOHDANOWICZITE, JUNOITE AND LAITAKARITE FROM THE KIDD CREEK MINE, TIMMINS, ONTARIO

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### ABSTRACT

Bohdanowiczite (ideally  $\text{AgBiSe}_2$ ) is a common but minor constituent of the selenide-bearing bornite-rich ore that forms a small zone in the Kidd Creek volcanogenic massive sulfide deposit, in the area of Timmins, Ontario. The lead-bismuth selenides junosite and laitakarite were identified in a single specimen from a drill hole that passes beneath the bornite zone. Some grains of junosite are partly rimmed by laitakarite, which contains inclusions and intergrowths of an unidentified phase that has higher lead and sulfur contents. A few minute blebs of an antimony-rich phase are also present in these intergrowths. Improved electron-microprobe analyses of bohdanowiczite ( $\text{Ag}_{1.01}\text{Bi}_{1.00}\text{Se}_{1.99}\text{S}_{0.01}$ ) and junosite ( $\text{Bi}_{7.99}\text{Pb}_{2.99}\text{Cu}_{1.99}\text{Ag}_{0.12}\text{S}_{10.08}\text{Se}_{5.94}$ ) have been achieved by the use of synthetic standards and a modified empirical matrix correction that is more suitable for lead-bismuth sulfosalts than the customary theoretical correction. The Kidd Creek junosite contains about 14.7 wt. % selenium, whereas 12 wt. % was the highest content reported for junosite from the Juno mine, Australia. Laitakarite ( $\text{Bi}_4\text{Se}_5\text{S}$ ) was semi-quantitatively analyzed by energy-dispersive techniques. X-ray powder data are presented for bohdanowiczite and junosite. The refined hexagonal cell for bohdanowiczite (Cu  $K\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ) is  $a$  8.412(6),  $c$  19.63(3)  $\text{\AA}$ ; for junosite (Co  $K\alpha$  radiation  $\lambda = 1.7900 \text{ \AA}$ ), the cell is  $a$  26.71(1),  $b$  4.060(2),  $c$  17.172(7),  $\text{\AA}$   $\beta = 127.65(3)^\circ$  [or  $a' = 21.17 \text{ \AA}$ ,  $b' = b$ ,  $c' = c$ ,  $\beta' = 92.32^\circ$  in the conventional setting]. The Kidd Creek mine is the first Canadian locality for bohdanowiczite, junosite and laitakarite.

**Keywords:** bismuth selenides, sulfosalts, bohdanowiczite, junosite, laitakarite, massive sulfide deposit, Kidd Creek, Timmins, Ontario.

### SOMMAIRE

La bohdanowiczite (idéalement  $\text{AgBiSe}_2$ ) constitue un minéral accessoire répandu dans le minerai sélénifère riche en bornite d'une petite zone du gisement de sulfures massifs volcanogéniques de Kidd Creek (Timmins, Ontario). Les séléniures de Pb et Bi junosite et laitakarite ont été identifiés dans une seule carotte, d'un trou de sondage foré sous la zone à bornite. Certains grains de junosite sont partiellement enrobés de laitakarite, qui ren-

ferme des inclusions et des intercroissances d'une espèce non-identifiée, enrichie en Pb et S. On trouve aussi dans les intercroissances quelques particules d'une phase riche en antimoine. Des analyses à la microsonde électronique, améliorées par l'emploi d'étalons synthétiques et d'une correction de matrice empirique modifiée, plus appropriée que la correction théorique à l'étude de sulfosels Pb-Bi, ont donné  $\text{Ag}_{1.01}\text{Bi}_{1.00}\text{Se}_{1.99}\text{S}_{0.01}$  pour la bohdanowiczite et  $\text{Bi}_{7.99}\text{Pb}_{2.99}\text{Cu}_{1.99}\text{Ag}_{0.12}\text{S}_{10.08}\text{Se}_{5.94}$  pour la junosite. Cette dernière contient environ 14.7% en poids de Se, surpassant ainsi le maximum (12%) trouvé à la mine Juno, en Australie. La laitakarite a pu être analysée semi-quantitativement par les techniques à dispersion d'énergie. Les dimensions de maille, affinées par diffraction X (méthode des poudres), sont: pour la maille hexagonale de la bohdanowiczite,  $a$  8.412(6),  $c$  19.63(3)  $\text{\AA}$  (radiation Cu  $K\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ); pour la junosite,  $a$  26.71(1),  $b$  4.060(2),  $c$  17.172(7)  $\text{\AA}$ ,  $\beta$  127.65(3)° (radiation Co  $K\alpha$ ,  $\lambda = 1.7900 \text{ \AA}$ ;  $a' = 21.17 \text{ \AA}$ ,  $b' = b$ ,  $c' = c$ ,  $\beta' = 92.32^\circ$  pour la maille conventionnelle). Pour chacune des trois espèces, la mine Kidd Creek constitue la première localité canadienne.

(Traduit par la Rédaction)

**Mots-clés:** séléniures de bismuth, sulfosels, bohdanowiczite, junosite, laitakarite, dépôt de sulfures massifs, Kidd Creek, Timmins, Ontario.

### INTRODUCTION

Bohdanowiczite (ideally  $\text{AgBiSe}_2$ , the selenium analogue of matildite) and an unidentified lead-bismuth selenide were encountered during the study of selenide-bearing specimens from a small zone of bornite ore in the Kidd Creek mine, Timmins area, Ontario (Thorpe *et al.* 1976). The unidentified lead-bismuth mineral subsequently has been found to correspond to junosite, a mineral defined by Large & Mumme (1975) and Mumme (1975a) from studies of material from the Juno mine, Australia. The Kidd Creek mine is the first Canadian locality for these two minerals and for laitakarite, a minor phase associated with junosite.

The general geology of the Kidd Creek volcanogenic massive sulfide deposit has been described by Walker & Mannard (1974) and

Walker *et al.* (1975). The deposit is generally concordant within a pile of steeply dipping, overturned Archean rhyolitic volcanoclastic rocks. Except that its size and silver grade are greater than average, the deposit is similar to other Archean deposits of this type in Canada (Sangster 1972). Production to the end of 1977 totaled 35,834,000 tonnes of ore containing 9.03% Zn, 1.62% Cu, 0.34% Pb and 131 g/tonne Ag. Ore reserves were then about 108 million tonnes, and the deposit has not yet been completely delimited at depth.

Included within the Kidd Creek deposit and forming a small part of the South orebody is a bornite zone that has a stratigraphic thickness of about 12 m and a strike length of about 30 m on the 1200 level of the mine. The zone plunges steeply to the north-northeast, but its extension to depth has not been completely defined. This bornite zone lies between Zn-Cu massive ore to the west and Cu-Zn stringer ore to the east and forms the uppermost part of a stringer zone. The bornite zone thus appears to lie at the very top of a small hydrothermal vent; however, the adjacent massive ore shows evidence of transport to its depositional site above the vent, and it is likely that the metals of this ore were supplied from another feeder vent. The general mineralogy of the bornite ore has been reported by Thorpe *et al.* (1976). As well as being very rich in copper, the bornite zone is enriched in selenium, silver and cobalt. The margins of the zone are enriched in arsenic and, less regularly, in gold. On the 1200 level the bornite zone is partly surrounded by chalcopyrite-rich ore containing some arsenopyrite and cobaltite. Drillholes below the 1200 level intersected similar chalcopyrite-rich ore that in places contains a little tennantite, selenide minerals and large crystals of cobaltian pyrite.

Thorpe *et al.* (1976) found grains of a lead-bismuth selenide, with rims of different composition, in a specimen from diamond drill-hole K1010 at a depth of 72.6 m. Subsequent studies have shown that these grains are junoitite and that the rims consist of laitarakite and another, unidentified phase.

This paper presents more information on the occurrence and associations of these bismuth selenides in the Kidd Creek ore, and provides more highly accurate analyses for these minerals by using an improved matrix correction for microprobe data (Pringle 1979). X-ray powder data for bohdanowiczite and junoitite are also presented.

## ASSOCIATION AND DISTRIBUTION

### *Bohdanowiczite*

The name *bohdanowiczite* was proposed by Banaś & Ottemann (1967) for a silver-bismuth selenide present in polymetallic ores from the Kletno deposit in Poland, and the mineral was accepted as a valid species following publication of additional data (Banaś & Ottemann 1969, 1971). Banaś *et al.* (1979) have presented better chemical and X-ray data for the mineral. Bohdanowiczite occurs in a polymetallic uranium zone near magnetite-bearing skarns that in turn form part of the Kletno fluorite deposit. The selenides and uranium minerals are concentrated in association with quartz and black fluorite (Banaś & Ottemann 1971). The bohdanowiczite is associated with clausenthalite, tiemannite, umangite, naumannite, eskebornite(?) and traces of klockmannite, and with emplectite, pitchblende, chalcocite, secondary uranium minerals and traces of native silver, bornite and chalcopyrite. Banaś & Ottemann (1971) noted that the bohdanowiczite is commonly intergrown with clausenthalite or emplectite and that bohdanowiczite has been identified in the Julianehaab deposit in Greenland (1) in association with clausenthalite and bornite, (2) as inclusions within lamellar chalcocite, and (3) as intergrowths with clausenthalite and eucairite in bornite.

Bohdanowiczite, with associated tennantite, carrollite and an unidentified Cu-Co-Fe-As-S phase, is particularly concentrated around the margin of the small bornite-rich body within the Kidd Creek mine. Naumannite is the most abundant silver-bearing mineral in the bornite ore, but bohdanowiczite also contributes a significant proportion of the silver. Bohdanowiczite occurs most commonly as small, irregular to round blebs in bornite and, more rarely, in chalcopyrite, chalcocite and tennantite. The bohdanowiczite is in most cases associated with the other silver selenides (naumannite and eucairite) or with clausenthalite. Specimens S246, K1010-231 and K1286-377.5 contain grains of bohdanowiczite as large as 200 x 600  $\mu\text{m}$ . In specimen K1010-231, these contain inclusions and lamellar intergrowths of clausenthalite. In the larger bohdanowiczite grains there is some evidence of cleavage in one direction, and a few fine, planar twin lamellae can be seen (Fig. 1).

Specimen K1010-231 also contains fine intergrowths of cobaltite, bohdanowiczite and clausenthalite and of cobaltite, bohdanowiczite

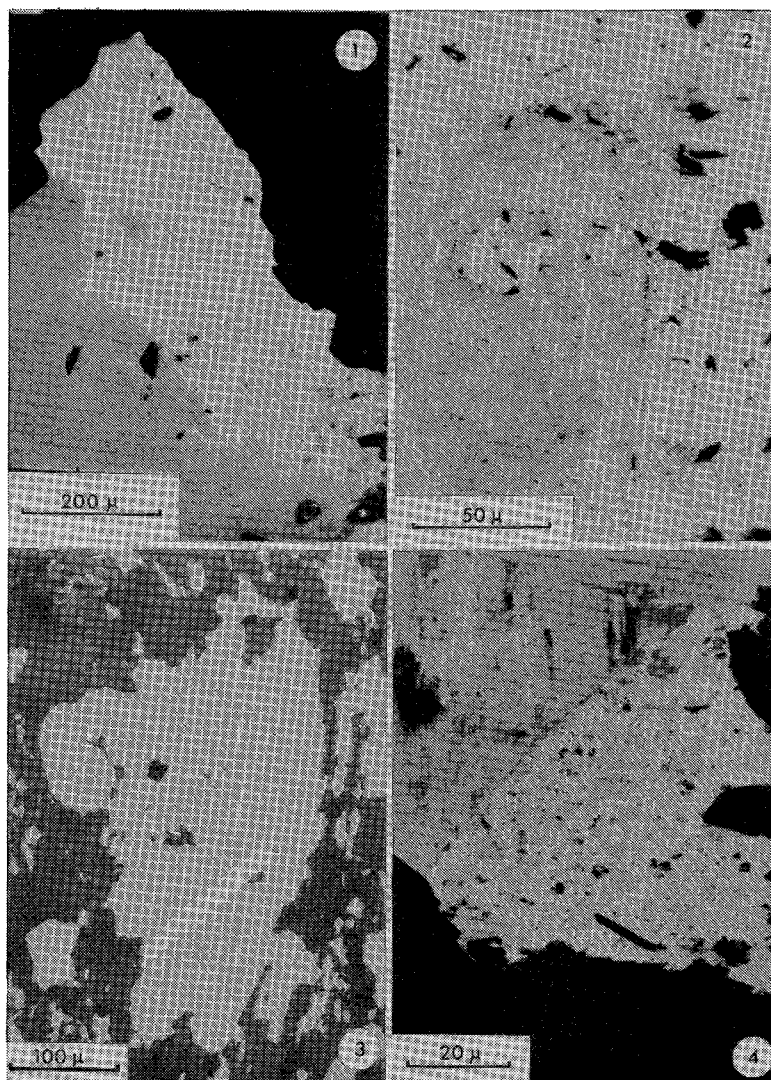


FIG. 1. Large bohdanowiczite grain showing planar twin lamellae. Nicols partly crossed. Darker grey at lower left is chalcopyrite.

FIG. 2. Intergrowths of cobaltite, bohdanowiczite and clausthalite (lighter area at right and top), and of cobaltite, bohdanowiczite and chalcopyrite.

FIG. 3. Lath-like grain of junosite included in sphalerite.

FIG. 4. Rim on junosite grain. Back-scattered electron image on the scanning-electron microscope. The light grey patchy area is the laitarakite rim with included blebs of a phase with high lead and sulfur contents. The uniform medium grey material is junosite and the dark grey patches (upper right) are the antimony-rich phase.

and chalcopyrite. These two unusual types of intergrowth are in continuous areas up to 0.5 x 2.5 mm (Fig. 2). It is not obvious whether chalcopyrite has replaced clausthalite or *vice versa* in the intergrowths.

#### *Junosite*

At the Juno mine, Tennant Creek Goldfield, Northern Territory, Australia, junosite, gold, chalcopyrite and other bismuth sulfosalt min-

erals are concentrated in two ellipsoidal to pipelike bodies of magnetite within a Lower Proterozoic pile of felsic metasediments and pyroclastic rocks (Large & Mumme 1975). The Juno deposit consists of a magnetite-chlorite core enclosed upward by a talc-magnetite zone with minor pyrite. Gold is concentrated at the centre of the magnetite-chlorite core and is succeeded upward by bismuth sulfosalts and then by chalcopyrite (Large 1975). Selenium is concentrated at the base of the bismuth-rich zone, where it overlaps the lower gold zone.

Junoite is the most abundant bismuth-bearing mineral at the Juno mine and occurs in association with magnetite, chalcopyrite, "wit-tite" ( $(\text{Bi}_{10}\text{Pb}_8[\text{S},\text{Se}]_{28})$ , subsequently named proudite: Mumme 1976) and members of the bismuthinite-aikinite mineral series (Large & Mumme 1975). Selenian heyrovskyite and emplectite are other bismuth sulfosalts that have been identified from the mine. Two members of the Juno aikinite-bismuthinite series have been named krupkaite (Žak *et al.* 1974, Large & Mumme 1975, Mumme 1975b), another has been named pekoite (Mumme & Watts 1976), and a third has been identified as gladite (Mumme & Watts 1976).

Junoite has been found in only one specimen from the Kidd Creek mine. This specimen is from borehole K1010, which was drilled to study the extension to depth of the selenide mineralization associated with bornite- and tennantite-bearing ore. The main opaque mineral in this specimen is chalcopyrite, whereas sphalerite is less abundant and junoite, cobaltite, kesterite and mawsonite are minor constituents. Cobaltite occurs as small grains included in chalcopyrite, less commonly in sphalerite, and in some cases associated with and included in junoite. Small blebs of kesterite are present as inclusions in chalcopyrite, and rarely in sphalerite. Mawsonite is present as a few blebs in chalcopyrite, and in one case, it was observed as a very fine partial rim on kesterite. Junoite generally forms discrete grains up to about 0.5 mm long and 0.3 mm wide that are isolated in gangue or included in chalcopyrite. Less commonly, junoite lamellae about 20  $\mu\text{m}$  wide

and 150  $\mu\text{m}$  long occur in chalcopyrite and, rarely, in sphalerite (Fig. 3). Small blebs of junoite, although not abundant, are present as inclusions in chalcopyrite and sphalerite.

### Laitakarite

Pitted and patchy rims are present on some junoite grains, and were found by X-ray-diffraction and scanning-electron-microscope (SEM) studies to be composed of laitarakite and intergrown junoite (in part platy). A few other minor unidentified phases are also finely intergrown with laitarakite in these rims (Fig. 4).

## PHYSICAL AND CHEMICAL PROPERTIES

### Bohdanowiczite

In polished sections of the Kidd Creek selenide-bearing ore, bohdanowiczite is creamy pink with weak anisotropism. Reflectance measurements on two orientations of a grain in sample K1010-231 are given in Table 1. Silicon was used as the reflectance standard. Vickers hardness, as determined on a Durimet microhardness tester with a 25 g load, is in the range 81-88 kg/mm<sup>2</sup>. These values are similar to those published by Banaś & Ottemann (1971) and Banaś *et al.* (1979).

Microprobe analyses were obtained with a MAC instrument operated at 25 kV, 0.03 mA sample current on chalcopyrite and using synthetic  $\text{AgBiSe}_2$ ,  $\text{AgBiS}_2$  and  $\text{CuSe}$  as standards. Element lines and analyzing crystals were as follows: Bi  $M\alpha$  (PET), Se  $K\alpha$  (LiF), Ag  $L\alpha$  (PET), S  $K\alpha$  (PET) and Cu  $K\alpha$  (LiF).

TABLE 1. REFLECTANCE VALUES FOR BOHDANOWICZITE

Wave length	$R_{\text{min.}}$	$R_{\text{max.}}$
470	51.2	52.9
546	49.8	51.5
589	50.1	51.5
650	50.1	51.6

TABLE 2. MICROPROBE ANALYSES OF BOHDANOWICZITE

	K1010-231	S(246)	679(3)	679(4a)	
Wt. %	(a)	(b)			
Ag	22.5	22.9	22.9	21.7	22.1
Cu	.0	.2	.3	.7	.7
Bi	44.5	44.7	43.9	44.0	43.6
Se	32.5	30.8	32.9	33.8	33.1
S	1.2	1.2	.1	.1	.2
Total	100.7	99.8	100.1	100.3	99.7
Formula with (Se, S) = 2					
Ag	.93	.99	1.01	.93	.96
Cu	.00	.02	.02	.05	.05
Bi	.95	1.00	1.00	.98	.98
Se	1.83	1.83	1.99	1.99	1.97
S	.17	.17	.01	.01	.03

(a) Thorpe *et al.* (1976); (b) same grain, analyses versus synthetic  $\text{AgBiSe}_2$ .

The matrix correction applied was by ERPMAG, a program developed at CANMET by combining EMPADR VII (Rucklidge & Gasparrini 1969) and MAGIC IV (Colby 1971). Four analyses of individual grains of bohdanowiczite, as well as a previously reported analysis (Thorpe *et al.* 1976), are listed in Table 2. The previously reported analysis deviates from stoichiometry because of errors in the matrix correction (Pringle 1979). The use of synthetic AgBiSe<sub>2</sub> as a standard in the more recent analyses has greatly reduced the magnitude of the matrix correction and accounts for the improved stoichiometry. Four recent analyses of type bohdanowiczite from the Kletno deposit, Poland, indicate an average of 2.5% sulfur substituting for selenium, and an average of 1.3% lead (Banaś *et al.* 1979). Lead was not detected in the Kidd Creek bohdanowiczite.

Cell dimensions were obtained by measuring X-ray powder-diffraction patterns of material from samples K1010-231 and S(246) and by using the least-squares refinement program of Stewart *et al.* (1972). The patterns were indexed by analogy with matildite (Harris & Thorpe 1969) and correspond to β-AgBiSe<sub>2</sub> (Geller & Wernick 1959). The X-ray powder-diffraction pattern from sample K1010-231 contains additional lines from inclusions of clausenthalite, and is similar, in this respect and by its appreciable substitution of sulfur for selenium, to the type material (Banaś *et al.* 1979). Bohdanowiczite from sample S(246) is very close to end-member composition and has no clausenthalite inclusions. The substitution of 1.2 wt. % sulfur for selenium in sample K1010-231 is reflected by a change in cell dimensions (Table 3).

### Junoite

Further X-ray-diffraction and electron-microprobe investigations of the unidentified Pb-Bi-Se-S phase reported in Thorpe *et al.* (1976, anal. 15) have shown it to be junosite. Optical measurements and hardness determinations have not been made on the Kidd Creek material, and for these the reader should consult the original descriptions by Large & Mumme (1975).

Junoite is ideally Bi<sub>8</sub>Pb<sub>3</sub>Cu<sub>2</sub>(S,Se)<sub>16</sub>, but published microprobe analyses of Australian and Kidd Creek specimens deviate significantly from this formula and also have consistently high totals. It can be shown that these deviations are due primarily to errors in the matrix correction provided by fundamental-parameter

TABLE 3. X-RAY POWDER DATA FOR BOHDANOWICZITE

K1010-231 <sup>1</sup>			S(246) <sup>2</sup>				
<i>I</i> <sub>est</sub>	<i>d</i> <sub>meas</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>est</sub>	<i>d</i> <sub>meas</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	
20	6.53	6.52	10	6.53	6.54	003	
30*	3.53	3.57	30†	3.57	3.58	021	
50†	3.39	3.40	60†	3.42	3.42	022	
10†	3.27	3.26	20†	3.28	3.27	006	
			10†	3.17	3.18	023	
100†	2.912	2.913	100†	2.926	2.925	024	
10†	2.659	2.660	20†	2.671	2.671	025	
			<5	2.439	2.434	026	
5	2.208	2.213	5	2.222	2.222	027	
			<5	2.186	2.182	009	
70†	2.094	2.095	80†	2.101	2.103	220	
70†	2.026	2.027	80†	2.036	2.035	028	
			10	2.004	2.002	223	
			5	1.810	1.813	041	
5	1.781	1.790	20	1.796	1.797	135	
40*	1.760	1.762	30†	1.770	1.769	226	
5†	1.725	1.719	10†	1.728	1.726	038	
30†	1.702	1.701	50†	1.705	1.707	044	
			<5	1.679	1.683	227	
10b	1.683	1.646	10	1.653	1.652	045	
20†	1.634	1.633	20†	1.637	1.639	137	
10*	1.522	1.521	5	1.530	1.528	047	
			10†	1.514	1.514	229	
40†	1.454	1.457	50†	1.462	1.462	048	
			<5	1.436	several		
			<5	1.399	1.398	049,331	
30*	1.362	1.358	10	1.361	1.361	242	
20†	1.319	1.321	30†	1.325	1.327	239	
			5	1.309	1.309	0015,0214	
			<5	1.299	1.299	245	
30†	1.286		40†	1.292	1.292	057,2212	
			<5	1.269	1.269	246	
5b	1.209		5	1.213	several		
20b	1.193	1.196	20b	1.201	1.201	248	
10†	1.159	1.160	20b	1.164	1.164	249	

1. Ag<sub>0.99</sub>Cu<sub>0.02</sub>Bi<sub>1.00</sub>Se<sub>1.93</sub>S<sub>0.17</sub>; hexagonal, *a* 8.379(8), *c* 19.55(4) Å, Cu Kα radiation (λ = 1.5418 Å), 114.6 mm Debye-Scherrer camera. Refinement based on 13 lines.

2. Ag<sub>1.01</sub>Cu<sub>0.02</sub>Bi<sub>1.00</sub>Se<sub>1.99</sub>S<sub>0.01</sub>; hexagonal, *a* 8.412(6), *c* 19.63(3) Å, Cu Kα radiation, 114.6 mm Gandolfi camera. Refinement based on 16 lines.

\* Mixture with clausenthalite. The additional lines from clausenthalite have been removed from the pattern except where they are combined with bohdanowiczite lines.

† Least-squares refinement.

TABLE 4. MICROPROBE ANALYSES OF JUNOITE

Wt. %	(1)	(2)	(3)	(4)
Bi	54.1	52.3	56.5	54.7
Pb	19.6	18.8	20.3	19.3
Cu	3.7	3.9	4.2	4.1
Ag	.4	.4	.1	.1
Se	14.9	14.7	7.8	7.6
S	9.9	10.1	13.5	13.5
Total	102.6	100.2	102.4	99.3
			Basis 16 (Se, S)	
Bi	8.33	7.99	8.32	8.09
Pb	3.04	2.89	3.02	2.88
Cu	1.87	1.96	2.03	1.99
Ag	.12	.12	.03	.03
Se	6.07	5.94	3.04	2.98
S	9.93	10.06	12.96	13.02

(1) K1010-238, ZAF correction

(2) K1010-238, correction based on measured coefficients (Pringle 1979)

(3) Juno mine, Australia (Large & Mumme 1975), ZAF correction. Average analysis, selenium variation from 4 to 12 wt. %.

(4) Juno mine, Australia. Estimated correction based on factors measured for (2).

(ZAF) methods, and that matrix corrections derived from measured correction factors give an improved result for lead-bismuth sulfosalts

TABLE 5. X-RAY POWDER DATA FOR JUNOITE

Kidd Creek <sup>1</sup>			Juno Mine <sup>2</sup>			Kidd Creek			Juno Mine			
I <sub>est</sub>	d <sub>meas</sub>	d <sub>calc</sub>	I <sub>est</sub>	d <sub>meas</sub>	hkl <sup>†</sup>	I <sub>est</sub>	d <sub>meas</sub>	d <sub>calc</sub>	I <sub>est</sub>	d <sub>meas</sub>	hkl	
20	13.04	13.07			201			2.316			1001	
5	8.56	8.58			202	20	2.312	2.315			716,	
		6.53			401						205	
30b	6.51	{ 6.43	20	6.515	402						912	
		5.47			403*			2.313			1007	
50	5.45	4.58	20	5.433	202*	5	2.284	2.287			006	
20	4.58	4.58	5	4.595	401	<5	2.27	2.266			316	
<5	4.14	4.15			601	10	2.241	2.241			1205	
5	4.06	4.07	10	4.084	204	<5	2.23	2.223			1204	
		4.03	5	4.005	604*			2.211			711	
80	3.92	3.92	80	3.904	311*	30b	2.208	{ 2.207	40	2.213	603	
5b	3.69	3.69	10	3.681	312*			2.205			916	
20	3.61	3.61	10	3.590	600	<5	2.18	2.178			1206	
90	3.52	{ 3.53	100	3.545	310			2.159			207	
		3.52			203	20	2.142	2.143		10	2.141	1203
<5	3.46	3.47	5	3.471	405			2.140			314	
60	3.40	{ 3.41	40	3.388	004	20	2.120	2.119		20	2.103	608*
		3.40	10	3.314	313,	20	2.090	2.090		30	2.095	513*
10b	3.31	3.31			402			2.073		40	2.070	802,
		{ 3.28	5	3.271	112	60	2.072	{ 2.072			1115	
		3.27			804			2.043			517	
10	3.27	3.27	50	3.229	802*	<5	2.04	2.043			1113	
30	3.216	3.215			113	20	2.030	2.030		20	2.026	020
60	3.182	{ 3.181	30	3.175	311	20	1.995	1.995		20	1.999	712*
		3.179			511	<5	1.98	1.976			405	
		3.151	10	3.131	513	5	1.960	{ 1.964			1112	
10	3.135	3.139			205	10	1.930	1.960			1208	
<5	3.04	3.037			805			1.928			604,	
<5	2.00	2.996			601						1117	
20	2.954	2.955	50	2.970	801*			1.903			1405,	
		2.955			314*	10	1.903				1406,	
100	2.930	{ 2.932	70	2.919	510						423	
		2.929			606			1.902			1201	
<5	2.87	2.860			312*	20	1.882	{ 1.883			918	
20	2.839	2.836	10	2.796	112,			1.879			116	
20	2.795	2.796			714,	10	1.857	1.859			609	
20	2.749	2.748			806			1.857			1111	
20	2.729	2.733	10	2.712	714			1.856			222	
<5	2.68	2.694			714	<5	1.84	1.845			803	
5	2.644	2.642			511	5	1.820	1.820			1316	
		2.621			515			1.802			524,	
30	2.617	2.618	20	2.606	711						713	
		2.614			1005	10	1.800	1.801			1403	
10	2.562	{ 2.562	10	2.538	315*			1.800			1408	
		2.559			206	10	1.758	{ 1.759			620	
20	2.499	2.498	20	2.506	1002*			1.754			318	
10	2.468	2.474	10	2.462	1006	<5	1.74	{ 1.744			425	
<5	2.43	2.424			807			1.743			024	
40	2.387	2.388	20	2.384	914*			1.734			823,	
10	2.347	2.345			407	5	1.732	1.732			406	
5	2.338	2.332	15	2.320	516			1.730			207	
						10	1.714	1.713			422	
											1402	

1. Debye-Scherrer camera, 114.6 mm, Co K $\alpha$  radiation ( $\lambda = 1.7900 \text{ \AA}$ ). Cell parameters [refined using Mumme's (1975a) convention]:  $a = 26.71(1)$ ,  $b = 4.060(2)$ ,  $c = 17.172(7) \text{ \AA}$ ,  $\beta = 127.65(3)^\circ$ . Conventional setting:  $a' = 21.17 \text{ \AA}$ ,  $b' = b$ ,  $c' = c$ ,  $\beta' = 92.32^\circ$ .

2. Data from Mumme (1975a); cell parameters:  $a = 26.73(3)$ ,  $b = 4.044(5)$ ,  $c = 17.03(2) \text{ \AA}$ ,  $\beta = 127.27(7)^\circ$ . Conventional setting:  $a' = 21.29 \text{ \AA}$ ,  $b' = b$ ,  $c' = c$ ,  $\beta' = 92.27^\circ$ .

<sup>†</sup> Indices include all significant lines from the structure-factor table in Mumme (1975a).

\* Both cells were refined using 15 lines.

(Pringle 1979). Table 4 compares analyses of junioite corrected by both methods. The Kidd Creek junioite has 14.7 wt. % selenium, whereas the maximum reported in the Australian junioite is 12 wt. %.

An X-ray powder-diffraction pattern from analyzed material in sample K1010-238 was prepared for measurement and comparison with published data (Table 5). The table of structure factors in Mumme (1975a) was a guide for the selection of lines used to calculate a refined cell. To make our results comparable to those of Mumme, we used his indexing convention. The agreement between  $d_{\text{meas}}$  and  $d_{\text{calc}}$  for the pattern published by Large & Mumme

(1975) can be improved by using the same selection of lines for refinement.

#### Laitakarite

The initial report on the Kidd Creek samples (Thorpe *et al.* 1976) listed two analyses of a phase rimming the mineral identified as junioite. Subsequent investigations have shown that these rims are laitakarite [(Bi,Pb)<sub>4</sub>Se<sub>2</sub>S] with inclusions of at least two other unidentified phases (Fig. 4), one characterized by higher lead and sulfur contents and the other by major antimony. An X-ray powder-diffraction pattern of a portion of the material shown

TABLE 6. SEMIQUANTITATIVE MICROPROBE ANALYSES, LAITAKARITE RIMS

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Wt. %						
S*	3.0	2.5	4.0	3.5	7.0	11.5
Se	17.5	16.5	16.0	16.5	15.0	13.0
Sb	.0	.0	.0	.5	1.0	2.0
Pb	7.0	8.5	11.0	12.5	16.5	22.5
Bi	72.5	72.5	69.0	67.0	60.5	51.0
Basist Sb + Pb + Bi = 4						
S	.98	.80	1.30	1.13	2.31	3.89
Se	2.33	2.16	2.11	2.17	2.01	1.78
Sb	.00	.00	.00	.04	.09	.18
Pb	.36	.42	.55	.63	.84	1.18
Bi	3.64	3.58	3.45	3.33	3.07	2.64
S+Se	3.31	2.96	3.41	3.30	4.32	5.67

\* Sulfur was calculated by difference, owing to nonresolution of S  $\alpha_1$ , Pb  $\alpha_2$  and Bi  $\alpha_1$ . 1, 2: laitakarite; 3, 4, 5: laitakarite with inclusions (Fig. 4); 6: inclusion with some laitakarite.

in Figure 4 had no lines other than those attributable to laitakarite. It was not possible to obtain fragments sufficiently rich in the lead-sulfur-rich phase to determine its diffraction properties.

Conventional microprobe analysis with wavelength spectrometers requires relatively high sample currents, and beam diameters are therefore not appropriate for grains of the size found in these rims. With reduced sample currents (2–3 nA), the minimum beam diameter on the MAC instrument used for these studies becomes marginally smaller than the largest inclusions in the laitakarite rims. Using these conditions and an energy-dispersive spectrometer, it was possible to obtain semi-quantitative analyses of some of these areas, provided that the sulfur content was calculated by difference. Analyses 1 and 2 (Table 6) represent small areas of laitakarite that are essentially free of inclusions. Analyses 3, 4 and 5 represent mixtures of laitakarite and the phase that is richer in lead and sulfur (Fig. 4). Analysis 6, of the largest inclusion of the lead-sulfur-rich phase shown in the SEM image, is certainly diluted somewhat by the presence of laitakarite, but should approach the true composition. As the SEM image shows that the phase with major antimony has a limited distribution, it is probable that the minor antimony in the lead-sulfur-rich phase (anal. 4, 5 and 6) is an essential constituent.

Qualitative microprobe analysis of the phase with major antimony showed sulfur as the only other major element, and the few grains present were too small for quantitative analysis. This phase is not believed to be stibnite because the grains reacted visibly to the electron beam.

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