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Bismuth minerals from the Karkonosze massif

ABSTRACT: The paper presents the results of ore microscopy, chemical, and X-ray studies of emplectite, nuffieldite, bismuthinite and native bismuth from a tungsten-tin-sulfide mineralization in aplite-granites exposed at Szklarska Poręba Huta, NW part of the Karkonosze massif, Sudetes. Implications of importance of these minerals for geothermometry are also evaluated.

INTRODUCTION

Among bismuth minerals noted in the territory of Poland, native bismuth and bismuthinite are the most common species, known from Miedzianka, Kowary, Czarnów, Zbójeckie Skąły, Stara Kamienica schist zone, Martwy Kamień Hill, Kletno, Paszowice, Strzelin, Chełmiec and Mrzyglód (Traube 1888, Jaskólski & Mochnacka 1958, Gajda 1960, Fedak & Lindner 1966, Górecka 1972, Karwowski 1972, Olszyński 1972, Sałaciński 1973, Karwowski & Kozłowski 1974, Kozłowski & Karwowski 1975, Stępisiewicz 1977). Bismuth sulfosalts are rarer: cosalite occurs at Strzegom (Wiewióra & al. 1967), emplectite, schapbachite and bohdanowiczite at Kowary and Kletno (Banaś & Mochnacka 1974), and aikinite, hammarite and rezbanyite at Pilica (Harańczyk 1975). Moreover, Bolewski (1975) listed matildite and cosalite from Kletno, aikinite from Kowary and wittichenite from Lower Silesian copper-bearing shales. Sałaciński (1972) described a mineral of Pb, Bi and S from Strzegom as probably beegerite.

BISMUTH MINERALS

In the Karkonosze massif, the writers have earlier noted (Karwowski, Olszyński & Kozłowski 1973; Kozłowski, Karwowski & Olszyński 1975) the occurrence of native bismuth, bismuthinite and bismuth sulfosalts at Szklarska Poręba Huta (Fig. 1; see also Fig. 1 in Kozłowski, Karwowski & Olszyński 1975) in a typical paragenesis of wolframite,

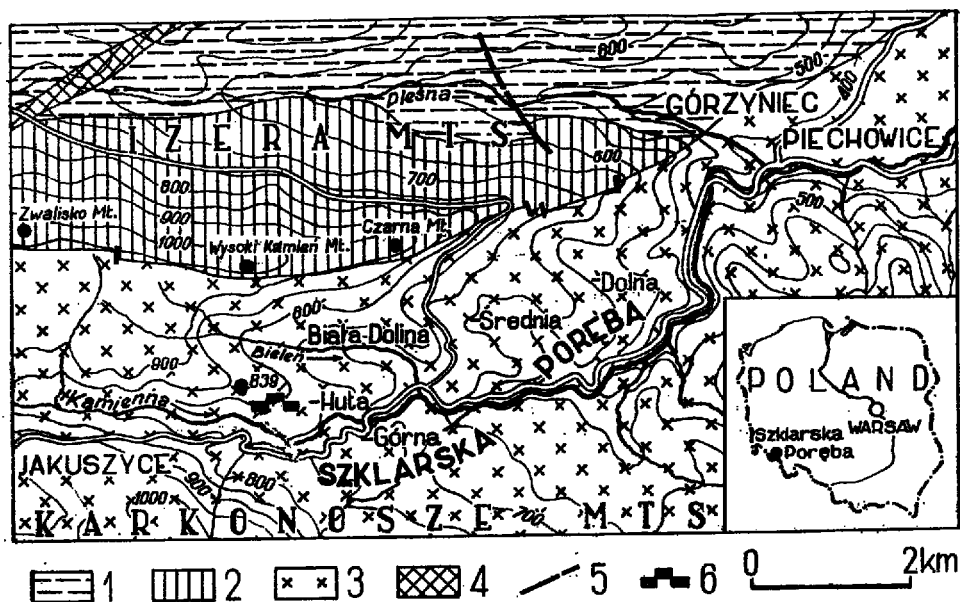


Fig. 1. Geological sketch-map of the vicinity of Szklarska Poręba

1 gneiss, 2 hornfels, 3 granite, 4 quartz vein, 5 faults, 6 quarry at Szklarska Poręba Huta

cassiterite and sulfides, connected with aplite-granites and quartz veins; the authors gave also the detailed description of geological setting, petrography, mineralogy and geochemistry of the wall rocks, as well as of ore and barren minerals. Following studies permitted the two of the previously mentioned sulfosalts (cf. Kozłowski, Karwowski & Olszyński 1975, p. 424) to determine as emplectite and nuffieldite.

EMPLECTITE

Emplectite forms very compact aggregates with nuffieldite (Pl. 1, Figs 1–2), or more commonly it occurs individually. In comparison with nuffieldite it is white-brownish in reflected light, strongly anisotropic and with high birefractance; its microhardness (H) varies from 177 to 187, rarer to 203 kg/cm² (PMT-3 apparatus); its R value at λ 589.3 nm = 37.9–39.8%. Emplectite is often associated with molybdenite (Pl. 1, Fig. 3), filling interstices between plates of the latter mineral (Pl. 1, Fig. 4). Chalcopyrite with distinct anisotropy is the second paragenetic mineral for emplectite, and it forms characteristic intergrowths (Pl. 2, Fig. 1). Emplectite is distinctly younger than magnetite, wolframite and scheelite, corroding them and cutting with veinlets; it is usually replaced by bismuthinite (Pl. 2, Figs 2–3), chalcopyrite II and native bismuth II, the both latter minerals being the secondary varieties (cf. Kozłowski, Karwowski & Olszyński 1975). The X-ray powder pattern (Table 1; VEM-TUR apparatus, CuK α radiation) agrees well with the pattern given by Berry & Thompson, and with synthetic emplectite of Godovikov (1972). Electron microprobe analysis (Fig. 2) has proved the composition as having significant amounts of silver and lead, but being suitable for a very exact calculation for the

formula of emplectite (Table 2). Slightly lowered content of Bi is probably connected with the presence of the bivalent ion Pb that replaces in part the monovalent ion Cu.

NUFFIELDITE

Nuffieldite is the mineral species established by Kingston (1968), and references on other occurrences of this mineral are unknown to the writers. That from Szklarska Poręba Huta was observed only in aggregates with emplectite (Pl. 1; Figs 1-2). It is creamy-white without brownish tint; birefractance lacks, anisotropy weak without colour effects. The studied nuffieldite commonly entrappes grains of native bismuth (Pl. 1, Figs 1, 1a and 2), but it does not alter into bismuthinite. Chemical composition of nuffieldite (Fig. 2 and Table 2) is also characterized by the presence of silver in structure. The determined element composition may be calculated for 27 ions of sulfur by two modes: either the lacking Cu is compensated by 0.1 Ag as well as lacking Pb — by 0.8 Ag (Table 2, formula 2), or one may accept that 0.8 Cu is oxidized to the bivalent ion, and then the whole 0.9 Ag ought to be included in the position of Cu^+ (Table 2, formula 3). The writers suggest rather the formula No. 2 as being correct, taking into account the similar ionic radii of Ag^+ and Pb^{2+} .

Kingston (1968) established the formula of nuffieldite as $Cu_4Pb_{10}Bi_{10}S_{27}$, but Godovikov (1972) suggested that rather $Cu_2Pb_4Bi_4S_{11}$ is the most probable. Calculating the analysis of nuffieldite from Szklarska Poręba Huta for 11 ions of sulfur (Table 2, formula 4), there occurs the lack of 5.3% of lead versus the lack of 2% of bismuth in formula bearing 27 ions of sulfur. The writers therefore suppose that the formula presented by Kingston should be accepted.

Table 1
X-ray powder patterns of emplectites

No.	Szklarska Poręba Huta		Berry & Thompson 1962*		No.	Szklarska Poręba Huta		Berry & Thompson 1962*		No.	Szklarska Poręba Huta		Berry & Thompson 1962*		No.	Szklarska Poręba Huta		Berry & Thompson 1962*			
	I	d/n	I	d/n		I	d/n	I	d/n		I	d/n	I	d/n		I	d/n	I	d/n	I	d/n
1					2		9.08	27			2		1.784								
2					2		8.20	28			2		1.759			1				1	1.757
3			5	7.38	3		7.15	29			0.5		1.716			1				1	1.726
4					1		6.37	30	7		3		1.658			6				6	1.657
5					1		5.41	31			0.5		1.616			2				2	1.618
6	4	4.63	2	4.72	2		4.76	32	3		2		1.561			2				2	1.562
7					1		4.44	33			0.5		1.544			1				1	1.534
8	1	4.03			1		3.96	34								1				1	1.494
9	4	3.60	0.5	3.65	2		3.66	35	3		0.5		1.475			1				1	1.473
10					1		3.44	36	3		2		1.453			4				4	1.447
11	10	3.21	9	3.23	10		3.21	37	1		1		1.407			1				1	1.405
12			7	3.13	3		3.12	38	1		1		1.369			1				1	1.365
13	10	3.03	10	3.05	10		3.06	39	1		1		1.33			0.5				2	1.336
14	2	2.80	0.5	2.83	2		2.85	40			1		1.320			1					
15			0.5	2.73	2		2.74	41			0.5		1.290			2				2	1.304
16			0.5	2.61	1		2.60	42			0.5		1.272								
17			0.5	2.42	1		2.41	43			0.5		1.256								
18	5	2.33	5	2.34	7		2.33	44	1		0.5		1.255			1				1	1.254
19	2	2.26	1	2.25	2		2.24	45	1		1		1.226			1					
20	5	2.16	4	2.17	7		2.16	46								3				3	1.221
21					1		2.09	47	1		1		1.206			1				3	1.205
22					1		2.03	48			1		1.192								
23	2	1.953	2	1.965	4		1.958	49								3				3	1.188
24					2		1.902	50	2		1		1.168			4				4	1.165
25	5	1.866	3	1.863	5		1.850	51	1		1		1.117								
26	6	1.811	3	1.804	6		1.798														

*fide Godovikov 1972

NATIVE BISMUTH

This mineral occurs in two generations; native bismuth *I* forms either individual grains up to 0.3 mm in diameter, or grained aggregates. Commonly, in the neighbourhood of pyrrhotite and both the above-described bismuth sulfosalts (Pl. 1, Figs 1-2) it accumulates as oval or elongated grains and drop-like ones in quartz (Kozłowski, Karwowski & Olszyński 1975). This bismuth bears internal twins (Pl. 2, Fig. 4), proving its precipitation in liquid state (cf. Godovikov & Kolonin 1965). Chemically, it consists of 96% Bi, 3% Pb and 1% Ag (Fig. 2). Native bismuth *II* occurs only in bismuthinite as fine-grained porous aggregates that form intergrowths with bismuthinite and chalcopyrite *II* during the process of alteration of emplectite into bismuthinite.

BISMUTHINITE

The group of secondary minerals in the studied association is represented mainly by bismuthinite, replacing at first the external parts of emplectite grains (Pl. 2, Fig. 2), and in the final stage forming almost complete pseudomorphs with

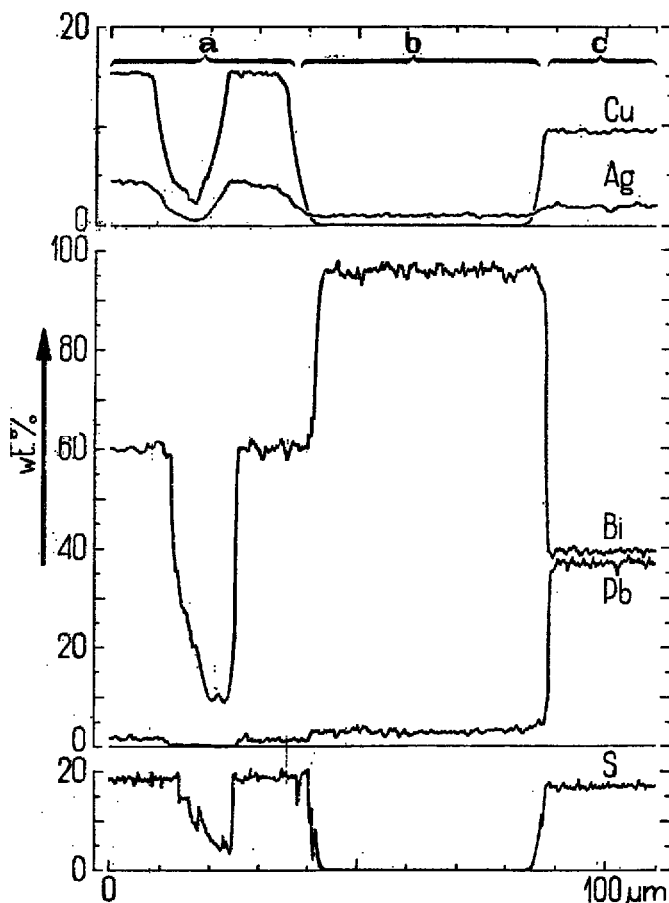
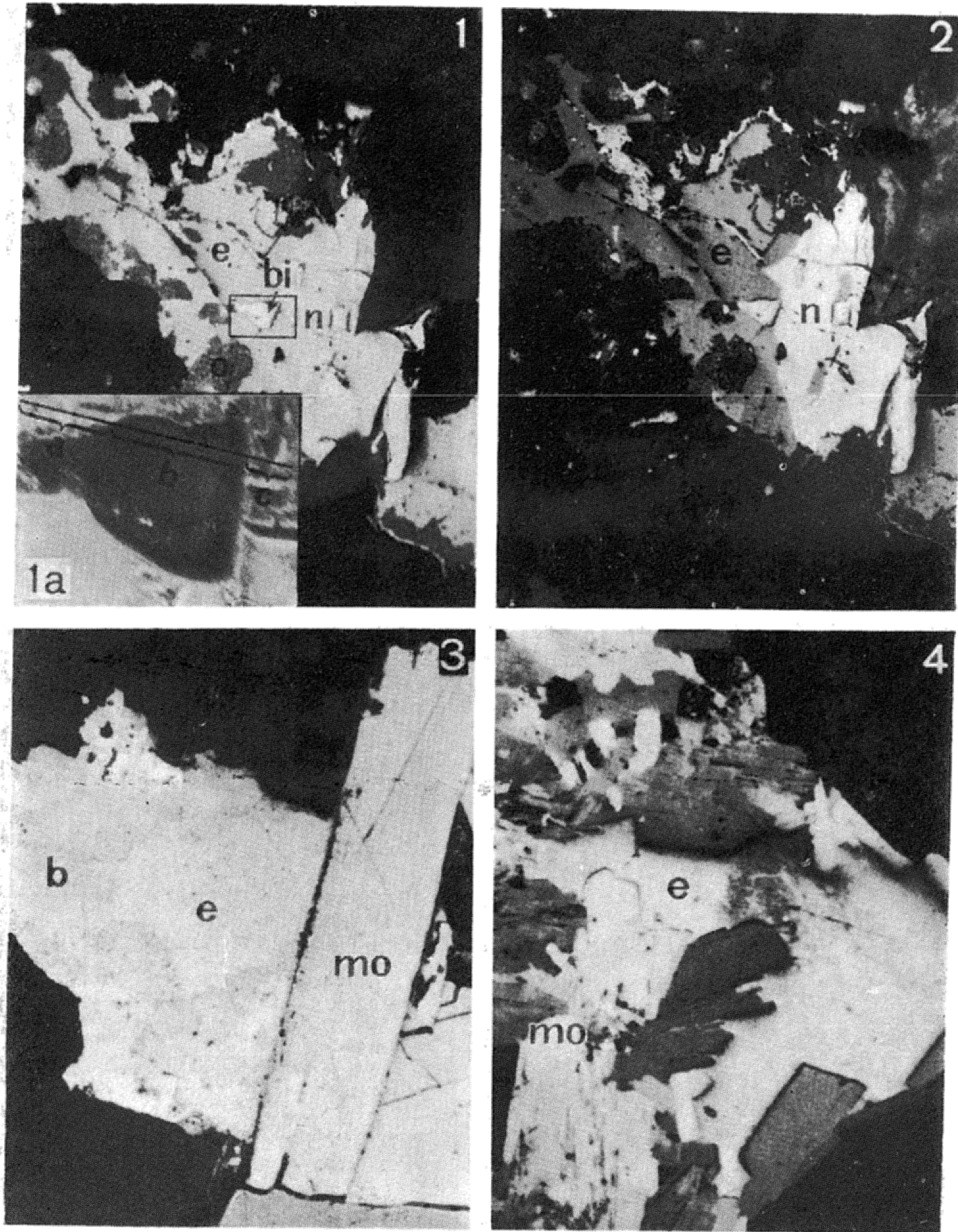
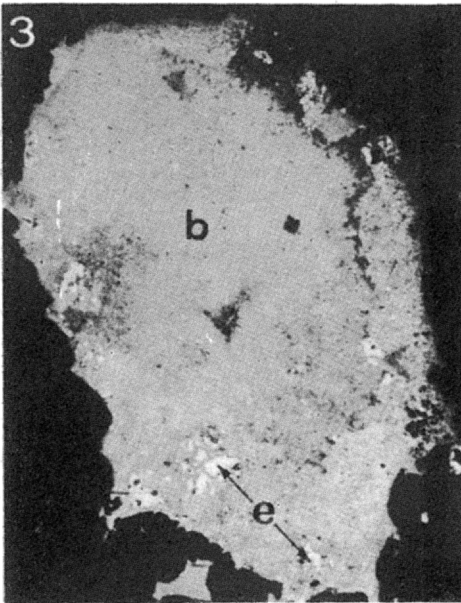
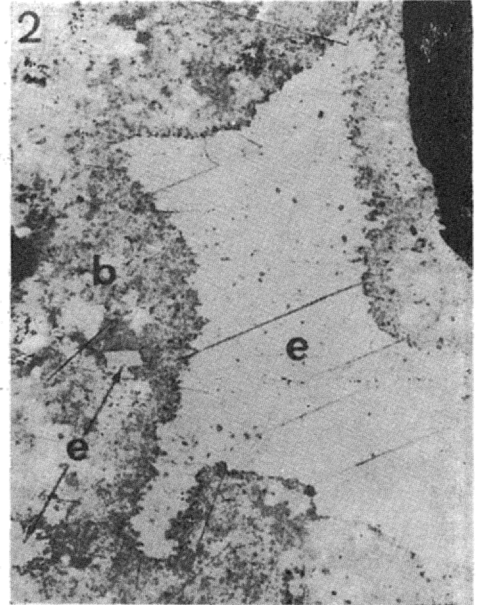
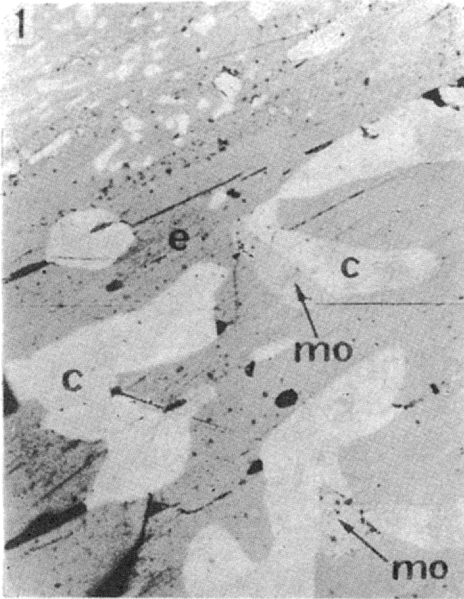


Fig. 2. Concentration curves of copper, silver, bismuth, lead and sulfur in emplectite (a), native bismuth (b), and nuffieldite (c); for route of analysis see Pl. 1, Fig. 1a. Electron microprobe analysis performed at the Institute of Precision Mechanics, JEOL apparatus.



1 — Emplectite (*e*), nuffieldite (*n*) and native bismuth (*bi*); emplectite is replaced by bismuth ochres (*o*); reflected light, one nicol, $\times 60$.
 1a — detail of Fig. 1, image in absorbed electrons; the line marks the route of electron-microprobe analysis (cf. Text-fig. 2): *a* emplectite, *b* native bismuth, *c* nuffieldite; $\times 330$.
 2 — Same as Fig. 1, nicols oblique.
 3 — Molybdenite (*mo*), and emplectite (*e*) replaced partly by bismuthinite (*b*); reflected light, one nicol, $\times 250$.
 4 — Emplectite (*e*) between plates of molybdenite (*mo*); reflected light, one nicol, $\times 120$.



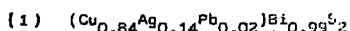
- 1 — Emplectite (e) intergrown with chalcopyrite (c); mo molybdenite; reflected light, one nicol, X 370.
- 2 — Emplectite (e) replaced partly by bismuthinite (b); reflected light, one nicol, X 250.
- 3 — Bismuthinite (b) with relics of emplectite (e); reflected light, one nicol, X 250.
- 4 — Internal twins in native bismuth; reflected light, nicols oblique, X 500.

Table 2

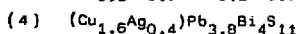
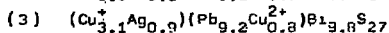
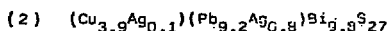
Chemical composition and formulae of emplectite and nuffieldite; electron microprobe analyses

Elements	Emplectite CuBiS_2		Nuffieldite		
	calculated	determined	calculated as		determined
			$\text{Cu}_4\text{Pb}_{10}\text{Bi}_{10}\text{S}_{27}$	$\text{Cu}_7\text{Pb}_4\text{Bi}_4\text{S}_{11}$	
Cu	18.87	15.4	4.84	5.92	4.8
Pb	-	1.5	39.23	38.58	37.0
Bi	62.08	60.0	39.57	39.05	39.6
Ag	-	4.5	-	-	1.8
S	19.05	18.6	16.39	16.45	15.3
Total	100.00	100.0	100.00	100.00	100.0

Formula of emplectite:



Formulae of nuffieldite:



minute relics of emplectite (Pl. 2, Fig. 3). It is usually fine-grained with tendency to recrystallization and enlarging of grains. Microhardness (H) of aggregates equals 167 kg/cm^2 . Bismuthinite develops together with bismuth II and fine-grained aggregates of isotropic chalcopyrite.

FINAL REMARKS

The investigated association of bismuth minerals bears two geological thermometers: emplectite and native bismuth. The upper range of the stability of emplectite equals 366°C (Godovikov 1972), and at higher temperature the assemblage of cuprobismuthite and wittichenite is stable. It therefore appears that the temperature of crystallization ought to be lower than the above value. However, the temperature of crystallization had to be higher than 271°C , because native bismuth has morphology and twinnings characteristic of the precipitation in liquid state, i.e. above 271°C . In fact, the association of bismuth minerals has crystallized subsequently to wolframite and scheelite, contemporaneously with sulfide minerals, and the temperatures of decrepitation and homogenization of fluid inclusions (Kozłowski, Karwowski & Olszyński 1975) in paragenetic ore and barren minerals confirm the presented conclusions.

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MINERAŁY BIZMUTU ZE SZKLARSKIEJ PORĘBY**(Streszczenie)**

Przedmiotem pracy jest opis minerałów bizmutu — emplektytu, bizmutu rodzimego, bizmutynitu oraz po raz pierwszy stwierdzonego w Polsce nufieldytu (pl. 1–2), występujących w aplogranicie odsłoniętym w kamieniołomie w Szklarskiej Porębie Hucie (fig. 1). Minerale te zostały zidentyfikowane metodą rentgenowską (tab. 1), co zostało potwierdzone oznaczeniami składu chemicznego metodą mikrosondy (fig. 2 i tab. 2). Na podstawie badań w świetle odbitym określono ich pozycję paragenetyczną w asocjacji minerałów wolframu, cyny oraz siarczków, a także oceniono możliwość użycia emplektytu i bizmutu rodzimego jako geotermometrów w obrębie badanej paragenety.
