

## FRIEDRICHITE FROM BĂIȚA BIHOR, ROMANIA

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### ABSTRACT

Friedrichite is reported from three western Romanian localities: the Antoniu magnesian skarn deposit, the "Blidar Contact" and "Secundar Contact" calcic skarn deposits, in Băița Bihor, in the northern Apuseni Mountains, Romania. Friedrichite occurs as isolated, short-prismatic grains up to  $500 \times 100 \mu\text{m}$  in size, usually included in cuprobismutite or cupropavonite, and as aggregates with Ag- and Bi-bearing galena. In plane-polarized light in air, fiedrichite is creamy yellowish white with a brownish tint. Bireflectance and pleochroism are weak, and anisotropism is strong. No internal reflections were noted. The average chemical compositions of fiedrichite from the three skarn deposits (basis of calculation: S + Se = 18) are, respectively:  $(\text{Cu}_{5.40}\text{Ag}_{0.01})_{\Sigma 5.41}(\text{Pb}_{5.03}\text{Fe}_{0.01})_{\Sigma 5.04}(\text{Bi}_{6.82}\text{Sb}_{0.02})_{\Sigma 6.84}\text{S}_{18}$  (Antoniu),  $(\text{Cu}_{4.99}\text{Ag}_{0.01})_{\Sigma 5.00}(\text{Pb}_{4.62}\text{Fe}_{0.01})_{\Sigma 4.63}(\text{Bi}_{7.22}\text{Sb}_{0.03})_{\Sigma 7.25}(\text{S}_{17.96}\text{Se}_{0.04})_{\Sigma 18}$  ("Blidar Contact") and  $(\text{Cu}_{5.26}\text{Ag}_{0.01})_{\Sigma 5.27}(\text{Pb}_{4.91}\text{Fe}_{0.02})_{\Sigma 4.93}(\text{Bi}_{6.95}\text{Sb}_{0.01})_{\Sigma 6.96}\text{S}_{18}$  ("Secundar Contact"). All of them deviate slightly from the ideal formula,  $\text{Cu}_5\text{Pb}_5\text{Bi}_7\text{S}_{18}$ . X-ray powder pattern and reflectance spectra for the Antoniu fiedrichite are given. The calculated unit-cell parameters are:  $a 3 \times 11.299(5)$ ,  $b 11.640(5)$ ,  $c 4.034(2)$  Å. Electron-microprobe-derived compositions of sulfosalts in the system  $\text{Cu}_2\text{S} - \text{PbS} - \text{Bi}_2\text{S}_3$  from the above deposits are concentrated on the join  $\text{Bi}_2\text{S}_3$  (bismuthinite) –  $\text{CuPbBiS}_3$  (aikinite), with a deviation to the Cu-excess side, as pointed out by Cook (1997) on northern Romanian materials.

**Keywords:** fiedrichite, X-ray diffraction, chemical data, optical data, Antoniu deposit, magnesian skarn, "Blidar Contact" deposit, "Secundar Contact" deposit, calcic skarn, Băița Bihor, Romania.

### SOMMAIRE

Nous décrivons ici la fiedrichite de trois endroits en Roumanie occidentale: les cornéennes magnésiennes d'Antoniu, et les cornéennes calciques de "Blidar Contact" et "Secundar Contact", dans le Băița Bihor, dans le nord des montagnes Apuseni. La fiedrichite se présente en amas isolés de grains prismatiques trappus jusqu'à  $500 \times 100 \mu\text{m}$  de taille, généralement inclus dans la cuprobismutite ou la cupropavonite, et en agrégats avec la galène enrichie en Ag et Bi. En lumière polarisée en plan et dans l'air, la fiedrichite est blanc jaunâtre crémeux avec une teinte brunâtre. La biréflexion et le pléochroïsme sont faibles, mais l'anisotropie est marquée. Nous n'avons pas décelé de réflexions internes. La composition chimique moyenne de la fiedrichite provenant de ces trois gisements est recalculée sur une base de S + Se = 18:  $(\text{Cu}_{5.40}\text{Ag}_{0.01})_{\Sigma 5.41}(\text{Pb}_{5.03}\text{Fe}_{0.01})_{\Sigma 5.04}(\text{Bi}_{6.82}\text{Sb}_{0.02})_{\Sigma 6.84}\text{S}_{18}$  (Antoniu),  $(\text{Cu}_{4.99}\text{Ag}_{0.01})_{\Sigma 5.00}(\text{Pb}_{4.62}\text{Fe}_{0.01})_{\Sigma 4.63}(\text{Bi}_{7.22}\text{Sb}_{0.03})_{\Sigma 7.25}(\text{S}_{17.96}\text{Se}_{0.04})_{\Sigma 18}$  ("Blidar Contact") et  $(\text{Cu}_{5.26}\text{Ag}_{0.01})_{\Sigma 5.27}(\text{Pb}_{4.91}\text{Fe}_{0.02})_{\Sigma 4.93}(\text{Bi}_{6.95}\text{Sb}_{0.01})_{\Sigma 6.96}\text{S}_{18}$  ("Secundar Contact"). Dans chaque cas, il y a de légers écarts à la formule

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idéale,  $\text{Cu}_5\text{Pb}_3\text{Bi}_7\text{S}_{18}$ . Nous présentons des données de diffraction X et les spectres de réflectance pour la friedrichite d'Antoniou. Les paramètres réticulaires calculés sont:  $a\ 3 \times 11.299(5)$ ,  $b\ 11.640(5)$ ,  $c\ 4.034(2)$  Å. En termes du système  $\text{Cu}_2\text{S} - \text{PbS} - \text{Bi}_2\text{S}_3$ , les compositions de sulfosels de ces trois gisements, telle que dérivée des données de microsonde électronique, montrent une concentration le long de la série  $\text{Bi}_2\text{S}_3$  (bismuthinite) –  $\text{CuPbBiS}_3$  (aikinite), avec une déviation vers un excédent de Cu, comme l'avaient indiqués les résultats de Cook (1997) sur des échantillons du nord de la Roumanie.

(Traduit par la Rédaction)

**Mots-clés:** friedrichite, diffraction X, données chimiques, données optiques, gisement d'Antoniou, cornéennes magnésiennes, gisement de "Blidar Contact", gisement de "Secundar Contact", cornéennes calciques, Băița Bihor, Roumanie.

## INTRODUCTION

The structural derivation of aikinite advocated by Moore (1967) has led to discoveries of new sulfosalts on the compositional join aikinite – bismuthinite, among which is friedrichite (Chen *et al.* 1978). The intermediate phases on the join are interpreted structurally as intergrowths of three fundamental ribbon-shaped units: bismuthinite ribbons, krupkaite ribbons, and aikinite ribbons (Pring 1989). Both ordered and disordered intergrowths are expected in natural phases (*e.g.*, Mumme & Watts 1976, Pring & Hyde 1987, Pring 1989).

Friedrichite, a member of the aikinite – bismuthinite series of the meneghinite homologous series, was first described by Chen *et al.* (1978) from the "Sedl" region, east of Habach Valley, Salzburg, Austria. It consists of an intergrowth of four ribbons of aikinite and two ribbons of krupkaite (*e.g.*, Pring 1989).

Recently, Romanian occurrences of friedrichite have been reported from Băița Bihor (Shimizu *et al.* 1995a, b) and Baia Borgia (Cook 1997). This work deals with materials from three skarn deposits in Băița Bihor, western Romania. We investigated these materials to establish the compositional range and to obtain reflectance spectra and an X-ray powder-diffraction pattern of good quality.

## OCCURRENCE

In the Apuseni Mountains, Poiana Ruscă Mountains, and in the Banat area in western Romania, late Cretaceous to Eocene magmatism gave rise to so-called "banatite" intrusive bodies (granodioritic products of such magmatism), considered to reflect Alpine subduction along the active continental margin. These granodioritic intrusions (65–43 Ma, *e.g.*, Russo-Sandulescu *et al.* 1984, Kräutner *et al.* 1986, Cioflica *et al.* 1994) are considered to be genetically responsible for Cu–Bi(–Mo–W) mineralization in Băița Bihor; there, the intrusive bodies are encountered, approximately 1 km below the current level of erosion, as evidenced by the data from eight drill cores. In this area, the formations of the Bihor Realm (Autochthon) and the Codru Nappe System (Codru, Arieșeni and Păiușeni Nappes) are widely distributed, and thermally and metasomatically affected by the intrusions.

The metallic mineralization is concentrated in the marginal zone of plutons. The ores are generally emplaced within skarns developed along the contacts of the intruded rocks with the plutons. In the Antoniu magnesian skarn deposit, the Bi–Cu(–W) mineralization is developed within Carnian recrystallized dolostones belonging to the Codru Nappe System. The most common member is a clinopyroxene skarn involving a diopside-dominant core passing to a narrow zone that includes chondrodite, clinohumite, and phlogopite. The clinopyroxene skarn is partly replaced by andradite skarn, similar to the situation at the Nakatatsu deposits in Japan (Shimizu & Iiyama 1982). The other constituents of the diopside-rich core include some magnesium borates like kotoite, fluoborite, and szaibelyite. The principal ore minerals are hosted in the skarns as disseminated masses and veinlets. They are chalcopyrite, aikinite, bismuth, wittichenite, cuprobismutite, cupropavonite, cosalite, tetradymite, sphalerite, galena, bornite, molybdenite, and scheelite. Cuprobismutite and tetradymite appear in direct association with friedrichite (Fig. 1A). In the upper part of the ore deposit, processes of weathering led to the formation of copper, cuprite, bismuth, malachite, and azurite.

The "Blidar Contact" and "Secundar Contact" skarn deposits contain Mo–Bi(–W) mineralization. Ores from the "Blidar Contact" deposit occur as veinlets in the central part of the skarns, these veinlets are mainly composed of wollastonite, grossular – andradite, diopside – hedenbergite, and vesuvianite. The skarn is about 15 m in average width and more than 100 m in extent. The ores from the "Secundar Contact" deposit are emplaced as veinlets within the skarn. The principal ore minerals in these two deposits are bismuthinite, molybdenite, scheelite, magnetite, hematite, pyrite, chalcopyrite, sphalerite, (Ag- and Bi-bearing) galena, galenobismutite, cosalite, bursaite (?), aikinite, hammarite, gladite, pekoite, paderaite, kobellite, emplectite, cuprobismutite, wittichenite, tetrahedrite, cupropavonite, tetradymite (including  $\gamma$ -tetradymite), altaite, joséite-A, bismuth, and gold. The materials examined from the "Blidar Contact" include tetradymite and, from the "Secundar Contact", Ag- and Bi-bearing galena (<1.1 wt.% Ag, <3.2 wt.% Bi) and tetradymite in direct association with friedrichite (Figs. 1B, C).

## OPTICAL PROPERTIES AND REFLECTANCE DATA

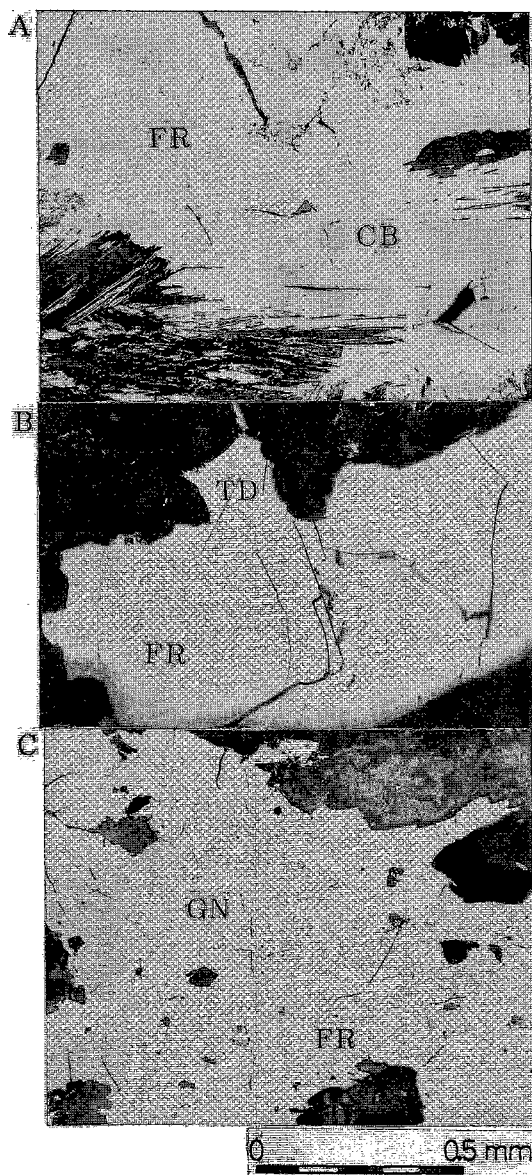


FIG. 1. Photomicrographs of fiedrichite. A. Friedrichite (FR, light grey), cuprobismutite (CB, dark grey) and tetradymite (greyish white) from the Antoniu magnesian skarn deposit, Băița Bihor, Romania. B. Friedrichite (FR, grey) and tetradymite (TD, greyish white) inclusion from the "Blidar Contact" calcic skarn deposit, Băița Bihor, Romania. C. Friedrichite (FR, light grey), Ag-, Bi-bearing galena (GN, dark grey) and tetradymite (greyish white) from the "Secundar Contact" calcic skarn deposit, Băița Bihor, Romania. All are in plane-polarized light.

Friedrichite is opaque with a metallic luster and black streak. Cleavage is developed on two directions,  $\{010\}$  and  $\{100\}$ , both perfect to good. Under the ore microscope, it is discernibly bireflectant and weakly pleochroic from creamy yellowish white to yellowish white with a brownish tint in oil. It is slightly lighter than cuprobismutite and Ag- and Bi-bearing galena (Fig. 1). It is strongly anisotropic from dark brownish gray to almost black with nearly crossed polars. Internal reflections are not observed.

Reflectance measurements were made against the SiC standard (Zeiss No. 851). Immersion measurements were made with Nikon oil,  $N_D$  1.515 at 20°C and Nikon photometry system P100 including Optiphot-2 microscope photometer with photometer-controller P101, monochromator G-70, and two-light-flux interference examination. The reflectance data for fiedrichite from the Antoniu deposit are summarized in Table 1 and Figure 2. Chen *et al.* (1978) also reported reflectance data measured in air. The present measurements give lower values than their results. The measurements in immersion are new data.

TABLE 1. REFLECTANCE VALUES FOR FRIEDRICHITE FROM THE ANTONIU DEPOSIT, BĂIȚA BIHOR, ROMANIA

nm	Air		Oil	
	$R_1$	$R_2$	$R_1$	$R_2$
470	34.5	40.7	13.5	16.3
546	36.3	43.0	13.7	16.0
589	37.1	43.1	14.5	16.5
650	38.3	42.9	14.7	16.4
400			7.0	8.3
420	29.7	35.4	10.7	12.6
440	31.9	37.8	13.0	15.6
460	34.1	39.8	13.6	16.3
480	34.8	41.5	13.4	16.2
500	35.4	42.9	13.3	15.9
520	35.5	42.7	13.3	15.8
540	36.0	43.0	13.5	16.0
560	36.2	42.8	14.0	16.2
580	37.1	43.1	14.3	16.4
600	37.4	43.1	14.6	16.6
620	37.8	43.0	14.8	16.7
640	38.0	42.8	14.8	16.5
660	38.6	42.9	14.5	16.2
680	38.8	42.5	14.1	15.5
700	38.9	42.3	13.4	14.7

## CHEMICAL COMPOSITIONS

The chemical compositions of fiedrichite and other minerals of the aikinite – bismuthinite series in Băița Bihor were determined using a JEOL 733II electron-microprobe analyzer at the Geological Institute, Faculty of Science, University of Tokyo, using the methods of Shimizu *et al.* (1986). The results of three electron-mi-

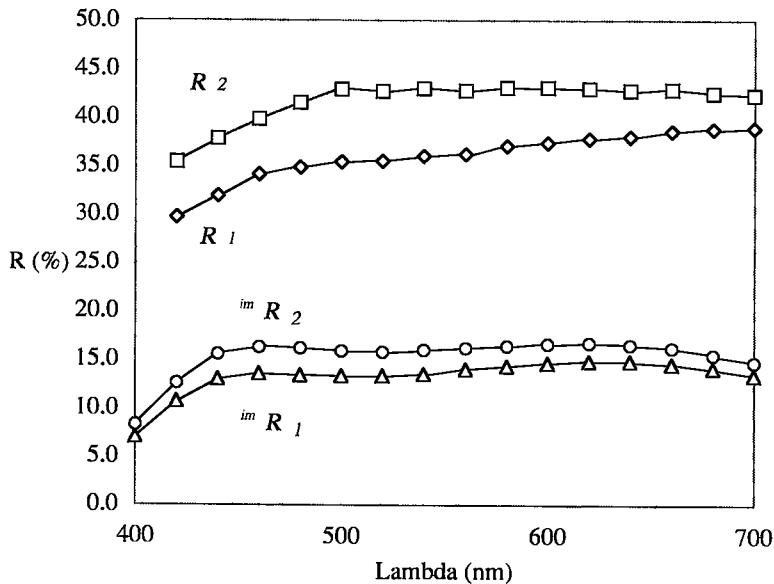
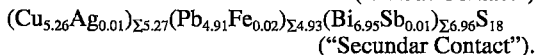
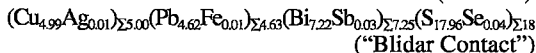
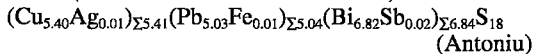
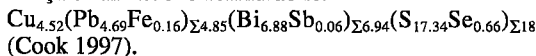


FIG. 2. Reflectance spectra of friedrichite from the Antoniu deposit, Băița Bihor, Romania, in air and in oil.

croprobe analyses of friedrichite from the Antoniu deposit, and two each from the "Blidar Contact" and "Secundar Contact" deposits, Băița Bihor, Romania are given in Table 2. The analyzed grains are large enough (>50 μm) that the results are not affected by neighboring minerals. The results lead to the following empirical formulae (basis of calculation: S + Se = 18):



The best fitting formula of the material from Baia Borsa to the above formulae is:



It is worthy of note that all the empirical formulae of friedrichite, including the one originally described by Chen *et al.* (1978), deviate from the ideal formula,  $\text{Cu}_5\text{Pb}_5\text{Bi}_7\text{S}_{18}$ , proposed by them. They discussed the crystal chemistry of phases in the aikinite – bismuthinite series, and proposed the general formula  $\text{Cu}_z\text{Pb}_z\text{Bi}_{8-z}\text{S}_{12+z}$ , where  $z$  represents an integer that represents the multiple of the  $a$  parameter of the superstructures in terms of that of the aikinite cell, friedrichite having  $z = 3$ . However, this needs revision in that the  $\text{Cu} > \text{Pb}$  relation exists in all of the examined materials, whereas Pb contents are less than those expected from the ideal formula. If the minor excess of  $\text{Pb} + \text{Fe}$  in the first empirical formula is neglected, the

most probable scheme of substitution, next to  $\square\text{Bi}^{3+}$  for  $\text{Cu}^{+}\text{Pb}^{2+}$ , is to be given as  $3\text{Cu}$  for  $\text{Bi}$ . According to Moore (1967), aikinite is regarded as a fully stuffed form in the aikinite – bismuthinite series, and has the relation that total cations = S + Se. Since all the empirical formulae of friedrichite here obey the relation total cations < S + Se, the Cu-excess state is still within the range of variation allowed. The  $\text{Cu} > \text{Pb}$  relation is also seen in the figure drawn by Cook (1997). Although the crystallochemical background of this off-series deviation needs further consideration, the present material has extended the degree of deviation, and the material with this characteristic coexists with a more Cu-bearing phase, cuprobismutite.

One of the electron micrographs of minerals of the krupkaite – aikinite series (Pring 1989) indicates the disordered intergrowths of krupkaite units in aikinite, and the other is interpreted as an intergrowth of units dimensionally corresponding to krupkaite and friedrichite in aikinite. This finding implies that a regular intergrowth of two bands, krupkaite and aikinite, can constitute a "phase" compositionally corresponding to friedrichite, where identification with the aid of an X-ray or electron micrographic study is necessary. In the present case, the Bi-rich material from the "Blidar Contact" is interpreted as having the composition of friedrichite. In the materials from the skarn deposits formed under similar genetic conditions, a different combination of bands is to be expected. It is likely that the formation of different combinations is controlled by such local factors as chemical environment.

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITIONS OF FRIEDRICHITE FROM THE ANTONIU DEPOSIT, BĂIȚA BIHOR, ROMANIA

	1	2	3	4	5	6	7	8	9	10	11	12
	Mean (1-3)			Mean (5-6)			Mean (8-9)					
Cu	10.13	10.16	10.12	10.14	9.28	9.54	9.41	9.79	9.84	9.82	8.66	9.1
Ag	0.05	0.00	0.04	0.03	0.03	0.00	0.02	0.03	0.00	0.02	0.00	0.0
Fe	0.03	0.00	0.00	0.01	0.00	0.01	0.01	0.05	0.01	0.03	0.18	0.0
Pb	30.78	30.80	30.78	30.79	27.91	28.91	28.41	29.99	29.91	29.95	29.30	29.7
Bi	42.31	42.36	41.76	42.14	45.69	43.80	44.75	42.96	42.44	42.70	43.34	44.2
Sb	0.07	0.07	0.04	0.06	0.14	0.06	0.10	0.00	0.07	0.04	0.21	0.0
S	17.11	17.11	16.95	17.06	17.23	16.92	17.08	17.04	16.92	16.98	16.77	17.2
Se	0.00	0.00	0.00	0.00	0.00	0.19	0.10	0.00	0.00	0.00	1.56	0.0
Total	100.48	100.50	99.69	100.23	100.28	99.43	99.88	99.86	99.19	99.54	100.02	100.2
Atomic proportions based on (S+Se) = 18												
Cu	5.378	5.395	5.424	5.401	4.891	5.100	4.994	5.222	5.285	5.255	4.521	4.806
Ag	0.016	0.000	0.013	0.009	0.009	0.000	0.006	0.009	0.000	0.006	0.000	0.000
Fe	0.018	0.000	0.000	0.006	0.000	0.006	0.006	0.030	0.006	0.018	0.161	0.000
Pb	5.011	5.015	5.059	5.029	4.511	4.740	4.623	4.905	4.926	4.914	4.690	4.810
Bi	6.830	6.839	6.804	6.823	7.321	7.119	7.220	6.966	6.930	6.947	6.879	7.099
Sb	0.019	0.019	0.011	0.017	0.039	0.017	0.028	0.000	0.020	0.011	0.056	0.000
S	18.000	18.000	18.000	18.000	18.000	17.918	17.957	18.000	18.000	18.000	17.343	18.000
Se	0.000	0.000	0.000	0.000	0.000	0.082	0.043	0.000	0.000	0.000	0.657	0.000

Provenance of the samples: columns 1 to 4: the Antoniu magnesian skarn deposit in Băița Bihor, 5 to 7: the "Blidar Contact" calcic skarn deposit in Băița Bihor, 8 to 10: the "Secundar Contact" calcic skarn deposit in Băița Bihor. Column 11: sample number [BB147 2.2] of Cook (1997). Column 12: average result of six analyses by Chen *et al.* (1978). Analytical conditions: Instrument: JEOL-733II, accelerating voltage: 20 kV, beam current:  $2.00 \times 10^{-8}$  amperes on Faraday cage. Standards used: analyzed chalcopyrite (Cu, Fe), synthetic  $\text{AgBiS}_2$  (Ag, Bi),  $\text{PbS}$  (Pb),  $\text{Cu}_{10}\text{Zn}_2\text{Sb}_{1.4}\text{As}_{2.4}\text{S}_{13}$  (Sb),  $\text{ZnS}$  (S), pure Se metal (Se), pure Te metal (Te).

Representative chemical compositions of the other minerals of aikinite – bismuthinite series in Băița Bihor, Romania are shown in Table 3. They are plotted in terms of  $\text{Bi}_2\text{S}_3$  (+  $\text{Sb}_2\text{S}_3$ ) –  $\text{Cu}_2\text{S}$  (+  $\text{Ag}_2\text{S}$ ) –  $\text{PbS}$  (+  $\text{FeS}$ ) in Figure 3. The presence of aikinite, friedrichite, hammarite, gladite and pekoite equivalent phases can be seen. The spread of compositions also extends along the narrow region between aikinite and bismuthinite, and Cu-excess phases are also in direct contact with such a high-Cu phase as cuprobismutite. Gladite and pekoite are observed to occur together, but other members of the series here do not coexist. Gladite and pekoite coexist with –tetradymite ( $\text{Bi}_8\text{Te}_4\text{S}_8$ ) and gold; where the other members of the series coexist with tetradymite and gold, tetradymite is normal ( $\text{Bi}_2\text{Te}_2\text{S}$ ).

#### X-RAY POWDER-DIFFRACTION STUDY

A sufficient quantity of available materials from the Antoniu deposit, Băița Bihor, Romania enabled the acquisition of X-ray powder pattern of good quality (Table 4). The diffraction maxima are indexed accord-

ing to a supercell with  $a' 3 \times 11.299(5)$ ,  $b 11.640(5)$ ,  $c 4.034(2)$  Å, where only the maxima with indices  $h$  equal to 0 or  $3n$  among the major peaks are observed. The  $c$  parameter seems to be longer than in other members of the aikinite – bismuthinite series, except aikinite [4.039(1) Å: Ohmasa & Nowacki (1970)].

The described materials from the two other localities were also examined by X-ray powder diffractometry. The results correspond to the tabulated one, though with fewer diffraction lines. The present data are in accordance with the previously reported patterns for friedrichite (Chen *et al.* 1978), but owing to the quality of the pattern, measurements are extended to  $d = 1.30$  Å.

#### ACKNOWLEDGEMENTS

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TABLE 3. REPRESENTATIVE CHEMICAL COMPOSITIONS OF MINERALS OF THE AIKINITE – BISMUTHINITE SERIES, BĂIȚA BIHOR, ROMANIA

	1	2	3	4	5	6	7
w%							
Cu	1.27	2.32	4.09	7.68	8.44	8.52	9.08
Ag	0.04	0.00	0.00	0.03	0.00	0.00	0.00
Fe	0.10	0.00	0.02	0.00	0.00	0.02	0.03
Pb	3.88	8.66	12.51	23.61	24.97	26.30	27.49
Bi	75.85	70.05	65.22	51.15	49.13	47.93	46.27
Sb	0.08	0.11	0.11	0.00	0.06	0.06	0.07
S	18.47	18.09	18.03	17.37	17.32	17.29	17.24
Te	0.00	0.00	0.00	0.00	0.01	0.00	0.00
total	99.69	99.23	99.98	99.84	99.93	100.12	100.18
Atomic proportions based on (S+Te) = 18							
Cu	0.625	1.165	2.060	4.017	4.425	4.477	4.785
Ag	0.012	0.000	0.000	0.009	0.000	0.000	0.000
Fe	0.056	0.000	0.011	0.000	0.000	0.012	0.018
Pb	0.585	1.333	1.932	3.787	4.015	4.238	4.442
Bi	11.340	10.694	9.988	8.133	7.832	7.658	7.413
Sb	0.021	0.029	0.029	0.000	0.016	0.016	0.019
S	18.000	18.000	18.000	18.000	17.997	18.000	18.000
Te	0.000	0.000	0.000	0.000	0.003	0.000	0.000
Cu+Ag	0.636	1.165	2.060	4.026	4.425	4.477	4.785
Pb+Fe	0.641	1.333	1.944	3.787	4.015	4.250	4.460
Bi+Sb	11.361	10.723	10.017	8.133	7.848	7.674	7.432

Analytical conditions are the same as those in Table 2.

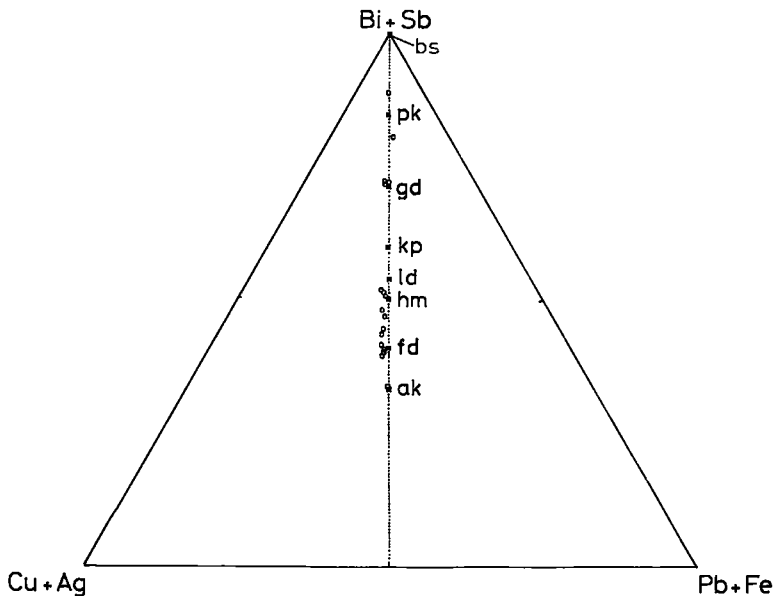


FIG. 3. Chemical compositions of aikinite – bismuthinite series in Băița Bihor, Romania in terms of the system  $\text{Bi}_2\text{S}_3$  (+  $\text{Sb}_2\text{S}_3$ ) –  $\text{Cu}_2\text{S}$  (+  $\text{Ag}_2\text{S}$ ) –  $\text{PbS}$  (+  $\text{FeS}$ ). Symbols: bs: bismuthinite  $\text{Bi}_2\text{S}_3$ , pk: pekoite  $\text{CuPbBi}_7\text{S}_{18}$ , gd: gladite  $\text{CuPbBi}_5\text{S}_9$ , kp: krupkaite  $\text{CuPbBi}_3\text{S}_6$ , ld: lindströmite  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ , hm: hammarite  $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$ , fd: friedrichite  $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{18}$ , ak: aikinite  $\text{CuPbBiS}_3$ .

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR FRIEDRICHITE FROM THE ANTONIU DEPOSIT, BĂIȚA BIHOR, ROMANIA

1				2		3		
l	d meas	d calc	h k l	l	d meas	l	d meas	h k l
1	8.16	8.11	3 1 0			10	8.1	3 1 0
2	5.86	5.82	0 2 0			5	5.79	0 2 0
10	5.19	5.17	3 2 0			20	5.13	3 2 0
60	4.06	4.05	6 2 0			40	4.05	6 2 0
10	3.808	3.799	3 0 1		10	4.03		
100	3.669	3.670	3 3 0		5	3.782		10 3.782 3 0 1
50	3.613	3.612	3 1 1		30	3.670	100	3.644 3 3 0
90	3.584	3.583	9 1 0		40	3.580	100	3.584 9 1 0 . 3 1 1
10	3.316	3.315	0 2 1		5	3.306	10	3.301 0 2 1
55	3.182	3.181	3 2 1					
45	3.162	3.162	9 2 0		100	3.160	100	3.161 3 2 1 . 6 1 1
		3.160	6 1 1					
					10	2.970		5 2 1
4	2.910	2.910	0 4 0					
65	2.861	2.859	6 2 1		50	2.850	80	2.850 6 2 1
8	2.827	2.825	12 0 0				5	2.815 12 0 0
10	2.754	2.753	9 0 1		30	2.742	20	2.741 9 0 1 . 12 1 0
30	2.680	2.679	9 1 1		30	2.672	30	2.675 9 1 1
60	2.584	2.587	6 4 0		20	2.590	40	2.577 6 4 0
20	2.540	2.541	12 2 0		5	2.539	20	2.533 12 2 0
15	2.506	2.506	6 3 1		5	2.484	20	2.495 6 3 1 . 9 2 1
15	2.360	2.360	0 4 1		20	2.356	10	2.351 0 4 1
15	2.309	2.310	3 4 1		10	2.303	20	2.302 9 4 0
20	2.270	2.269	12 1 1		10	2.262	30	2.264 12 1 1
5	2.247	2.245	9 3 1					
1	2.221	2.218	15 1 0					
5	2.178	2.178	6 4 1				5	2.168 6 4 1
					5	2.155		6 5 0
20	2.150	2.150	12 2 1		20	2.141	20	2.146 12 2 1
							5	2.098 15 2 0
20	2.019	2.017	0 0 2		10	2.005	20	2.011 0 0 2
25	1.985	1.987	12 3 1		30	1.981	40	1.979 9 5 0 . 3 5 1 . 12 3 1
		1.985	3 5 1					
25	1.980	1.980	9 5 0					
25	1.951	1.953	15 3 0					
5	1.940	1.940	0 6 0		10	1.940	30	1.943 0 6 0 . 15 1 1
1	1.912	1.912	3 6 0					
5	1.899	1.900	6 0 2					
		1.899	6 5 1					
5	1.883	1.883	18 0 0		30	1.879	10	1.884 18 0 0
1	1.834	1.835	6 6 0					
5	1.806	1.806	6 2 2		10	1.806	10	1.805 12 4 1
<1	1.776	1.778	9 0 2 etc.					
<1	1.767	1.768	3 3 2					
10	1.758	1.758	9 1 2		30	1.760	30	1.757 3 3 2
5	1.748	1.748	0 6 1					
5	1.726	1.725	9 6 0					
<1	1.708	1.706	18 0 1					
		1.706	6 3 2					
<1	1.669	1.670	6 6 1					
1	1.642	1.641	12 0 2					
<1	1.598	1.599	21 1 0					
10	1.591	1.591	6 4 2					
1	1.580	1.580	12 2 2					
2	1.555	1.555	21 2 0					
10	1.521	1.521	9 7 0					
2	1.487	1.487	12 6 1 etc.					
2	1.482	1.483	6 7 1					
5	1.471	1.472	6 5 2					
2	1.451	1.451	21 2 1					
1	1.413	1.413	9 5 2					
		1.412	24 0 0					
10	1.402	1.403	15 3 2 etc.					
<1	1.382	1.383	15 6 1					
1	1.377	1.376	18 0 2 etc.					
1	1.372	1.373	24 2 0					
2	1.350	1.350	12 7 1					
5	1.330	1.330	6 8 1					
1	1.300	1.300	6 1 3					

1 Friedrichite from the Antoniu magnesian skarn deposit, Băița Bihor, the Apseni Mountains, Romania.

Diffraction method. Cu/Ni radiation. This study. Calculated cell parameters of friedrichite:  $a$  3 x 11.299 = 33.897,  $b$  11.640,  $c$  4.034 Å.  $Ph$  2,  $m$ .

2 Friedrichite from the "Sedl" region, Salzburg, Austria.

114.6mm Gandolfi camera method. Cu/Ni radiation. Chen et al. (1978). Given cell parameters:

$a$  3 x 11.28 = 33.84,  $b$  11.65,  $c$  4.01 Å.

3 Friedrichite from the "Sedl" region, Salzburg, Austria.

114.6mm Debye-Scherrer camera method. Cu/Ni radiation. Chen et al. (1978). Given cell parameters:

$a$  3 x 11.28 = 33.84,  $b$  11.65,  $c$  4.01 Å.

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