

BENJAMINITE, REINSTATED AS A VALID SPECIES

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ABSTRACT

Benjaminite from Nevada, U.S.A., Camsell River, N.W.T. and Cobalt, Ontario, gives a general composition, $(\text{Ag,Cu})_3(\text{Bi,Pb})_7\text{S}_{12}$, and space group $C2/m$, Cm or $C2$, with $a = 13.25$, $b = 4.04$, $c = 20.18\text{Å}$, $\beta = 103.21^\circ$ and $Z = 2$, supporting the existence of benjaminite reported by Nuffield (1975), and reinstating benjaminite as a valid species.

Benjaminite is compositionally similar to pavonite. These two minerals cannot be identified infallibly without x -ray single-crystal data. Reports of "pavonite", "alaskaite", and "benjaminite" in the literature should be re-examined.

RÉSUMÉ

La benjaminite du Nevada, E.U., de Camsell River, T.N.O. et de Cobalt, Ontario a été étudiée. Les résultats ont donné comme composition générale, $(\text{Ag,Cu})_3(\text{Bi,Pb})_7\text{S}_{12}$, et une maille élémentaire de $C2/m$, Cm ou $C2$, $a = 13.25$, $b = 4.04$, $c = 20.18\text{Å}$, $\beta = 103.21^\circ$ et $Z = 2$, ce qui soutient l'existence de la benjaminite rapportée par Nuffield (1975) et rétablit la benjaminite comme une espèce valable.

La benjaminite est de composition semblable à la pavonite. Ces deux minéraux ne peuvent être identifiés infailliblement des données de cristal simple obtenues par rayons-x. Les rapports publiés sur la "pavonite", l'"alaskaite" et la "benjaminite" devraient être ré-étudiés.

INTRODUCTION

"Benjaminite" was originally described by Shannon (1925) on a specimen from the Outlaw mine, Nye County, Nevada, associated with muscovite, fluorite, chalcopyrite, molybdenite, and pyrite in a quartz vein near the contact of granite and rhyolite. The mineral resembled massive tetrahedrite except that it showed a fair cleavage in one direction. The formula $(\text{Cu, Ag})_2\text{Pb}_2\text{Bi}_4\text{S}_9$ was proposed by Shannon.

Shannon's type material (U.S. Nat. Mus. 95058; Harvard University, HMM 85749) was re-examined by Nuffield (1953) and found to be a mixture of aikinite and a possible silver-

bearing mineral with distinct x -ray crystallographical data. As the inspiration of Shannon's investigation was probably the "silver-bearing mineral", the name benjaminite was retained by Nuffield, though the chemical composition was undefined.

In a study of material from the Adrasman deposit, Central Asia, Mintser (1967) assigned the name benjaminite to a mineral with composition $(\text{Cu,Ag})_2\text{Pb}_2\text{Bi}_4\text{S}_9$, even though its x -ray powder diffraction pattern was not identical to Nuffield's (1953) data, and despite $(\text{Cu,Ag})_2\text{Pb}_2\text{Bi}_4\text{S}_9$ for benjaminite having been discredited by Nuffield. On re-examining Mintser's material, Borodaev & Mozgowa (1971) found that the grains considered homogeneous by Mintser were intergrowths of berryite, matildite and lindströmite. Borodaev & Mozgowa thus concluded that "benjaminite of Shannon and Mintser must once again be discredited" and that "the powder pattern obtained by Nuffield should not be identified with the material which was chemically analyzed by Shannon". It was on this basis that the Commission on New Minerals and Mineral Names (IMA) voted in 1973 to discredit the name "benjaminite", regardless of the fact that the name had been assigned by Nuffield (1953) to the distinct species ($C2/m$, $a' = 13.34$, $b' = 4.06$, $c' = 20.25\text{Å}$, and $\beta = 104^\circ$) of unknown composition in Shannon's type material. Borodaev & Mozgowa further concluded that there were not sufficient grounds for distinguishing individual mineral species among low-Pb, *i.e.* $(\text{Ag,Cu,Pb})_3\text{Bi}_7\text{S}_{12}$, and Pb-free (*e.g.* $\text{AgCu}_4\text{Bi}_7\text{S}_{12}$) phases, and suggested that all be considered as a single series of benjaminite with discontinuous, isomorphous miscibility of a general formula $(\text{Ag,Cu,Pb})_3\text{Bi}_7\text{S}_{12}$.

Nuffield (1975), on re-examination of the type specimen from Nye County, Nevada (U.S. Nat. Mus. 95058), found that the phase previously identified as benjaminite by him consisted of two finely intergrown silver-bearing phases of which one, a low-Pb phase $(\text{Ag}_{2.66}\text{Cu}_{0.32})_{23.18}(\text{Bi}_{17.08}\text{Pb}_{0.40})_{27.46}\text{S}_{11.64}$ was predominant and contributed most of his original x -ray data. The present investigations have also found this low-Pb phase in material from Nevada, U.S.A.,

TABLE 1. REFLECTANCE AND MICRO-INDENTATION HARDNESS OF BENJAMINITE

Wavelength	Nevada		Camseil River, N.W.T.
	Gr. 1.	Gr. 2.	
470 nm	47.9-42.6	47.5-44.3	44.8-44.5
546	45.6-40.4	44.9-41.9	42.7-42.0
589	44.7-39.4	44.6-41.6	42.0-41.5
650	43.9-39.4	43.5-40.4	41.6-41.0
Micro-Indentation Hardness (kg/mm ²)	186-251	225-239	164-218
VHN50g =	Av. 219	Av. 232	Av. 186

Results of five to six measurements.

TABLE 2. UNIT CELL OF BENJAMINITE - (Ag,Cu)₃(Bi,Pb)₇S₁₂ AND PAVONITE - (Ag,Cu)(Bi,Pb)₃S₅

Space Group	Benjaminite			Pavonite
	Nevada	Camseil River N.W.T.	Nye County* Nevada	Bolivia†
	<i>C</i> 2/ <i>m</i> , <i>Cm</i> , <i>C</i> 2	<i>C</i> 2/ <i>m</i> , <i>Cm</i> , <i>C</i> 2	<i>C</i> 2/ <i>m</i> , <i>Cm</i> , <i>C</i> 2	<i>C</i> 2/ <i>m</i> , <i>Cm</i> , <i>C</i> 2
<i>a</i> Å	13.363(8)	13.246(5)	13.39	13.36
<i>b</i>	4.051(3)	4.044(2)	4.06	4.02
<i>c</i>	20.187(9)	20.179(8)	20.21	16.38
β	103.29(5)°	103.21(3)°	103.45°	94.2°
<i>Z</i>	2	2	2	4

* Pseudo-cell. True-cell has *b* = 8.12Å according to Nuffield (1975).

† Harris & Chen (1975). Type material.

TABLE 3. X-RAY POWDER DIFFRACTION DATA OF BENJAMINITE AND PAVONITE

<i>h k l</i>	Benjaminite				Pavonite	
	Camseil R., N.W.T.	Nevada (Gr. 1)	Bolivia (Nuffield 1954)			
	<i>d</i> _{calc} Å	<i>d</i> _{obs} Å	<i>I</i> _{est}	<i>d</i> _{obs} Å	<i>I</i> _{est}	
2 0 1	6.588	6.594	2	6.625	2	
2 0 1	5.749	5.753	1	5.787	1	5.36
0 0 4	4.911	4.907	2	4.920	2	
2 0 2	4.901					
0 0 5	3.929	3.935	†			4.03
1 1 1	3.837	3.832	†	3.840	†	3.85
2 0 5	3.758	3.754	2	3.776	2	
2 0 4	3.537	3.539	8	3.551	6	3.58
1 1 3	3.429	3.427	8	3.435	8	3.44
4 0 2	3.294	3.302	5	3.322	5	3.33
2 0 6	3.233	3.234	4	3.230	4	
4 0 3	3.196	3.194	1			
1 1 4	3.141	3.148	2	3.139	1	
3 1 1	2.982	2.983	2	2.992	1	
3 1 0	2.946	2.944	5	2.966	5	
3 1 3	2.859					2.96
3 1 5	2.852	2.851	10	2.862	10	2.84
3 1 1	2.848					
2 0 7	2.820	2.813	6	2.821	5	
3 1 4	2.721	2.723	3	2.731	2	
1 1 6	2.585	2.586	3	2.587	2	2.58
1 1 6	2.417	2.417	†	2.417	†	
3 1 6	2.383	2.388	†	2.386	†	
1 1 7	2.199	2.201	5	2.203	4	2.25
5 1 4	2.147			2.166		2.19
1 1 8	2.139	2.143	3	2.140	2	
1 0 1	2.086					
1 1 5	2.080	2.083	3	2.097	3	2.10
0 2 0	2.022					
6 0 6	2.021	2.022	6	2.028	6	
1 1 9	2.011					
6 0 2	2.006	2.007	6	2.009	6	2.01
5 1 6	1.997	1.997	1			
0 0 7	1.965	1.965	3	1.962	3	1.963
6 0 9	1.933	1.934	1			1.893
4 0 8	1.839	1.839	1	1.849	1	
4 0 8	1.768	1.769	4	1.773	4	
3 1 8	1.756	1.754	4	1.756	4	1.753
0 2 6	1.721	1.720	4	1.722	4	1.721
7 1 1	1.701	1.701	4	1.713	3	
6 0 10	1.650	1.648	4	1.660	3	
0 0 12	1.637	1.636	3	1.638	4	1.637
8 0 5	1.628	1.628	†			
4 0 11	1.430	1.429	2	1.434	3	1.484
4 0 14	1.410	1.411	2	1.413	2	1.457
						1.423

CuKα radiation (λ=1.5418Å), 114.6mm camera; *d*_{calc} obtained from *a*=13.246, *b*=4.044, *c*=20.179Å, β =103.21°. Index on benjaminite patterns.

from Camseil River, Northwest Territories, Canada, and from Cobalt, Ontario. Because of the misunderstanding about the identification, and the subsequent discrediting of benjaminite by the IMA Commission, and in view of more recent studies by Nuffield (1975) and ourselves, a proposal was submitted jointly to reinstate the name benjaminite to represent the low-Pb phase. The proposal has been approved by the Commission on New Minerals and Mineral Names (IMA). The material from N.W.T., Nevada, and Ontario are described here in detail.

DESCRIPTIONS OF SAMPLES

A specimen labelled "alaskaite" and argenterous galenobismutite" from Nevada, U.S.A. (exact locality unknown), was obtained from the reference collection of the Geological Survey of Canada. The specimen consists primarily of massive quartz and small amounts of sulpho-salt minerals. The opaque minerals observed under reflected light were benjaminite, an aikinite-type phase, and minor amounts of bismuthinite and chalcopyrite. The benjaminite occurs as laths up to 6 mm in length. It usually shows alteration along cracks, whereas the aikinite-type phase occurs in a few cases as fine lamellae which resemble twinning, intergrown with benjaminite.

The specimen from the mine of Terra Mining and Exploration Company, Camseil River, N.W.T., Canada was obtained from Dr. R. I. Thorpe, Geological Survey of Canada. Under reflected light, the specimen was observed to consist of several arsenides and sulphides, including safflorite, skutterudite, rammelsbergite, arsenopyrite, nickeline, matildite, bismuthinite, chalcopyrite, pyrite, benjaminite, sphalerite, galena, and minor amounts of native bismuth. The benjaminite occurs as finely disseminated grains and irregular shapes up to 100 microns in size, associated closely with matildite and in contact with the arsenides. Native silver fills fractures in arsenides, and native bismuth occurs within the arsenides.

A fine-grained pavonite-type mineral from the Canadian Keeley mine, Cobalt, Ontario, Canada has been re-examined and identified as benjaminite. The mineral was first identified by Petruk and staff (1971) on the basis of its x-ray powder pattern, which is similar to that of pavonite, although the composition did not correspond to AgBi₃S₅. The mineral occurs as veinlets in calcite in the mineralized Keewatin interflow rocks. It is intergrown with bismuthinite, matildite, native bismuth, chalcopyrite, sphalerite and pyrite.

MICROSCOPIC OBSERVATIONS

Under a reflected-light microscope, benjaminite in air is greyish white, or slightly bluish, distinctly anisotropic (white to grey), and weakly birefracting. It usually shows lath-like form and a fair cleavage parallel to the elongation. Polysynthetic twinning, and lamellar intergrowths with aikinite that resemble twinning, are very common. The mineral has optical properties very similar to those of pavonite, whereas it can be readily distinguished from aikinite which is creamy white to very pale brownish in color, granular, and more or less fractured.

The reflectance measured with a Leitz MPE microscope photometer using a silicon reference standard (N 2538.42, issued by the IMA Commission on Ore Microscopy) for four standard wavelengths, and the micro-indentation hardness determined with a Leitz Durimet hardness tester at 50 g and 15 seconds are listed in Table 1.

Tests show that HNO_3 (1:1) etches very slowly and stains iridescently or blackens the surface. Aikinite is etched more easily. FeCl_3 (20%) gives a light brown surface with effervescence; HCl does not show detectable reaction.

X-RAY CRYSTALLOGRAPHY

Specimens from Camsell River, N.W.T., and Nevada, U.S.A., were studied by the precession method using $\text{MoK}\alpha$ radiation. The crystals were pre-analyzed by electron microprobe and identified with a Gandolfi camera.

The diffraction symbol gives $2/mC/-$ corresponding to space groups $C2/m$, Cm , or $C2$. The cell parameters, refined by a least-squares method using powder data, are compared with those from Nye County, Nevada (Nuffield 1975) in Table 2. A b -axis precession cone-axis photograph taken with $\mu = 12^\circ$, $s = 25$ mm and 24 hours exposure failed to reveal the doubling of the b -dimension described by Nuffield (1953, 1975).

X -ray powder diffraction data (Table 3) were indexed by comparison of the observed d -values with the calculated values obtained from single-crystal data, and only the strong reflections on single-crystal photographs were used to index the patterns. The x -ray data for specimens from Camsell River, and Nevada, and the powder pattern obtained by Petruk and staff (1971) for the Cobalt, Ontario material are the same except that the Nevada patterns are slightly diffuse. The small differences from the pattern given by Nuffield (1953) are apparently due to

TABLE 4: ELECTRON MICROPROBE ANALYSES OF BENJAMINITE

	Nevada			Camsell River N.W.T.	Cobalt Ontario (this study)	Nye County* Nevada
	Gr.1	Gr.2	Gr.3			
Cu	1.1	2.3	1.0	1.3	2.9	1.4
Ag	12.4	11.4	12.5	13.6	9.6	12.6
Pb	9.7	10.8	8.7	2.3	1.3	3.7
Bi	59.0	57.8	61.5	65.4	69.0	65.1
S	17.1	17.3	17.8	17.7	18.1	16.4
Tot. wt%	99.3	99.6	101.5	100.3	100.9	99.2

Atomic contents per unit cell assuming $D = 6.7 \text{ g/cm}^3$

Cu	0.75	1.56	0.67	0.87	1.92	0.96
Ag	4.98	4.57	4.91	5.34	3.75	5.08
Pb	2.03	2.25	1.78	0.47	0.26	0.78
Bi	12.24	11.95	12.48	13.25	13.90	13.54
S	23.12	23.32	23.54	23.37	23.76	22.34

Atomic ratios based on $\text{Pb} + \text{Bi} = 7.00$

Cu	0.37	0.77	0.33	0.44	0.95	0.47
Ag	2.44	2.25	2.41	2.72	1.85	2.48
Pb	1.00	1.11	0.87	0.24	0.13	0.38
Bi	6.00	5.89	6.13	6.76	6.87	6.62
S	11.34	11.49	11.56	11.93	11.75	10.87

* Average of low-Pb phase analyses, Nuffield (1975). Recalculated.

the presence of a second phase in Nuffield's material (Nuffield 1975).

Although the powder patterns of benjaminite and pavonite are similar, the two minerals can be distinguished by the presence of the following strong doublets (in terms of $d\text{\AA}$, h): 1.77(4), 1.75(4); 1.72(4); 1.70(4), 1.65(4), 1.64(3); and 1.43(2), 1.41(2) in benjaminite, instead of only three broad strong lines at 1.72(3), 1.64(3), and 1.42(2) in pavonite (Table 3). Pavonite has a unit cell (Table 2) with $a = 13.36$, $b = 4.02$, $c = 16.38\text{\AA}$, $\beta = 94.2^\circ$, space group $C2/m$ (Nuffield 1954; Harris & Chen 1975). Although the c -dimension and the β -angle of pavonite are distinctly different from those of benjaminite, the strong reflections on zero-level b -axis precession photographs of both minerals correspond closely and result in the strong similarity of their powder patterns.

CHEMICAL COMPOSITIONS AND THE POSSIBLE GENERAL FORMULA

Electron microprobe determination of Cu, Ag, Pb, Bi, and S were performed at 25 kilovolts with a Material Analysis Company (MAC) Model 400 electron-probe microanalyzer using synthetic CuS , PbS and AgBiS_2 as standards. The x -ray intensity data were processed with the computer program of Rucklidge & Gasparini (1969). The results (Table 4) are compared with the average analysis reported by Nuffield (1975) for benjaminite from Nye County, Nevada.

The atomic contents per unit cell were cal-

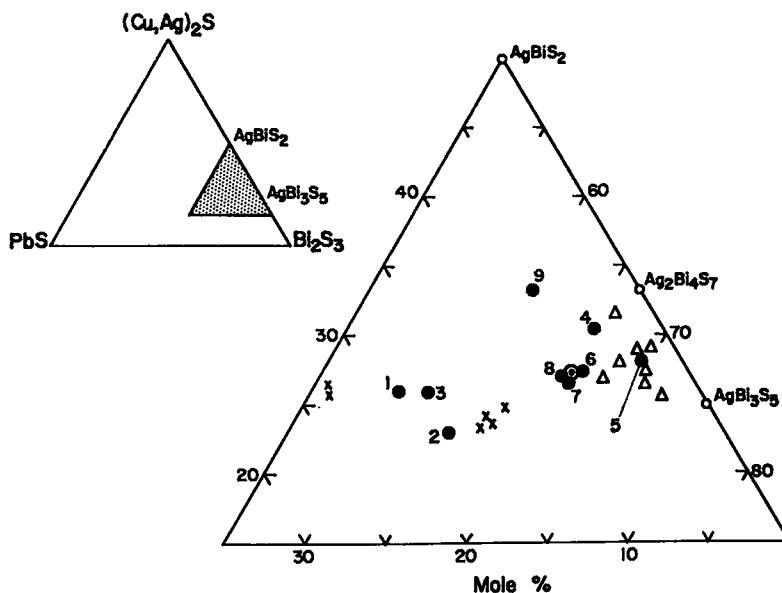


FIG. 1. Distributions of benjaminite and some compositionally-related phases in the $(\text{Cu,Ag})_2\text{S-PbS-Bi}_2\text{S}_3$ diagram.

- benjaminite: 1-3 Nevada; 4 Camsell River, N.W.T.; 5 Cobalt, Ontario; 6-9 Nye County, Nevada (Nuffield 1975);
- × pavonite: ROM 21003, No 1124 (Karup-Møller 1972);
- △ low-Pb phases (Borodaev & Mozgowa 1971);
- ⊙ pavonite, type material, Bolivia (Harris & Chen 1975).

culated using a density of 6.7 g/cm^3 . If one assumes that Cu and Ag occupy the same structural site, as do Pb and Bi, the observed analyses agree very well with the general formula, $(\text{Ag, Cu})_8(\text{Bi, Pb})_{14}\text{S}_{24}$ *, proposed by Nuffield (1975). The slight deficiency of S, as usually observed in probe analyses, is most likely due to the imperfect calibration of the sulphur intensity data. The formula corresponds to $(\text{Ag, Cu})_8(\text{Bi, Pb})_7\text{S}_{12}$. The atomic ratios calculated on the basis of $\text{Pb} + \text{Bi} = 7.0$ are also listed in Table 4.

The general formula requires the presence of Pb. This is further supported by the fact that the Pb-free compound, $\text{Ag}_8\text{Bi}_7\text{S}_{12}$, has never been synthesized in the system $\text{Ag}_2\text{S-Bi}_2\text{S}_3$ (Van Hook 1960; Craig 1967; Chen & Chang 1974). The high-Pb content usually corresponds to a low-Bi content, indicating a substitution relationship between Bi and Pb.

The substitutions are most probably of the type, $\text{Ag}^+\text{Bi}^{3+} \rightleftharpoons 2\text{Pb}^{2+}$. This is also evident from the fact that a similar, though not identical, substitution was found between benjaminite

and its intergrown phase, $\text{Pb}_2(\text{Ag, Cu})_2(\text{Bi, Pb})_2\text{S}_{12}$, in the type specimen from Nye County, Nevada (Nuffield 1975).

Crystal-structure studies have confirmed that Ag and Cu can occupy the same structural site, as in tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (Wuensch 1964). Disorder of Pb and Bi is not uncommon, as for example in nuffieldite, $\text{Pb}_2\text{Cu}(\text{Pb, Bi})\text{Bi}_5\text{S}_7$ (Kohatsu & Wuensch 1973). The general formula $(\text{Ag, Cu})_8(\text{Bi, Pb})_7\text{S}_{12}$ is preferred for benjaminite. However, as the Pb content per unit cell can be up to 2.3 atoms, and because Ag, Pb and Bi can also occupy the same structural location (Kupcik & Makovicky 1968), the formula $(\text{Ag, Cu, Pb})_8(\text{Bi, Pb})_7\text{S}_{12}$ is also possible. The true formula can be determined only by crystal-structure analysis.

Based on the data available, *i.e.* including Nuffield's analyses, the compositions show a range with $\text{Ag} = 1.85\text{-}2.72$ atoms, and $\text{Bi} = 5.89\text{-}6.87$ atoms in the formula $(\text{Ag, Cu})_8(\text{Bi, Pb})_7\text{S}_{12}$. The range of compositions are shown in a $(\text{Cu, Ag})_2\text{S-PbS-Bi}_2\text{S}_3$ diagram (Fig. 1); a composition of pavonite from Cerro Bonete, Sur Lipez, Bolivia (Harris & Chen 1975), and some analyses (Karup-Møller 1972; Borodaev & Mozgowa 1971) which are similar to those of benjaminite, are included.

*The same formula will be derived by using a density in the range of 6.7 to 7.0 g/cm^3 , which is very common for Bi-sulphosalts.

OTHER POSSIBLE OCCURRENCES
OF BENJAMINITE

Borodaev & Mozgowa (1971) reported three low-Pb phases, I, II, III, with compositions, $(Ag_{2.0}Cu_{0.9}Pb_{0.1})Bi_7S_{12}$, $(Ag_{1.5}Cu_{1.5}Pb_{0.5})Bi_7S_{12}$ and $(Ag_{1.2}Cu_{1.7}Pb_{0.1})Bi_7S_{12}$ respectively, from Odrasman, Central Asia and North Kounrad, Kazakhstan (Fig. 1). The compositions of the first two phases are close to that of benjaminite from Cobalt, Ontario, whereas phase III has $Cu > Ag$ in contrast to $Ag > Cu$ observed for benjaminite. Pavonite can also have a similar composition but with a different unit cell (Harris & Chen 1975). The *x*-ray powder diffraction patterns of these three phases show variations from sample to sample, but the patterns are more similar to that of benjaminite than to pavonite. The identification of these phases can only be made by single-crystal work.

A medium-Pb phase, $(Ag_{1.5}Cu_{2.5})PbBi_6S_{12}$, was also reported by Borodaev & Mozgowa. The composition is somewhat similar to that of the benjaminite from Nevada (analysis No. 1) except for a very high Cu and a low Ag content. This phase is apparently not benjaminite because the *x*-ray powder pattern is distinctively different.

A phase, $Pb(Cu,Ag)_{2.2}Bi_{4.6}S_{7.6}$, from Kaptarkhan deposits, Central Asia was reported by Lur'ye *et al.* (1971). Its *x*-ray powder pattern is similar to some extent to that of benjaminite. The chemical analyses correspond to $(Ag_{2.0}Cu_{0.9})(Bi_{6.0}Pb_{1.0})S_{9.6}$ and $(Ag_{1.7}Cu_{1.0})(Bi_{5.5}Pb_{1.5})S_{9.5}$ and indicate that this phase is not benjaminite.

Karup-Møller (1972) reported several pavonite minerals from Bolivia, Nevada, and Colorado. Their compositions and *x*-ray powder patterns are very close to those of benjaminite, especially those labelled "alaskaite" from Alaska mine, Colorado, and "benjaminite and aikinite" from Cerro Bonete, Sur Lipez, Bolivia. The "alaskaite" consists of two pavonite phases, with one exsolved from the other as lamellae. The host corresponds to $(Ag_{1.64}Cu_{0.71})(Bi_{6.25}Pb_{0.75})S_{11.42}$, similar to that of benjaminite from Nevada (Fig. 1), whereas the lamellae have the composition $(Ag_{1.15}Cu_{1.71})(Bi_{5.72}Pb_{1.28})S_{11.48}$. Both phases were reported to have triclinic symmetry, and the *x*-ray powder data obtained from a mixture of these two phases are similar to those of benjaminite. The pavonite mineral in "benjaminite and aikinite" from Cerro Bonete also shows a similar exsolution in which the host compositions fall in the range of benjaminite from Nevada. It would not be surprising if some of these phases are found to be benjaminite by

x-ray single-crystal studies.

Re-examination of materials identified as "alaskaite" or "benjaminite" in old literature have often proved to be pavonite, or benjaminite (this study; Nuffield 1954, 1975; Karup-Møller 1972). The "alaskaite" and "benjaminite" from Alaska mine (Colorado), Nevada, and Cerro Bonete (Bolivia) should be re-examined.

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