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FRIEDRICHITE, $Cu_5Pb_5Bi_7S_{18}$, A NEW MEMBER OF THE AIKINITE–BISMUTHINITE SERIES

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ABSTRACT

Friedrichite was found near the well-known emerald deposit in the "Sedl" region, east of Habach Valley, Salzburg, Austria. It occurs as aggregates of granular-shaped crystals, associated with chalcopyrite, covellite, chlorite and mica, in vein-quartz boulders. The mineral is a new superstructure of the aikinite-bismuthinite series: $Pb2_1m$, *a* 3×11.28, *b* 11.65, *c* 4.01A. The average composition, Cu 9.1, Pb 29.7, Bi 44.2, S 17.2 wt% (total 100.2) and the measured density, 6.98 g/cm^3, suggest an ideal cell content $Cu_{10}Pb_{10}Bi_{14}S_{36}$, between those of aikinite and hammarite. The mineral is creamy yellowish-white in air, more pinkish in oil; bireflectance is moderate and distinct, anisotropism is distinct and strong in air and in oil, respectively; micro-indentation hardness VHN_{50} is 201-244 (av. 224).

SOMMAIRE

Découverte près du gisement d'émeraude bien connu de la région Sedl, à l'est de la vallée de Habach, à Salzbourg, en Autriche, la friedrichite se présente sous forme d'agrégats de cristaux granulaires associés à la chalcopyrite, à la covelline, à la chlorite et au mica dans des blocs de quartz filonien. Ce minéral est une nouvelle surstructure de la série aikinite-bismuthine: $Pb2_1m$, *a* 3×11.28, *b* 11.65, *c* 4.01Å. Sa composition moyenne (Cu 9.1, Pb 29.7, Bi 44.2, S 17.2% en poids; total, 100.2) et sa densité mesurée (6.98) conduisent à $Cu_{10}Pb_{10}Bi_{14}S_{36}$, ce qui situe la friedrichite entre l'aikinite et l'hammarite. La friedrichite est d'un blanc jaunâtre crémeux dans l'air, de teinte plus rosâtre dans l'huile; la biréflectance est modérée mais nette; l'anisotropie est nette dans l'air et forte dans l'huile; la microdureté VHN_{50} va de 201 à 244 (moyenne 224).

INTRODUCTION

Hammarite ($Cu_8Pb_8Bi_{16}S_{36}$), lindströmite ($Cu_{12}Pb_{12}Bi_{28}S_{60}$), krupkaite ($Cu_2Pb_2Bi_6S_{12}$), gladite ($Cu_4Pb_4Bi_{20}S_{36}$) and pekoite ($Cu_2Pb_2Bi_{22}S_{36}$) are known as superstructures in the aikinite-bismuthinite series (Harris & Chen 1976; Mumme *et al.* 1976). Each superstructure usually has a small range of compositions and is characterized by either *Pbnm* or $Pb2_1m$ space-group symmetry, and by an *a* parameter equivalent to a multiple of that of bismuthinite (or aikinite). The *b* and *c* parameters are similar to those in the bismuthinite (or aikinite) cell. The cell dimensions of the phases in this series generally increase systematically from those of bismuthinite to aikinite according to the amount of Cu and Pb substituting for Bi. Cu and Pb atoms tend to distribute among the maximum possible number of bismuthinite ribbons. Thus, the superstructures with compositions between krupkaite and bismuthinite (*e.g.*, gladite and pekoite) were found to consist entirely of bismuthinite (Bi_4S_6) and krupkaite ($CuPbBi_3S_6$) ribbons (Kohatsu & Wuensch 1973; Synec̆ek & Hybler 1975; Mumme & Watts 1976), whereas those with compositions between krupkaite and aikinite (*e.g.*, hammarite and lindströmite) consist entirely of krupkaite and aikinite ($Cu_2Pb_2Bi_2S_6$) ribbons (Horiuchi & Wuensch 1976; 1977). Prior to the present study, during which the new member friedrichite ($Cu_{10}Pb_{10}Bi_{14}S_{36}$) was discovered, only the five phases mentioned above were known as intermediate members in this series. The mineral and name have been approved by the Commission on New Minerals and Mineral Names, I.M.A.

GENERAL DESCRIPTION

The mineral was first found by two mineral collectors, E. Schnitzer and P. Ogris, and later by two of the present authors (W. P. and E. K.) in a locality below the well-known emerald deposit of the "Sedl" region, at the east side of the Habach Valley, Salzburg, Austria. The mineral was found in the screes of a landslip, 1700m above sea level. The geology in this region is characterized by schists and gneisses,

FIG. 1. Friedrichite showing alteration along cracks to cerussite, hydrous (?) Cu-Bi sulfate and hydrous Bi carbonate-sulfate mineral. Matrix is quartz.

metamorphic rocks of the Paleozoic "Habach Series" (Frasl 1958). Nothing is known about the host rocks of friedrichite. Other sulfides, *e.g.*, galena, cosalite, phases $Pb_6Bi_2S_9$ (heyrovskyite?) and $Pb_{1.38}Bi_{1.00}S_{2.38}$ (lillianite type), were also found in the nearby screes.

Friedrichite occurs as isolated crystals or, more commonly, as aggregates of granular-shaped to column-like crystals, 0.2 to more than 1.5 mm in size, embedded in head-sized vein-quartz boulders. Friedrichite shows alteration (Fig. 1), most commonly along cracks, but also randomly. Some friedrichite grains have been completely altered to cerussite, a hydrous (?) Cu-Bi sulfate and a wax-colored hydrous carbonate-sulfate of Bi that shows a bismoclite-type X-ray powder diffraction pattern, whereas some other grains show a relict core surrounded by zones of these secondary minerals. Trace amounts of chalcopyrite, covellite, chlorite and mica are also associated with friedrichite.

In polished section, the color of the mineral is creamy yellowish-white in air, more pinkish in oil. Bireflectance is moderate in air, distinct in oil: from creamy yellowish-white with a pink tint to pinkish grey-white or light bluish yellow-white. Anisotropism is distinct in air, strong in oil: from light creamy yellow or pinkish yellow to pink-grey or bluish grey at 15° from crossed polars, from grey to dark with crossed polars. HNO_3 (1:1) burned with effervescence and darkened the surface with seconds. $FeCl_3$ (20%) gave a light brown stain, whereas 1:1 HCl showed no effect.

Reflectances were determined with a Leitz MPE microscope photometer using a calibrated silicon standard *N*2538.42, issued by IMA Commission on Ore Microscopy). The results measured on five grains in air gave as maximum and minimum values: at 470 nm, 46.7-41.0 (av. 44.2); 546 nm, 46.2-40.1 (av. 43.5); 589 nm, 45.8-39.9 (av. 43.0); 650 nm, 45.6-39.9 (av. 42.9). Micro-indentation hardness values were determined with a Leitz Durimet hardness tester; the results on seven grains gave VHN_{50}= 201-244 (av. 224).

X-RAY CRYSTAL DATA

Two crystals pre-analyzed with the electron probe were studied with a precession camera using Mo$K\alpha$ radiation. The results showed the mineral to be a new superstructure of the aikinite-bismuthinite series; a $3\times11.28\pm0.021$, b 11.65 ± 0.007, c 4.01 ± 0.003Å, Pb^{**} ($Pb2_1m$ based on the structure of the aikinite-bismuthinite series). The X-ray powder diffraction data obtained using a 114.6 mm Gandolfi camera and Ni-filtered Cu radiation (λ=1.5418Å) from these two crystals are compared with those obtained using a 114.6 mm Debye-Scherrer camera in Table 1. The data are very similar to those for aikinite.

CHEMICAL COMPOSITION

Electron probe analyses were performed by T.T.C. using an MAC model 400 probe, at 25kV, with the following standards and emission lines: synthetic Bi_2S_3(Bi$L\alpha$), synthetic PbS (Pb$L\alpha$), and chalcostibite (Cu$K\alpha$,S$K\alpha$). The X-ray intensity data were processed using a computer program modified from EMPADR VII (Rucklidge & Gasparrini 1969). Sb was analyzed for but not detected. Other elements were not detected by the energy-dispersive X-ray analyzer. Six grains were analyzed. The results were calculated to 36 S atoms, and are listed in Table 2. The average analysis gives Cu 9.1, Pb 29.7, Bi 44.2 and S 17.2 (total 100.2 wt %), corresponding to $Cu_{9.61}Pb_{9.62}Bi_{14.19}S_{36}$; this gives a calculated density 7.06 g/cm^3, comparable with the measured density 6.98 g/cm^3 obtained by

TABLE 1. X-RAY POWDER DIFFRACTION DATA OF FRIEDRICHITE

h	k	ℓ	d_{calc} [1]	d_{meas} [2]	I_{est}	d_{meas} [3]	I_{est}
3	1	0	8.10			8.10	1
0	2	0	5.83			5.79	½
3	2	0	5.18			5.13	2
6	2	0	4.05	4.03	1	4.05	4
3	0	1	3.778	3.782	½	3.782	1
3	3	0	3.672	3.670	3	3.644	10
3	1	1	3.594	3.580	4	3.584	10
9	1	0	3.578				
0	2	1	3.303	3.306	½	3.301	1
3	2	1	3.170	3.160	10	3.161	10
6	1	1	3.147				
5	2	1	2.968	2.970	1		
6	2	1	2.850	2.850	5	2.850	8
12.	0.	0	2.820			2.815	½
9	0	1	2.743	2.742	3	2.741	2
12.	1.	0	2.741				
9	1	1	2.670	2.672	3	2.675	3
6	4	0	2.588	2.590	2	2.577	4
12.	2.	0	2.538	2.539	½	2.533	2
6	3	1	2.500	2.484	½	2.495	2
9	2	1	2.482				
0	4	1	2.357	2.356	2	2.351	1
9	4	0	2.303	2.303	1	2.302	2
12.	1.	1	2.263	2.262	1	2.264	3
6	4	1	2.174			2.168	½
6	5	0	2.153	2.155	½		
12.	2.	1	2.145	2.141	2	2.146	2
15.	2.	0	2.104			2.098	½
0	0	2	2.005	2.005	1	2.011	2
3	5	1	1.983	1.981	3	1.979	4
12.	3.	1	1.983				
9	5	0	1.981				
0	6	0	1.942	1.940	1	1.943	3
15.	1.	1	1.939				
18.	0.	0	1.880	1.879	3	1.884	1
12.	4.	1	1.808	1.806	1	1.805	1
3	3	2	1.760	1.760	3	1.757	3

CuKα radiation (λ = 1.5418Å); (1) calculated from a = 33.84, b = 11.65, c = 4.01Å; (2) 114.6mm Gandolfi camera, film taken at CANMET; (3) 114.6mm Debye-Scherrer camera, film taken at Univ. Salzburg. There is no explanation for differences between the Gandolfi and Debye-Scherrer films for (330) and (640) reflections.

Berman balance and toluene. The small variation in compositions possibly indicates a narrow range of solid solution, usually found in the members of the aikinite-bismuthinite series. The structural cell formula for phases of the aikinite-bismuthinite series in general can be represented by $Cu_xPb_xBi_{8z-2x}S_{12z}$, where z represents the integer multiple factor for the a parameter of the superstructures in terms of that of the aikinite cell. The z value is 3 for friedrichite. The compositions observed (Table 2) thus suggest an ideal structural cell formula $Cu_{10}Pb_{10}Bi_{14}S_{36}$ for this mineral.

TABLE 2. ELECTRON PROBE ANALYSES OF FRIEDRICHITE

	Weight percent					Atomic proportions (S=36)			
No.	Cu	Pb	Bi	S	Total	Cu	Pb	Bi	S
1	8.8	29.6	44.5	17.4	100.3	9.19	9.48	14.13	36
2	8.9	29.6	44.1	17.5	100.1	9.24	9.42	13.92	36
3	9.4	29.5	44.0	17.0	99.9	10.04	9.67	14.30	36
4	9.2	29.7	44.1	17.0	100.0	9.83	9.73	14.33	36
5	9.0	29.9	44.2	17.1	100.2	9.56	9.74	14.28	36
6	9.1	29.6	44.0	17.2	99.9	9.61	9.59	14.13	36

DISCUSSION

Much has been reported on the crystal chemistry of phases in the aikinite-bismuthinite series (*e.g.*, Harris & Chen 1976; Mumme & Watts 1976). The crystal chemical data of friedrichite are closely related to those of aikinite (*Pbnm*, *a* 11.33Å) and hammarite (*Pbnm*, $a \simeq 3 \times 11.29$Å). Using the data provided by Harris & Chen, the observed compositions of friedrichite (with (Cu+Pb)/2Bi = 0.69-0.66) fall between those of aikinite ((Cu or Pb)/(Bi,Sb) = 0.85-0.71) and hammarite ((Cu or Pb)/Bi = 0.60-0.55). The proposed ideal formula gives a (Cu or Pb)/Bi ratio of 0.71, which overlaps the range of aikinite. There may be no compositional gap between the aikinite and friedrichite solid solution fields; as an alternative, the substitution of Bi by Sb may affect the stability fields of the phases in the aikinite-bismuthinite series.

Mumme & Watts suggested a general formula, $Cu_xPb_xBi_{12-x}S_{18}$, to represent the ideal compositions of some of the members in this series: $x=0$ for bismuthinite, 1 for pekoite, 2 for gladite, 3 for krupkaite, 4 for hammarite, and 6 for aikinite. Nothing was known for $x=5$. Lindströmite ($Cu_{12}Pb_{12}Bi_{28}S_{60}$, $a \sim 5 \times 11.2$Å) is the only known member which does not satisfy an integer x for this formula. The new mineral, friedrichite, corresponds to the phase with $x=5$.

The crystal structures of the seven phases previously known in this series, including aikinite and bismuthinite, have been summarized by Horiuchi & Wuensch (1977). Since the idealized cell content of each superstructure in this series can be defined by the general formula $Cu_xPb_xBi_{8z-2x}S_{12z}$ (x is an integer in this case), the ratio of the structural ribbons (*i.e.*, aikinite ($Cu_2Pb_2Bi_2S_6$), krupkaite ($CuPbBi_3S_6$), and bismuthinite (Bi_4S_6) ribbons) for each superstructure thus can be derived directly from the idealized cell content, on the basis that all the superstructures with compositions between bismuthinite and krupkaite would consist entirely of bismuthinite and krupkaite ribbons, whereas those with compositions between krupkaite and aikinite consist entirely of krupkaite and aikinite ribbons. Only one combination for the structural ribbons is found for each superstructure, *i.e.*, aikinite ribbons (aikinite); 1 aikinite:2 krupkaite (hammarite); 1 aikinite:4 krupkaite (lindströmite); krupkaite ribbons (krupkaite); 2 krupkaite:1 bismuthinite (gladite); 1 krupkaite:2 bismuthinite (pekoite); and bismuthinite ribbons (bismuthinite). The ratios (m:n, where $m+n=z$) derived are the same as those obtained by crystal structure analysis (see Horiuchi & Wuensch 1977). The ratio derived for friedrichite is 2 aikinite: 1 krupkaite ribbon.

The present finding of friedrichite perhaps implies that more new phases with structures consisting of combinations of bismuthinite and krupkaite ribbons or krupkaite and aikinite ribbons in ratios other than 1:2 and 2:1 exist in nature. Lindströmite, consisting of aikinite and krupkaite ribbons in the ratio 1:4, is one such phase. However, attempts to synthesize the intermediate phases in this series by Springer (1971) and Mumme & Watts (1976) were not successful but confirmed that a complete solid solution series exists above 300°C. The hypothetical phases $Cu_{20}Pb_{20}Bi_{28}S_{72}$ (composition equivalent to friedrichite) with $a \sim 6 \times 11.2$Å (Moore 1967) and $Cu_{16}Pb_{16}Bi_{24}S_{60}$ (composition between friedrichite and hammarite) with $a \sim 5 \times 11.2$Å (Welin 1966; Moore 1967; Syneček & Hybler 1975) have not as yet been found in nature.

PRESERVATION OF TYPE MATERIAL

The mineral is named in honor of Professor Emeritus, Dr.-Ing O. M. Friedrich, Mining University, Leoben, Styria, Austria for his contribution to the field of ore genesis in Austria during the past fifty years. Type materials will be preserved at Institute of Mineralogy, University of Salzburg, Salzburg, Austria, at the Museum of Landeskunde Joanneum, Graz, Styria, Austria, at the Royal Ontario Museum, Toronto, Canada, and at the U.S. National Museum, Smithsonian Institution, Washington, D.C., U.S.A.

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