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CUPROMAKOVICKYITE, $Cu_8Pb_4Ag_2Bi_{18}S_{36}$, A NEW MINERAL SPECIES OF THE PAVONITE HOMOLOGOUS SERIES

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ABSTRACT

Cupromakovickyite, ideally $Cu_8Pb_4Ag_2Bi_{18}S_{36}$, is a new mineral species that occurs at the skarn deposit of Băiţa Bihor, Romania, and at the scheelite deposit Felbertal, Salzburg Province, Austria. The associated minerals are makovickyite, bismuthinite derivatives (aikinite–friedrichite range), hodrušite, kupčikite, paděraite, emplectite, wittichenite and tetradymite (Băiţa Bihor), and makovickyite, bismuthinite derivatives (aikinite–krupkaite range), hodrušite, kupčikite, wittichenite and native bismuth (Felbertal). The opaque mineral is grey, has a metallic luster and is brittle without any discernable cleavage. The mean micro-indentation hardness is 295 kg/mm^2, corresponding to a Mohs hardness of 4. In reflected light, it is grayish white; the bireflectance is weak, and the anisotropy is moderate in air and strong in oil. Internal reflections are absent. The reflectance data (air) are: 42.1, 48.5 at 470 nm, 41.0, 46.9 at 546 nm, 40.2, 45.8 at 589 nm and 39.6, 45.0% at 650 nm. The average results of five electron-microprobe analyses are: Cu 7.66(1), Ag 4.01(3), Pb 9.45(3), Bi 60.02(9), Se 0.30(1), Te 0.76(3), S 17.55(2), total 99.75(7) wt.%, corresponding to $Cu_{7.79}Ag_{2.4}Pb_{2.95}Bi_{18.55}(Se_{0.24}Te_{0.39}S_{35.37})_{\Sigma 36}$, calculated on the basis of Σ(S + Se + Te) = 36 atoms per formula unit. The simplified formula, $Cu_8Pb_4Ag_2Bi_{18}S_{36}$, is in accordance with the empirical formula and that deduced from the crystal-structure analysis. The density, 6.78 g/cm^3, was calculated using the ideal (structural) formula and Z = 1. Cupromakovickyite has a monoclinic cell with a 13.405(8), b 4.016(3), c 29.949(19) Å, β 99.989(16)°, V 1587.8(17) Å^3, space group $C2/m$, and Z = 1. The strongest lines in the calculated powder-diffraction pattern [d in Å(I)(hkl)] are: 3.478(100)($\bar{1}$14), 2.842(94)(312), 3.646(57)(206), 3.486(41)($\bar{2}$08), 3.345(33)($\bar{4}$02), 2.964(33)(310), 2.282(31)(11$\underline{1}$0). Its c dimension is double the length of the c dimension of makovickyite, the N = 4 member of the pavonite homologous series. Cupromakovickyite is closely structurally related to makovickyite. The name of the new mineral expresses this relationship. Both the mineral and its name were approved by the Commission on New Minerals and Mineral Names (IMA 2002–58).

Keywords: cupromakovickyite, sulfosalt, new mineral species, single-crystal X-ray diffraction, electron-microprobe analyses, pavonite homologous series, Felbertal deposit, Austria, Băiţa Bihor skarn, Romania.

SOMMAIRE

Nous décrivons la cupromakovickyite, de formule idéale $Cu_8Pb_4Ag_2Bi_{18}S_{36}$, nouvelle espèce minérale trouvée dans le gisement de type skarn de Băiţa Bihor, en Roumanie, et le gisement de scheelite de Felbertal, Province de Salzburg, en Autriche. Lui sont associés makovickyite, dérivés de bismuthinite (intervalle aikinite–friedrichite), hodrušite, kupčikite, paděraïte, emplectite, wittichenite et tetradymite (Băiţa Bihor), et makovickyite, dérivés de bismuthinite (intervalle aikinite–krupkaïte), hodrušite, kupčikite, wittichenite et bismuth natif (Felbertal). Le minéral est opaque, gris, avec un éclat métallique, cassant, et apparemment sans clivage. La dureté déterminée par micro-indentations est 295 kg/mm^2, ce qui correspond à une dureté de Mohs de 4. En lumière réfléchie, la cupromackovickyite est blanc grisâtre, la biréflectance est faible, et l'anisotropie est modérée dans l'air et forte dans l'huile. Aucune réflexion interne n'est évidente. Les données de réflectance, déterminées dans l'air, sont: 42.1, 48.5 à 470 nm, 41.0, 46.9 à 546 nm, 40.2, 45.8 à 589 nm et 39.6, 45.0% à 650 nm. Les résultats moyens de cinq analyses effectuées avec une microsonde électronique sont: Cu 7.66(1), Ag 4.01(3), Pb 9.45(3), Bi 60.02(9), Se 0.30(1), Te 0.76(3), S 17.55(2), pour un total de 99.75(7)% (poids), ce qui correspond à la formule $Cu_{7.79}Ag_{2.4}Pb_{2.95}Bi_{18.55}(Se_{0.24}Te_{0.39}S_{35.37})_{\Sigma 36}$, calculée sur une base de Σ(S + Se + Te) = 36 atomes par formule unitaire. La formule simplifiée, $Cu_8Pb_4Ag_2Bi_{18}S_{36}$, concorde avec la formule empirique et celle qui découle de l'analyse structurale. La densité, 6.78 g/cm^3, a été calculée en utilisant la formule structurale idéale et Z = 1. La cupromakovickyite possède une maille élémentaire monoclinique ayant a 13.405(8), b 4.016(3), c 29.949(19) Å, β 99.989(16)°, V 1587.8(17) Å^3, groupe spatial $C2/m$, et Z = 1. Les sept raies les plus intenses du spectre de diffraction sur poudre calculé [d en Å(I)(hkl)] sont: 3.478(100)($\bar{1}$14), 2.842(94)(312), 3.646(57)(206), 3.486(41)($\bar{2}$08), 3.345(33)($\bar{4}$02), 2.964(33)(310), et 2.282(31)(11$\underline{1}$0). La dimension c est le double de la dimension c de la makovickyite, le membre de la série d'homologues de

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la pavonite ayant N = 4. Le nom exprime le lien structural étroit avec la makovickyite. Le nouveau minéral et son nom ont reçu l'approbation de la Commission des Nouveaux Minéraux et des Noms de Minéraux (IMA 2002–58).

(Traduit par la Rédaction)

Mots-clés: cupromakovickyite, sulfosel, nouvelle espèce minérale, diffraction X sur monocristal, analyses par microsonde électronique, série d'homologues de la pavonite, gisement de Felbertal, Autriche, skarn de Băiţa Bihor, Romanie.

Introduction

Several natural members of the pavonite homologous series, defined by Makovicky *et al.* (1977), are composed of exsolved lamellae (or lamellar intergrowths) of compounds respectively rich and poor in Cu (and Pb). A detailed X-ray-diffraction study of a pavonite-like material, with such a lamellar structure, revealed the presence of two phases, pavonite and cupropavonite, chemically and structurally different. Both phases have almost identical *a* and *b* parameters (13.4 and 4 Å, respectively), whereas the *c* axis is doubled for the Cu- (and Pb)-rich phase, named cupropavonite to denote its Cu content (Karup-Møller & Makovicky 1979, Nuffield 1980). Analogous exsolution phenomena, which are interpreted as the result of decomposition of a homogeneous high-temperature phase, were observed for homologue N = 4, makovickyite (Žák *et al.* 1994, Mumme 1990) and homologue N = 8, mummeite (Karup-Møller & Makovicky 1992). Such exsolution-related pairs represent two mineral species, separated by a definite miscibility-gap; consequently, the Cu- (and Pb)-rich varieties (for N = 4 and 8) received the modifier "cuproplumbian". However, no information about the expected doubling of the *c* axis was provided for either species.

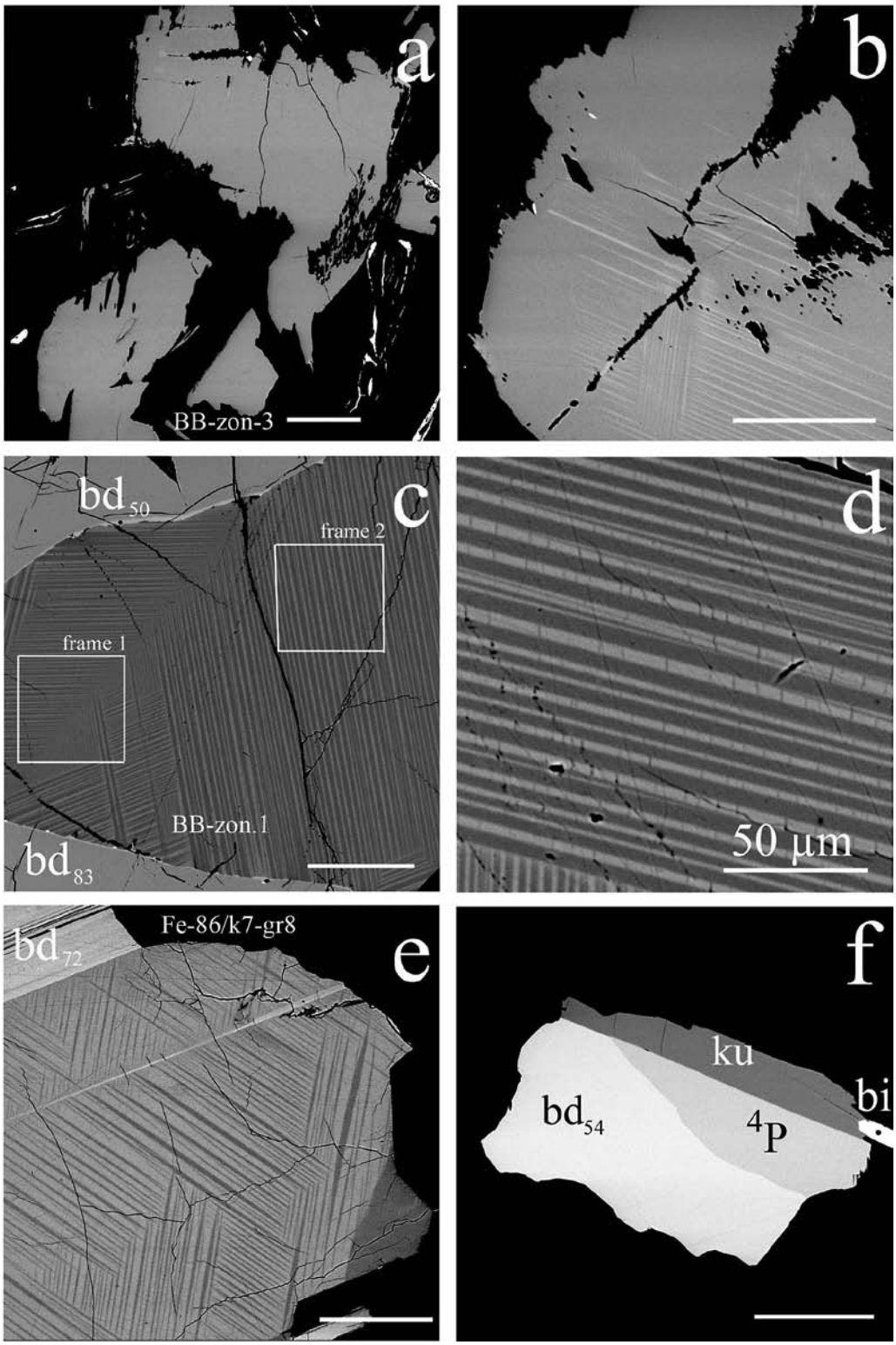
During a systematic study of mineral specimens from Băiţa Bihor and Felbertal deposits, we have found Cu-free and Cu-bearing makovickyite, lamellar intergrowths of makovickyite and "cuproplumbian" makovickyite, as well as homogeneous grains of "cuproplumbian" makovickyite. This led to an exhaustive study of their chemical composition and an intensive search for good-quality material on which a crystal-structure investigation could be done. In the present contribution, we provide the formal mineralogical description of the new mineral species, cupromakovickyite, the Cu- (and Pb)-rich phase ("cuproplumbian" makovickyite), whereas the discussion on the crystal structure of cupromakovickyite and makovickyite and the nature of their relation is the subject of a companion paper (Topa *et al.* 2008).

Provenance of the Samples

Cupromakovickyite has been detected in two genetically different ore deposits. At Băiţa Bihor, Apuseni Mountains, Romania, it occurs in a skarn that was created by the reaction of granitic magma (Cioflica & Vlad 1973, Žák *et al.* 1994) with Triassic dolomites. Samples kindly provided by Dr. P. Kolesar (Kempten, Germany) and by Prof. G. Cioflica (University of Bucharest, Romania) were analyzed. Cupromakovickyite occurs as rare homogeneous grains and in aggregates that consist of a lamellar intergrowth with makovickyite (Figs. 1a to d). The associated minerals are bismuthinite derivatives in the range aikinite (bd_{83}) – friedrichite (bd_{80}), hodrušite, paděraite, traces of kupčikite, emplectite, wittichenite, tetradymite, and abundant chalcopyrite in a matrix of dolomite. The Cu–Bi association appeared during the late stages of the skarn formation.

In the scheelite deposit of Felbertal, Hohe Tauern, Austria, pavonite homologues with N = 4 (cupromakovickyite and makovickyite) are known only in the orebodies K7 and K8 (Figs. 1e and f), whereas Cu-free makovickyite and pavonite (N = 5) occur in orebodies K1, K3 and K5 (Topa 2001, Topa *et al.* 2003b). The minerals associated with cupromakovickyite are bismuthinite derivatives in the range aikinite (bd_{92}) – krupkaite (bd_{56}), hodrušite, cuprobismutite, kupčikite, traces of wittichenite, native bismuth, chalcopyrite and pyrrhotite in a matrix of quartz. This mineralization formed by the recrystallization of quartz veins containing sulfides and sulfosalts and hosted within felsic gneisses and amphibolites. Recrystallization occurred during the retrograde stage of Alpine metamorphism (Topa *et al.* 2002).

FIG. 1. The association of sulfosalts with cupromakovickyite from Băiţa Bihor (a–d) and Felbertal (e–f). BSE photographs; the scale bars represent 100 μm. a) Homogeneous aggregate of cupromakovickyite. b) Homogeneous grain of cupromakovickyite with locally exsolved lamellae (bright) of makovickyite. c) Intergrowth of lamellar cupromakovickyite (dark lamellae) and makovickyite (bright lamellae) in a matrix of aikinite (bd_{83}) that is locally rimmed by krupkaite (bd_{50}); frame 1 and 2 denote the surfaces used for quantitative image-analysis. d) Detail of the lamellar intergrowth shown in c); the lamellae of makovickyite contain small and oriented fractures and a second generation of exsolved cupromakovickyite. e) Lamellar intergrowth of cupromakovickyite–makovickyite similar to that shown in b–d. A homogeneous grain of cupromakovickyite and another one of hammarite (bd_{72}) border the lamellar aggregate. f) A four-phase aggregate composed of krupkaite (bd_{54}), Cu-bearing makovickyite (^{4}P), kupčikite (ku) and native bismuth (bi).


a
BB-zon-3
b
bd50
c
frame 2
frame 1
BB-zon.1
bd83
d
50 μm
bd72
Fe-86/k7-gr8
e
f
ku
bi
bd54
4P

Physical Properties

Cupromakovickyite from Băiţa Bihor and Felbertal occurs as independent composite grains and as a constituent of exsolution-induced intergrowths with makovickyite. At Băiţa Bihor, the grain aggregates do not exceed 0.3 mm, whereas at Felbertal, such grains attain a size of 0.1 mm. Cupromakovickyite is opaque and metallic, has a grey color and a grey streak. The mineral is brittle, the fracture is uneven, and no cleavage or partings were observed. The Vickers hardness was determined using a Leitz Miniload 2 hardness tester with a load of 50 g. The Vickers hardness number ranges between 257 and 321 kg/mm^2, mean 295 kg/mm^2 (eight indentations). This corresponds to a Mohs hardness of 4, quite similar to that of makovickyite. The density could not be measured because no suitable grains were available. The calculated density is 6.78 g/cm^3, and is based on the ideal formula and $Z = 1$.

Optical Data

In polarized light, cupromakovickyite is greyish white, without internal reflections. Bireflectance is perceptible in air and moderate in oil; pleochroism is absent. Anisotropy is moderate in air and strong in oil. The rotation tints between crossed polars are dark bluish grey to yellowish brown for the most anisotropic grains. Reflectance data were obtained in air, using a Leitz MPV–SP microscope photometer and WTiC as standard. The observed R_{min} and R_{max} values are summarized in Table 1 and plotted in Figure 2. Both the R_{min} and the R_{max} curve are flat, with a weak maximum at 440–470 nm coincident with that of homogeneous Cu-bearing makovickyite from Felbertal.

TABLE 1. REFLECTANCE DATA (IN AIR) FOR CUPROMAKOVICKYITE FROM BĂIŢA BIHOR AND Cu-BEARING MAKOVICKYITE FROM FELBERTAL

	cupromakovickyite		makovickyite	
λ (nm)	R_{min}	R_{max}	R_{min}	R_{max}
400	42.37	48.05	41.85	48.80
420	42.42	48.19	41.95	48.95
440	42.47	48.40	42.00	49.10
460	42.26	48.51	42.07	49.19
470	42.15	48.45	42.13	49.25
480	41.95	48.29	42.05	49.07
500	41.62	47.85	41.76	48.87
520	41.35	47.50	41.55	48.52
540	41.15	47.10	41.21	48.33
546	41.02	46.93	40.91	48.15
560	40.60	46.49	40.65	47.87
580	40.36	46.02	40.45	47.60
589	40.25	45.83	40.35	47.45
600	40.13	45.74	40.25	47.16
620	39.93	45.42	40.07	46.95
640	39.82	45.23	39.92	46.70
650	39.66	45.01	39.90	46.57
660	39.53	44.80	39.80	46.30
680	39.46	44.52	39.66	46.14
700	39.38	44.44	39.54	45.95

Chemical Data

Quantitative chemical data for cupromakovickyite and the associated sulfosalts minerals were obtained with an electron microprobe (JEOL Superprobe JXA–8600, controlled by LINK–*eXL* system, operated at 25 kV and 35 nA, beam diameter 5 μm), installed at the Department of Geography and Geology, University of Salzburg. The following standards (all synthetic except galena) and emission lines were selected: Bi_2S_3 (Bi$L\alpha$, S$K\alpha$), galena (Pb$L\alpha$), chalcopyrite (Cu$K\alpha$, Fe$K\alpha$), Ag metal (Ag$L\alpha$), CdTe (Cd$L\beta$, Te$L\alpha$), and Bi_2Se_3 (Se$L\alpha$). The raw data were corrected with the on-line ZAF–4 procedure. The results of the electron-microprobe analyses for Cu-free makovickyite and Cu-free pavonite are compiled in Tables 2 and 3, whereas compositional data for Cu-bearing makovickyite and cupromakovickyite are presented in Tables 4 and 5. Most analyses show the absence of iron and antimony, minor amounts of tellurium (usually below 1 wt.%) and selenium (usually around 0.3 wt.%), and the systematic presence of cadmium (up to 3.2 wt.% in Cu-free makovickyite, 4.4 wt.% in Cu-free pavonite and around 1 wt.% in Cu-bearing makovickyite and cupromakovickyite). We assume that Cd and Fe substitute for Pb, Sb for Bi, and Se and Te for S. The trace amounts of Cu in Cu-free makovickyite and pavonite (Tables 2, 3) are considered to substitute for Ag and allow us to calculate the empirical formulae on the basis of the total number of atoms per formula unit (*i.e.*, 32 for makovickyite and 36 for pavonite).

The empirical formulae of Cu-bearing makovickyite and cupromakovickyite (Tables 4, 5) were calculated on the basis of S + Se + Te = 18 atoms per formula unit for makovickyite and S + Se + Te = 36 *apfu* for cupromakovickyite, and lead to $Cu_{7.79}Ag_{2.40}Pb_{2.95}Bi_{18.55}(S_{35.37}Se_{0.25}Te_{0.39})_{\Sigma 36}$ for Băiţa Bihor material (anal. 1, Table 5), and $Cu_{7.93}Ag_{2.43}(Pb_{2.73}Cd_{0.43})_{\Sigma 3.16}Bi_{18.45}(S_{35.95}Te_{0.05})_{\Sigma 36}$ for Felbertal material (anal. 5, Table 5), respectively.

The results, obtained from five aggregates in two polished sections of the holotype specimens (Băiţa Bihor and Felbertal material), show only minor variation of the chemical composition of cupromakovickyite (Table 5). On the basis of S = 36 and *Me* = 32 (from the single-crystal study), the ideal formula of cupromakovickyite for both occurrences can be written as $Cu_8Ag_2Pb_4Bi_{18}S_{36}$ and requires Cu 7.86, Ag 3.34, Pb 12.81, Bi 58.15, S 17.84, total 100.00 wt.%.

The analyses of exsolved lamellae (Tables 4, 5) were done with a slightly defocused beam of electrons (~2–3 μm) to avoid damage of the surface of the samples and thus, problems in sulfur determination. The results deviate from above-mentioned values, indicating clearly a mixture of the two components.

A combination of electron-microprobe data on Cu-bearing makovickyite and homogeneous cupromakovickyite with quantitative image-analysis on selected

TABLE 2. AVERAGE RESULTS OF ELECTRON-PROBE ANALYSES OF Cu-FREE MAKOVICKYITE (N_p = 4) FROM THE FELBERTAL DEPOSIT, AUSTRIA

No.	Cu	Ag	Fe	Pb	Cd	Bi	Te	S	Total	N_{p1}	N_{p2}	Σmet	*ch*	*ev*	Me^+	Me^{3+}
1	0.11(3)	6.60(8)	0.14(5)	5.45(11)	3.23(14)	66.05(12)	0.51(3)	17.92(5)	100.00(16)	3.82	3.85	13.98	0.01	0.04	2.94	11.04
2	0.40(4)	6.81(13)	0.11(1)	5.88(11)	2.55(3)	65.61(13)	0.56(2)	17.77(3)	99.68(15)	3.86	3.96	14.04	0.02	0.05	3.09	10.95
3	0.09(2)	7.07(4)	0.19(1)	4.42(12)	2.42(13)	67.07(23)	0.50(5)	17.92(3)	99.68(16)	3.78	3.80	13.94	-0.09	-0.26	2.89	11.04
4	0.15(1)	7.08(1)	0.41(2)	6.13(10)	0.97(9)	66.49(5)	-	17.82(1)	99.05(2)	3.80	3.84	13.99	0.07	0.20	2.94	11.05
5	0.57(2)	7.28(2)	0.18(3)	4.76(5)	1.59(27)	67.30(16)	0.53(4)	17.85(6)	100.05(27)	3.75	3.90	14.05	0.05	0.14	3.09	10.95
6	0.15(3)	7.73(13)	0.17(3)	4.37(4)	1.58(4)	67.51(21)	-	17.97(5)	99.48(36)	3.89	3.93	13.99	-0.03	-0.09	2.99	11.00
7	0.05(1)	8.36(7)	0.25(1)	2.74(6)	1.19(6)	68.97(10)	0.13(2)	18.09(4)	99.79(11)	3.90	3.92	13.95	-0.17	-0.46	2.96	10.99

Empirical formulae were calculated on the basis of 32 atoms per formula unit ($Me^+_3\ Me^{3+}_{11}S_{18}$).

1) $Cu_{0.06}Ag_{1.96}(Pb_{0.84}Cd_{1.00})_{\Sigma 1.84}Bi_{10.12}(S_{17.90}Te_{0.13})_{\Sigma 18.02}$
2) $Cu_{0.20}Ag_{2.03}(Pb_{0.91}Cd_{0.79})_{\Sigma 1.71}Bi_{10.10}(S_{17.82}Te_{0.14})_{\Sigma 17.96}$
3) $Cu_{0.05}Ag_{2.10}(Pb_{0.68}Cd_{0.80})_{\Sigma 1.49}Bi_{10.30}(S_{17.94}Te_{0.12})_{\Sigma 18.06}$
4) $Cu_{0.07}Ag_{2.13}(Pb_{0.96}Cd_{0.52})_{\Sigma 1.48}Bi_{10.31}S_{18.01}$
5) $Cu_{0.29}Ag_{2.16}(Pb_{0.74}Cd_{0.56})_{\Sigma 1.29}Bi_{10.31}(S_{17.82}Te_{0.13})_{\Sigma 17.95}$
6) $Cu_{0.08}Ag_{2.30}(Pb_{0.68}Cd_{0.55})_{\Sigma 1.23}Bi_{10.38}S_{18.01}$
7) $Cu_{0.03}Ag_{2.48}(Pb_{0.42}Cd_{0.48})_{\Sigma 0.90}Bi_{10.54}(S_{18.02}Te_{0.03})_{\Sigma 18.05}$

The compositions are expressed in wt.%. NA = number of analyses. Standard deviation for the last digit is shown in parentheses. N_{p1}, N_{p2} and N_{p3} represent the pavonite homologue number calculated from chemical data. *ch* and *ev* express the absolute and relative error in the charge balance based on the sum of cation and anion charges. Details about samples and location: 1) FE-97/3a-19d, NA= 6, 2) FE-97/3a-3d, NA = 4, 3) FE-97/3a-4d, NA = 3, 4) FE-97/3a-4d, NA = 3, 5) FE-97/3a-6, NA = 4, 6) FE-99/68-g4d, NA = 5, 7) FE-89/9-3-g13d, NA = 4.

TABLE 3. AVERAGE RESULTS OF ELECTRON-PROBE ANALYSES OF Cu-FREE PAVONITE (N_p = 5) FROM THE FELBERTAL DEPOSIT, AUSTRIA

No.	Cu	Ag	Fe	Pb	Cd	Bi	Sb	Te	S	Total	N_{p1}	N_{p2}	Σmet	*ch*	*ev*	Me^+	Me^{3+}
1	-	6.79(9)	-	10.62(12)	3.86(4)	60.06(13)	-	-	17.60(6)	99.08(15)	4.84	4.84	15.96	0.00	-0.01	3.91	12.05
2	-	7.17(13)	-	9.10(24)	4.45(22)	60.85(28)	-	-	17.71(13)	99.28(42)	4.85	4.85	15.99	0.09	0.21	3.92	12.06
3	-	7.23(6)	-	9.42(9)	4.30(2)	60.24(15)	-	-	17.76(7)	98.96(16)	4.92	4.92	15.98	-0.02	-0.04	3.96	12.02
4	-	7.36(12)	-	9.26(9)	3.85(8)	60.56(20)	0.12(1)	-	17.53(18)	98.68(15)	4.87	4.87	16.01	0.18	0.46	3.94	12.07
5	0.06(1)	7.77(11)	0.04(1)	7.34(16)	3.71(9)	63.06(26)	-	0.37(3)	17.87(8)	99.68(16)	4.71	4.73	15.91	-0.14	-0.35	3.86	12.06
6	-	8.03(8)	0.21(1)	7.15(30)	3.13(6)	63.61(18)	-	-	17.96(12)	100.22(47)	4.74	4.74	15.94	-0.02	-0.05	3.85	12.09
7	0.05(1)	8.22(4)	0.15(1)	8.19(9)	2.02(2)	63.00(27)	-	-	17.64(4)	100.08(19)	4.78	4.79	15.97	0.05	0.12	3.90	12.07
8	0.06(1)	9.71(9)	0.30(4)	4.85(11)	1.71(8)	65.19(27)	-	0.14(2)	18.10(8)	100.06(31)	5.04	5.05	15.89	-0.59	-1.46	4.02	11.87

Empirical formulae were calculated on the basis of 36 atoms per formula unit ($Me^+_4\ Me^{3+}_{12}S_{20}$).

1) $Cu_{0.00}Ag_{2.35}(Pb_{1.87}Cd_{1.25})_{\Sigma 3.12}Bi_{10.49}S_{20.04}$
2) $Cu_{0.00}Ag_{2.41}(Pb_{1.59}Cd_{1.43})_{\Sigma 3.02}Bi_{10.55}S_{20.01}$
3) $Cu_{0.00}Ag_{2.44}(Pb_{1.65}Cd_{1.39})_{\Sigma 3.04}Bi_{10.50}S_{20.02}$
4) $Cu_{0.00}Ag_{2.49}(Pb_{1.63}Cd_{1.25})_{\Sigma 2.88}Bi_{10.63}S_{19.99}$
5) $Cu_{0.04}Ag_{2.58}(Pb_{1.27}Cd_{1.21})_{\Sigma 2.48}Bi_{10.82}(S_{19.98}Te_{0.10})_{\Sigma 20.09}$
6) $Cu_{0.00}Ag_{2.67}(Pb_{1.24}Cd_{1.13})_{\Sigma 2.37}Bi_{10.90}S_{20.06}$
7) $Cu_{0.03}Ag_{2.78}(Pb_{1.44}Cd_{0.75})_{\Sigma 2.19}Bi_{10.98}S_{20.03}$
8) $Cu_{0.03}Ag_{3.20}(Pb_{0.83}Cd_{0.73})_{\Sigma 1.56}Bi_{11.09}(S_{20.07}Te_{0.04})_{\Sigma 20.11}$

NA: number of analyses. Compositions are reported in wt.%. Details about samples and location: 1) FE-89/11-1dk, NA = 5, 2) FE-wa, NA = 6, 3) FE-89/11-5d, NA = 3, 4) FE-89/11-14d, NA = 5, 5) FE-97/3a-1d, NA = 9, 6) FE-86/k7-5-G1d, NA = 4, 7) FE-89/9-sg42d, NA = 2, 8) FE-89/9n-A-d, NA = 3.

TABLE 4. AVERAGE RESULTS OF ELECTRON-PROBE ANALYSES OF Cu-BEARING MAKOVICKYITE (N_p = 4) FROM FELBERTAL (FE) AND BĂIŢA BIHOR (BB) DEPOSITS

No.	NA	Cu	Ag	Fe	Pb	Cd	Bi	Sb	Te	Se	S	Total	N_{p2}	N_{p3}	Σmet	ch	ev
Homogeneous grains, K8																	
1	3	2.81(14)	6.92(9)	0.02(1)	2.53(14)	0.38(3)	68.60(49)	0.00	0.12(3)	0.00	18.05(2)	99.45(39)	3.86	3.52	14.45	-0.27	-0.24
2	3	3.49(5)	6.68(2)		2.05(16)	0.76(14)	69.13(8)	0.00	0.00	0.00	18.28(4)	100.40(26)	3.91	3.50	14.66	0.21	0.19
3	7	4.08(8)	5.81(5)		2.11(10)	0.50(5)	68.63(19)	0.00	0.11(3)	0.00	18.25(6)	99.47(22)	3.72	3.25	14.56	-0.74	-0.67
4	9	4.55(3)	5.37(9)		1.79(10)	0.45(7)	69.41(10)	0.11(2)	0.20(3)	0.00	18.29(3)	100.16(26)	3.59	3.09	14.69	0.13	0.12
5	3	4.92(3)	5.73(9)		1.14(2)	0.00	69.61(8)	0.00	0.11(2)	0.00	18.19(2)	99.70(20)	3.70	3.15	14.86	0.43	0.39
Homogeneous grains, K7																	
6	7	1.60(9)	7.39(7)	0.13(3)	2.77(8)	1.63(5)	68.28(5)	0.08(1)	0.10(1)	0.00	18.15(3)	100.12(18)	3.97	3.78	14.32	0.21	0.19
7	4	2.42(5)	6.18(9)		4.10(5)	1.07(4)	68.88(28)	0.00	0.00	0.00	18.25(2)	100.91(23)	3.67	3.40	14.36	0.41	0.37
Bright lamellae as in Figures 1c, e																	
8	7	4.27(4)	5.52(5)		2.03(8)	0.99(8)	68.38(11)	0.00	0.00	0.00	18.24(3)	99.44(9)	3.74	3.25	14.69	0.10	0.09
9	5	4.39(10)	5.53(7)		2.10(18)	0.91(8)	68.35(18)	0.00	0.04(7)	0.00	18.24(2)	99.57(12)	3.75	3.25	14.73	-0.02	-0.02
10	7	4.50(12)	5.25(7)		2.47(38)	0.86(4)	68.05(44)	0.00	0.00	0.00	18.26(4)	99.40(21)	3.71	3.20	14.69	-0.31	-0.28
11	5	4.41(12)	5.25(10)	0.06(1)	2.14(22)	0.77(6)	68.95(12)	0.00	0.00	0.00	18.28(3)	99.85(01)	3.63	3.14	14.71	0.36	0.33
12	3	5.25(12)	4.57(4)		1.83(8)		69.07(9)	0.00	0.90(2)	0.29(2)	18.06(4)	99.98(13)	3.44	2.87	14.56	-1.37	-1.24
13	4	5.00(11)	5.03(12)		2.45(27)	0.05(8)	68.10(21)	0.14(3)	1.05(5)	0.31(1)	17.75(8)	99.88(17)	3.63	3.07	14.78	-0.05	-0.05

Empirical formulae were calculated on the basis of Σ(S + Se + Te) = 18 *apfu*.

1) $Cu_{1.41}Ag_{2.05}(Pb_{0.39}Cd_{0.12})_{\Sigma 0.51}Bi_{10.48}(S_{17.97}Te_{0.03})_{\Sigma 18}$
2) $Cu_{1.73}Ag_{1.95}(Pb_{0.31}Cd_{0.21})_{\Sigma 0.52}Bi_{10.44}S_{18}$
3) $Cu_{2.03}Ag_{1.70}(Pb_{0.32}Cd_{0.14})_{\Sigma 0.46}Bi_{10.37}(S_{17.97}Te_{0.03})_{\Sigma 18}$
4) $Cu_{2.25}Ag_{1.56}(Pb_{0.27}Cd_{0.13})_{\Sigma 0.40}Bi_{10.48}(S_{17.95}Te_{0.05})_{\Sigma 18}$
5) $Cu_{2.45}Ag_{1.68}(Pb_{0.17}Cd_{0.00})_{\Sigma 0.17}Bi_{10.55}(S_{17.97}Te_{0.03})_{\Sigma 18}$
6) $Cu_{0.80}Ag_{2.17}(Pb_{0.42}Cd_{0.53})_{\Sigma 0.95}Bi_{10.39}(S_{17.97}Te_{0.03})_{\Sigma 18}$
7) $Cu_{1.20}Ag_{1.81}(Pb_{0.63}Cd_{0.30})_{\Sigma 0.93}Bi_{10.42}S_{18}$
8) $Cu_{2.13}Ag_{1.62}(Pb_{0.31}Cd_{0.28})_{\Sigma 0.59}Bi_{10.35}S_{18}$
9) $Cu_{2.19}Ag_{1.62}(Pb_{0.32}Cd_{0.26})_{\Sigma 0.58}Bi_{10.34}(S_{17.99}Te_{0.01})_{\Sigma 18}$
10) $Cu_{2.24}Ag_{1.54}(Pb_{0.38}Cd_{0.24})_{\Sigma 0.62}Bi_{10.29}S_{18}$
11) $Cu_{2.19}Ag_{1.54}(Pb_{0.33}Cd_{0.25})_{\Sigma 0.58}Bi_{10.41}S_{18}$
12) $Cu_{2.59}Ag_{1.33}(Pb_{0.28}Cd_{0.00})_{\Sigma 0.28}Bi_{10.36}(S_{17.66}Se_{0.12}Te_{0.22})_{\Sigma 18}$
13) $Cu_{2.51}Ag_{1.48}(Pb_{0.38}Cd_{0.01})_{\Sigma 0.39}Bi_{10.40}(S_{17.62}Se_{0.12}Te_{0.26})_{\Sigma 18}$

NA: number of analyses. Compositions are reported in wt.%. Details about samples and location: 1) FE-89/9-sg2, 2) FE-89-9-A, 3) FE-89/9-sg14, 4) FE-89/9-sm5-gr1*, 5) FE-89/9-4-g6m, 6) FE-86/K7-sg2-gr2d, 7) FE-86/K7-V29-gr9d, 8) FE-86/K7-2-gr2m, 9) FE-86/K7-2-gr13m, 10) FE-86/K7-2-gr8b, 11) FE-86/K7-3-gr17b, 12) BB-zon.1b, 13) BB-zon.5b. * indicates a crystal used in the single-crystal investigation of the structure.

TABLE 5. AVERAGE RESULTS OF ELECTRON-PROBE ANALYSES OF CUPROMAKOVICKYITE (Np = 4) FROM BĂIŢA BIHOR (BB) AND FELBERTAL (FE) DEPOSITS

No.	NA	Cu	Ag	Fe	Pb	Cd	Bi	Sb	Te	Se	S	Total	N_{p2}	N_{p3}	Σmet	ch	ev
Homogeneous grains																	
1	5	7.66(1)	4.01(3)	-	9.45(3)	-	60.02(9)	-	0.76(2)	0.30(1)	17.55(2)	99.75(7)	4.85	3.88	31.69	-0.37	-0.35
2	7	7.87(6)	4.16(10)	-	9.61(32)	0.15(3)	59.32(17)	-	0.73(3)	0.30(1)	17.43(8)	99.57(28)	5.06	4.05	32.15	0.30	0.28
3	4	7.97(8)	3.98(6)	-	10.44(13)	0.21(5)	59.23(23)	-	0.78(3)	0.30(1)	17.49(9)	100.40(48)	5.08	4.06	32.29	0.61	0.58
4	3	7.61(3)	4.14(1)	-	8.60(2)	0.64(8)	60.52(11)	-	-	-	18.02(2)	99.73(21)	4.88	3.93	31.72	-0.21	-0.20
5	3	7.89(2)	4.10(5)	-	8.85(5)	0.76(2)	60.35(11)	-	0.10(1)	-	18.05(2)	100.43(25)	4.98	3.99	31.96	0.03	0.03
Dark lamellae as in Figures 1c, e																	
6	3	7.16(2)	4.35(2)	-	7.41(3)	0.84(3)	61.54(5)	-	-	-	18.03(2)	99.29(29)	4.72	3.84	31.41	-0.18	-0.17
7	4	7.21(6)	4.20(11)	-	7.59(11)	0.79(3)	61.88(11)	-	-	-	18.12(2)	99.29(25)	4.66	3.78	31.37	-0.17	-0.16
8	4	8.07(3)	3.94(4)	-	8.68(19)	-	60.53(16)	-	0.64(3)	0.29(2)	17.88(5)	100.04(10)	4.82	3.82	31.45	-1.07	-1.49
9	4	7.90(10)	4.21(6)	0.12(2)	8.43(10)	0.27(5)	60.38(22)	0.11(3)	0.76(8)	0.31(3)	17.61(5)	100.10(14)	4.95	3.96	32.10	0.33	0.46
10		6.09	4.67	-	4.38	0.07	65.97	-	0.79	0.30	17.72	99.99	4.00	3.29	30.50	0.46	0.42
11		6.94	4.46	-	6.38	0.13	63.50	-	0.75	0.30	17.64	100.10	4.41	3.58	31.28	0.62	0.58
12		7.86	3.34		12.81		58.15				17.84	100.00	5.00	4.00	32.00		

Empirical formulae were calculated on the basis of Σ(S + Se + Te) = 36 *apfu* (from single-crystal study):

1) $Cu_{7.79}Ag_{2.40}(Pb_{2.95}Cd_{0.00})_{\Sigma 2.95}Bi_{18.55}(S_{35.37}Se_{0.25}Te_{0.39})_{\Sigma 36}$
2) $Cu_{8.06}Ag_{2.51}(Pb_{3.02}Cd_{0.09})_{\Sigma 3.11}Bi_{18.47}(S_{35.38}Se_{0.24}Te_{0.38})_{\Sigma 36}$
3) $Cu_{8.13}Ag_{2.39}(Pb_{3.27}Cd_{0.12})_{\Sigma 3.39}Bi_{18.37}(S_{35.36}Se_{0.26}Te_{0.39})_{\Sigma 36}$
4) $Cu_{7.68}Ag_{2.46}(Pb_{2.66}Cd_{0.37})_{\Sigma 3.03}Bi_{18.56}S_{36}$
5) $Cu_{7.93}Ag_{2.43}(Pb_{2.73}Cd_{0.43})_{\Sigma 3.16}Bi_{18.45}(S_{35.95}Te_{0.05})_{\Sigma 36}$
6) $Cu_{7.22}Ag_{2.58}(Pb_{2.29}Cd_{0.48})_{\Sigma 2.77}Bi_{18.85}S_{36}$
7) $Cu_{7.23}Ag_{2.48}(Pb_{2.34}Cd_{0.45})_{\Sigma 2.79}Bi_{18.87}S_{36}$
8) $Cu_{8.07}Ag_{2.32}(Pb_{2.62}Cd_{0.00})_{\Sigma 2.62}Bi_{18.41}(S_{35.44}Se_{0.24}Te_{0.32})_{\Sigma 36}$
9) $Cu_{8.01}Ag_{2.51}(Pb_{2.62}Cd_{0.29})_{\Sigma 2.91}Bi_{18.66}(S_{35.37}Se_{0.24}Te_{0.38})_{\Sigma 36}$
10) $Cu_{6.13}Ag_{2.77}(Pb_{1.35}Cd_{0.04})_{\Sigma 1.39}Bi_{20.20}(S_{35.36}Se_{0.24}Te_{0.40})_{\Sigma 36}$
11) $Cu_{7.02}Ag_{2.66}(Pb_{1.98}Cd_{0.08})_{\Sigma 2.06}Bi_{19.54}(S_{35.38}Se_{0.24}Te_{0.38})_{\Sigma 36}$
12) $Cu_8Ag_2Pb_4Bi_{18}S_{36}$

NA: number of analyses. Compositions are reported in wt.%. Details about samples and location: 1) BB-zon.3*, 2) BB-zon.k, 3) BB-zon.10, 4) FE-86/k7-2-gr8, 5) FE-86/k7-3-gr17, 6) FE-86/k7-2-gr8d, 7) FE-86/k7-2-gr17d, 8) BB-zon.1d, 9) BB-zon.5d, 10) BB frame-1, Fig. 1c#, 11) BB frame-2, Fig. 1c#, 12) ideal cupromackovickyite. * indicates a crystal used in the single-crystal investigation of the structure.

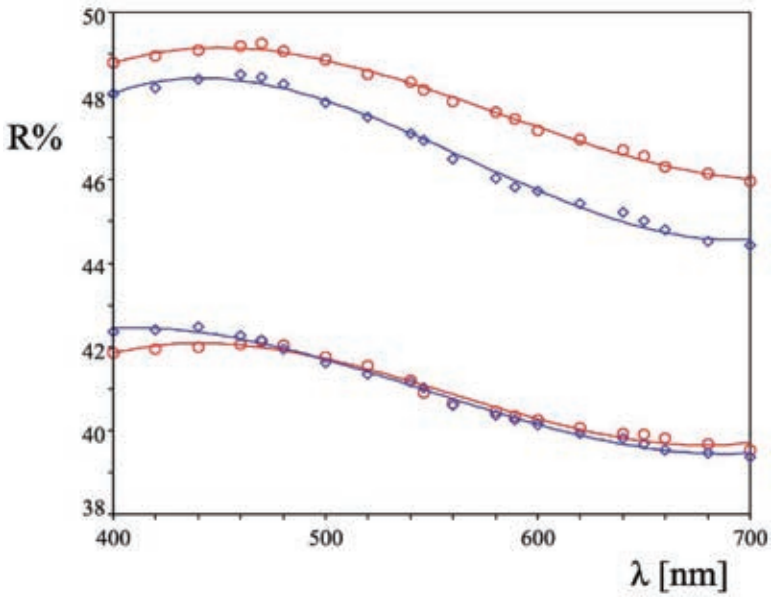


FIG. 2. Reflectance data (in air) for Cu-bearing makovickyite (open circles) from Felbertal and cupromakovickyite (diamonds) from Băiţa Bihor.

areas (Fig. 1c, frame 1 and 2) was used to evaluate the range of original, pre-exsolution chemical compositions of the high-temperature phase from which both minerals exsolved (anal. 9 and 10, Table 5).

Chemical data for the Cu-free, Cu-bearing makovickyite and cupromakovickyite (presented in Tables 2, 4 and 5) are plotted in the triangular diagram Bi – (Ag) – (Pb + Cu) in Figure 3.

The chemical composition of kupčikite, hodrušite and cuprobismutite is presented in detail in Topa *et al*. (2003a, b), whereas bismuthinite derivatives are treated in Topa *et al*. (2002).

X-RAY-DIFFRACTION DATA

Owing to the very small amount of pure cupromakovickyite material found, only a few single-crystal fragments (~ 0.06 × 0.05 × 0.04 mm) were obtained by dissolving the carbonate matrix. These were investigated only by single-crystal method. The X-ray-diffraction data were aquired with a CCD-equipped single-crystal diffractrometer (four-circle Bruker AXS diffractometer). Cupromakovickyite is monoclinic, space group *C*2/*m*, with *a* 13.396(9), *b* 4.013(3), *c* 29.93(2) Å, β 100.07(2), *V* 1584(3) Å^3, *Z* = 1, with a structural formula $Cu_8Ag_2Pb_4Bi_{18}S_{36}$. The unit-cell volume of cupromakovickyite is equal to double the unit-cell volume of Cu-bearing makovickyite, which has space group *C*2/*m*, *a* 13.239(3), *b* 4.0547(7), *c* 14.667(3) Å, β 100.07(2)°, *V* 776.7(3) Å^3, *Z* = 1, with a structural formula $Cu_{2.12}Ag_{1.36}Bi_{11.20}S_{18}$.

The crystal-structure determinations presented in a companion article (Topa *et al*. 2008) reveal that the doubling of the *c* parameter results from: (1) the oriented replacement of pairs of Bi pyramids by pairs of Pb–Bi pyramids (combined with the appearance of a new tetrahedrally coordinated Cu site), and (2) the replacement of the octahedrally coordinated Ag site by a tetrahedrally coordinated Cu site in the thin layers of the cupromakovickyite.

Theoretical powder-diffraction patterns for cupromakovickyite (Table 6) and makovickyite were calculated using POWDERCELL 2.3 software (Kraus & Nolze 1999) for a Debye–Scherrer configuration. They are plotted for comparison in Figure 4. We used Cu*K*α radiation (λ 1.540598 Å), a fixed slit, no anomalous dispersion correction and unit-cell parameters, space group, atom positions, site occupancy and anisotropic displacement factors from both single-crystal determinations of the structures (Topa *et al*. 2008).

DISCUSSION

The experience gained from numerous studies of the pavonite homologous series suggests an important structural role for silver and copper. The ideal formula of makovickyite unsubstituted by Pb or Cu (or both) (Žák *et al*. 1994, Makovicky *et al*. 1977) is $Ag_3Bi_{11}S_{18}$

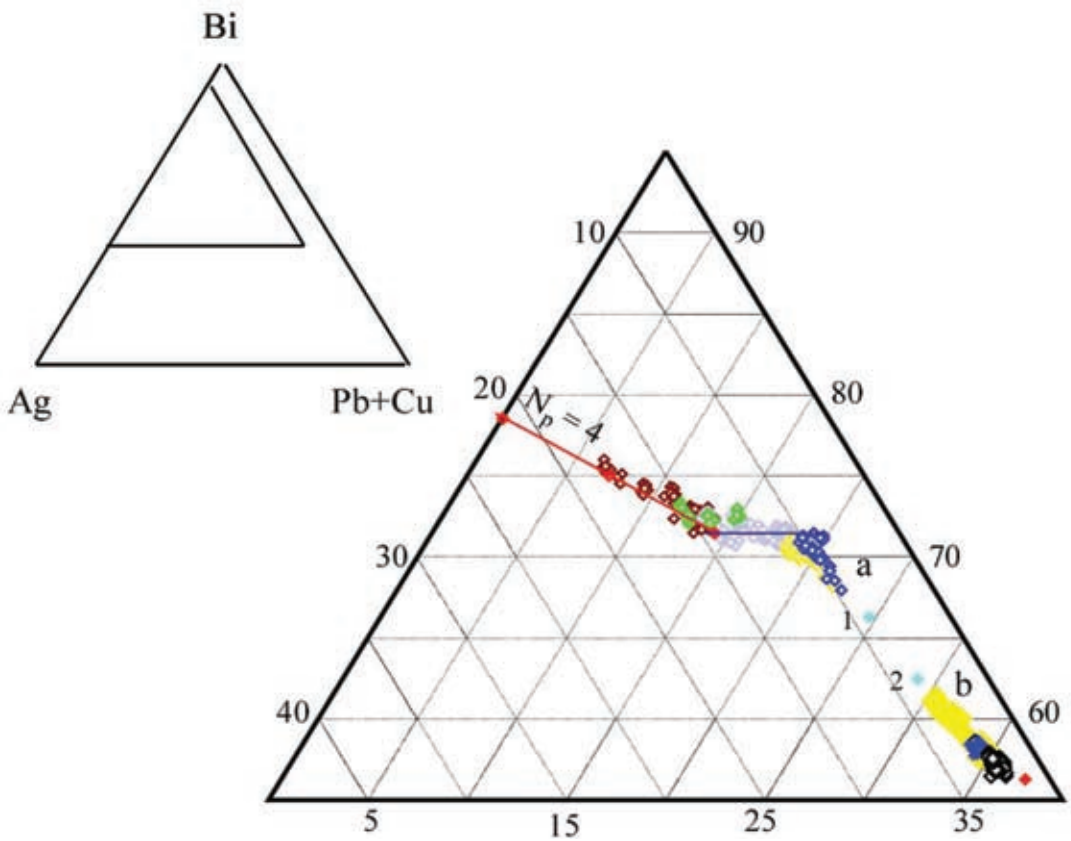


FIG. 3. Chemical composition of cupromakovickyite, Cu-bearing and Cu-free makovickyite in the diagram Bi – Ag – (Pb + Cd + Cu). Red line: Pb substitution, blue line: Cu and Pb substitution. The results of the image analysis: point 1 and 2. Analytical data affected by intimate mixture of makovickyite and cupromakovickyite are denoted by **a** and **b**. Color-coded symbols: open red diamond: ideal makovickyite; open brown diamond: Cu-free makovickyite (Felbertal); red diamond: ideal cupromakovickyite; open lavender diamond: homogeneous makovickyite, Felbertal, K8; open green diamond: homogeneous makovickyite, Feblertal, K7; open yellow diamond: exsolved lamellae, bright, makovickyite, Felbertal, K7; open blue diamond: exsolved lamellae, bright Băiţa Bihor; yellow diamond: exsolved lamellae, dark, cupromakovickyite, Felbertal, K7; open black diamond: homogeneous cupromakovickyite, Băiţa Bihor; blue diamond: exsolved lamellae, dark, Băiţa Bihor; turquoise diamonds mark a gap at Băiţa Bihor.

for Z = 1, or $^{\text{thin layer}}(Ag_2Bi_4)\ ^{\text{thick layer}}(AgBi_7)S_{18}$, with silver present in the separate octahedra of the thin layer and in a single octahedron of the thick layer. The well-known mechanism of substitution $Ag^+ + Bi^{3+} \rightarrow 2Pb^{2+}$ will introduce substitutional Pb into the thick layer (Table 2), leading to the substitutional trend presented as the red line in Figure 3.

Copper was found (Žák *et al.* 1994, Mumme 1990) in planar trigonal and tetrahedral coordinations, both replacing the flattened octahedrally coordinated Ag site of the thin layer. The combined influence of Cu-for-Ag and (Cu + Pb)-for-Bi mechanisms of substitution is presented as the blue line in Figure 3.

The formulae for the recognition of N_p (estimation of homologue number) from results of the chemical analyses, given by Karup-Møller & Makovicky (1979), are based on the following assumptions: (1) the total Cu recorded in the chemical data is assumed to represent *interstitial* ^{i}Cu (N_{p1}), (2) the total Cu is assumed to represent *substitutional* ^{s}Cu (N_{p2}), and (3) the total Cu is equally distributed between ^{i}Cu and ^{s}Cu (N_{p3}). Thus, the empirical formula for Cu-free makovickyite can be calculated (from electron-microprobe data) on the basis of total number of atoms (32) per formula unit, whereas the same principle will not function for Cu-bearing makovickyite, owing to the unknown percentage of interstitial Cu.

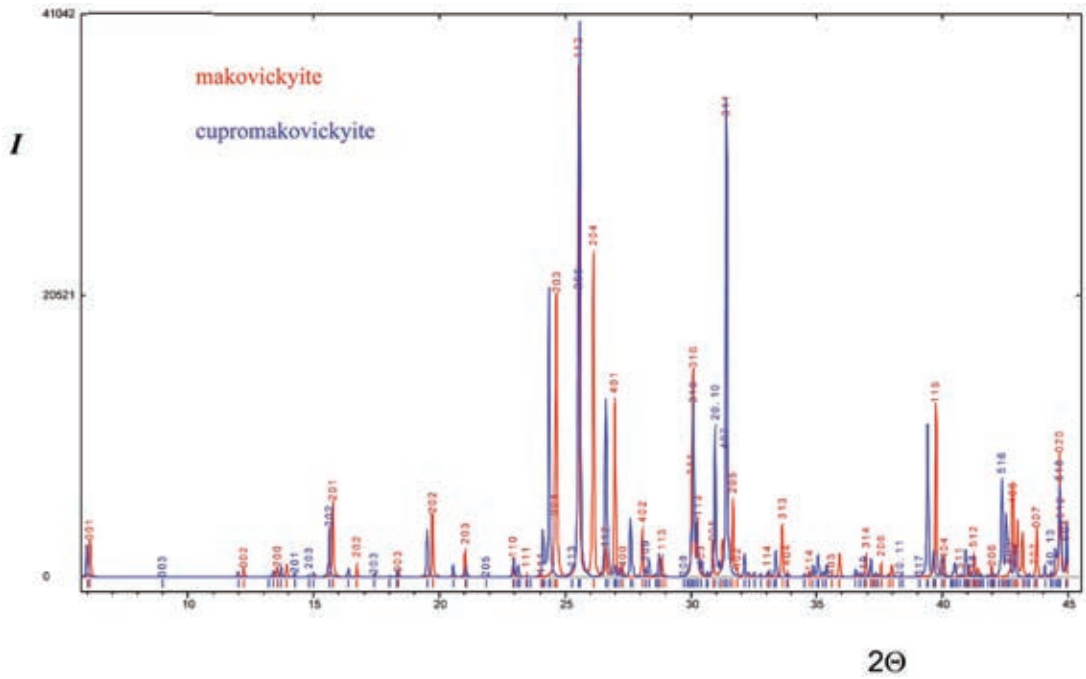


FIG. 4. Calculated X-ray-diffractometer patterns (Cu$K\alpha$) of makovickyite and cupromakovickyite for a 2θ range of 6–45°.

TABLE 6. CALCULATED X-RAY POWDER-DIFFRACTION PATTERN FOR CUPROMAKOVICKYITE FROM BĂIŢA BIHOR

h	*k*	*l*	*d*	*I*	*h*	*k*	*l*	*d*	*I*	*h*	*k*	*l*	*d*	*I*
0	0	4	7.37	1	3	1	2	2.8416	95	5	1	6	1.9095	15
2	0	0	6.60	1	$\bar{3}$	1	5	2.7828	5	$\bar{5}$	1	10	1.9035	4
$\bar{2}$	0	2	6.46	2	$\bar{4}$	0	8	2.7029	1	2	2	2	1.8911	1
0	0	5	5.89	1	$\bar{3}$	1	6	2.6812	5	$\bar{1}$	1	14	1.8866	2
2	0	2	5.66	11	$\bar{3}$	1	7	2.5703	3	3	1	11	1.8802	2
$\bar{2}$	0	4	5.41	2	$\bar{4}$	0	9	2.5578	2	$\bar{2}$	0	16	1.8601	3
$\bar{2}$	0	5	4.84	1	$\bar{1}$	1	9	2.5562	3	0	0	16	1.8418	2
2	0	4	4.54	9	2	0	10	2.5307	2	$\bar{5}$	1	11	1.8391	2
$\bar{2}$	0	6	4.32	3	$\bar{3}$	1	8	2.4548	2	2	2	4	1.8348	1
0	0	7	4.21	2	$\bar{4}$	0	10	2.4173	4	$\bar{4}$	0	15	1.8347	1
$\bar{2}$	0	7	3.871	4	1	1	10	2.2821	31	4	0	12	1.8228	5
1	1	0	3.839	2	4	0	8	2.2677	4	$\bar{3}$	1	14	1.8204	5
0	0	8	3.684	9	0	0	13	2.2668	1	1	1	14	1.8073	3
2	0	6	3.646	56	$\bar{1}$	1	11	2.2513	4	$\bar{6}$	0	12	1.8020	3
1	1	3	3.515	1	$\bar{3}$	1	10	2.2249	3	3	1	12	1.7901	6
$\bar{2}$	0	8	3.486	40	$\bar{5}$	1	4	2.2020	6	5	1	8	1.7803	3
$\bar{1}$	1	4	3.478	100	$\bar{5}$	1	6	2.1307	19	0	2	8	1.7619	2
$\bar{4}$	0	2	3.345	32	6	0	2	2.1208	12	2	2	6	1.7577	13
$\bar{4}$	0	1	3.342	3	$\bar{1}$	1	12	2.1182	6	$\bar{2}$	2	8	1.7389	10
1	1	4	3.336	6	$\bar{3}$	1	11	2.1153	2	$\bar{7}$	1	3	1.7272	1
4	0	0	3.298	2	0	0	14	2.1049	6	$\bar{7}$	1	2	1.7258	5
0	0	9	3.274	2	$\bar{6}$	0	8	2.0522	2	$\bar{4}$	2	2	1.7205	9
$\bar{4}$	0	4	3.228	11	5	1	4	2.0318	5	$\bar{5}$	1	13	1.7101	1
4	0	1	3.216	2	4	0	10	2.0281	3	7	1	0	1.7056	5
$\bar{2}$	0	9	3.161	1	$\bar{5}$	1	8	2.0264	17	$\bar{4}$	2	4	1.7039	3
1	1	5	3.144	4	1	1	12	2.0225	9	$\bar{8}$	0	4	1.6725	1
$\bar{1}$	1	6	3.102	4	6	0	4	2.0123	11	0	2	10	1.6584	2
$\bar{3}$	1	2	2.9742	7	$\bar{3}$	1	12	2.0110	9	$\bar{3}$	1	16	1.6542	1
3	1	0	2.9638	33	0	2	0	2.0063	27	$\bar{8}$	0	6	1.6526	7
1	1	6	2.9526	9	$\bar{1}$	1	13	1.9969	3	4	0	14	1.6483	2
0	0	10	2.9468	7	$\bar{2}$	0	15	1.9799	1	$\bar{2}$	2	10	1.6471	9
$\bar{3}$	1	3	2.9348	3	3	1	10	1.9765	4	$\bar{4}$	0	18	1.5805	2
$\bar{2}$	0	10	2.8849	29	$\bar{5}$	1	9	1.9665	1	$\bar{7}$	1	11	1.5545	1
$\bar{3}$	1	4	2.8693	2	0	0	15	1.9645	1	$\bar{4}$	2	10	1.5438	2
$\bar{4}$	0	7	2.8490	2	$\bar{6}$	0	10	1.9313	2	$\bar{1}$	1	18	1.5343	1

The only way to calculate the empirical formula is to base it on Σ cations = 18, for analytical datasets with good charge-balance (*ch* and *ev*). Several authors (*e.g.*, Žák *et al*. 1994, Karup-Møller & Makovicky 1992) have emphasized the fact that the sum of cations in the formula does not have to be an integral number. For N = 4, the "fundamental" sites give $Me_{14}S_{18}$. The electron-microprobe data indicate for Cu-bearing makovickyite (Table 4) a range from 14.32 to14.86 and 14.56 to 14.78 cations *pfu*, for Băiţa Bihor and Felbertal material, respectively. Thus, the possible interstitial Cu ranges between 0.32 and 0.86 cations *pfu*.

Cupromakovickyite has $N_{p2} \approx 5$ (meaningless, because from the single-crystal study, $N_p = 4$) and $N_{p3} \approx 4$ (Table 5), with a clear indication that Cu is equally distributed between ^{i}Cu and ^{s}Cu, and has a sum of anions equal to 32, in good agreement with the results of the single-crystal study. An attempt can be made to construct a simplified formula by applying a partial 2Pb-for-(Ag + Bi) substitution to the excess Ag and Bi. This gives a simplified model formula $Cu_8Ag_2Pb_4Bi_{18}S_{36}$ for both occurrences. On the one hand, this formula is richer in lead than the analytical data indicate; on the other hand, it shows that the high contents of Cu in cupromakovickyite are caused by the distribution of copper over more sites than the

"fundamental" ones that are universal for the entire series of pavonite homologues.

In no case is the cupromakovickyite analyzed a pure phase. Rather, it contains a certain proportion of the makovickyite phase, finely distributed as lamellae down to few unit cells in thickness. It is for this reason that the Pb content reported is lower than expected.

Mineral Name and Type Material

Cupromakovickyite is related to makovickyite in exactly the same way as cupropavonite is related to pavonite (Karup-Moller & Makovicky 1979). In order to articulate this relationship (we expect more such pairs in the pavonite homologous series), we proposed a name analogous to cupropavonite. The prefix "cupro" also expresses the primary chemical difference between the two species and replaces "cuproplumbian" as a modifier. Both the mineral and its name were approved by the Commission on New Minerals and Names (IMA 2002–58). The holotype material is deposited under No. 14943 and 14944 (two polished sections) in the reference collection (museum) of the Division of Mineralogy, University of Salzburg, Austria.

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