

Henryk KUCHA*, Ksenia MOCHNACKA*

PRELIMINARY REPORT ON BISMUTH MINERALS FROM THE GIERCZYN TIN DEPOSIT, LOWER SILESIA, POLAND

Abstract. In samples derived from the tin-bearing zones of the worked-out Gierczyn mine, bismuth minerals unreported so far from this area were detected. Besides native bismuth, bismuthinite, galenobismuthinite, Bi-bearing galena, cosalite and bismuth ochres, described or mentioned in earlier papers, the samples were found to contain bismuth antimonite, $Sb_{1.75}Bi_{0.25}S_3$, and a mineral with the formula Bi_2S_2Se . Their optical features were determined comparatively, and their chemical composition was established by electron microprobe analysis. Worth noting is the increased gold content, sometimes running up to more than 2%. The bismuth minerals are accompanied by ore minerals: pyrrhotite, chalcopyrite, arsenopyrite, pyrite, sphalerite, tetrahedrite and cassiterite.

INTRODUCTION

The occurrence of bismuth minerals in the Gierczyn tin deposit has been mentioned in several publications (Stehr 1933; Jaskólski, Mochnacka 1958; Kowalski *et al.* 1978; Wiszniewska 1982, 1984; Speczik, Wiszniewska 1984; Mochnacka 1985). Bismuthinite was described as forming grains in arsenopyrite or inclusions in chalcopyrite and tetrahedrite, or as coexisting with sphalerite. Native bismuth was reported as forming inclusions in bismuthinite (Stehr 1933). Discussing the mineralization of tin-bearing zones in the Kamiénica range, Kowalski *et al.* (1978) mentioned native bismuth as a common mineral occurring in quartz with galena, arsenopyrite and bismuthinite, and distinguished three generations of this mineral. According to these authors, bismuthinite is a rare mineral, occurring with or independently of chalcopyrite. They also mentioned some indefinite sulphosalts. A more detailed description of Bi minerals was given by Wiszniewska (1984), who defined precisely the three generations of native bismuth, distinguishing native Bi I, II and III. It appears from her studies that native Bi I is a high-temperature variety forming intergrowths with arsenopyrite, glaucodot and other Co minerals, as well as with pyrrhotite II. It also intercalates quartz in the vicinity of minerals with an increased Co and Bi content. Native bismuth I is confined to bismuth-bearing minerals. Native Bi II forms as a result of a decrease in temperature, and its usual carrier is bismuth-bearing galena. Native bismuth of the third generation occurs within super-

* Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy in Cracow (Kraków, al. Mickiewiczza 30).

gene minerals, replacing bismuth-bearing minerals. According to Wiszniewska (1984), bismuthinite is an accessory mineral accompanying Bi-bearing galena, galenobismuthinite and native bismuth. It was found as exsolutions in Bi-bearing chalcopyrite I besides native bismuth II and pyrrhotite, as well as in intergrowths with galena I and galenobismuthinite, with native bismuth II as an accompanying mineral. In the cementation zone bismuthinite is replaced by chalcocite. Galenobismuthinite appears in insignificant amounts, together with galena I, bismuthinite and native Bi I. Cosalite was found by Wiszniewska in the form of exsolutions in bismuth-bearing galena. Bismuth minerals occurring in association with tin minerals are (Wiszniewska 1983): Bi-bearing galena, bismuthinite, galenobismuthinite, cosalite, native bismuth II and III, and bismuth ochres.

The study of old samples from the Gierczyn mine with the application of more sophisticated methods gave new data on Bi mineralization in the area in question.

Bismuth mineralization was detected in samples characterized by the substantial concentration of sulphides and the presence of cassiterite (sulphide ore with cassiterite — cf. Mochnacka, 1985). However, it has not yet been possible to assign all the minerals studied to the definite mineral phases on the basis of their optical features or chemical composition. The association in question will be the object of further detailed studies, and the results will be published in a separate paper. The aim of this paper is to give some preliminary information on the occurrence of these minerals and their chemical composition, in which worth noting is the increased gold content.

DESCRIPTION OF BISMUTH MINERALS

Bismuth minerals were detected in seven samples. According to the archival data of the Gierczyn mine, two samples from which thin sections were made represent tin-bearing zones in which Sn content was 0.98% and 0.01%, respectively. No precise data are available for the other samples. In one of them cassiterite was found, while the structures and textures of the others imply that they also represent poor tin-bearing zones.

The dominant ore minerals in the samples studied are pyrrhotite and chalcopyrite, sometimes accompanied by subordinate arsenopyrite, pyrite, sphalerite, tetrahedrite and cassiterite.

Bismuth minerals form concentrations, intergrowing chalcopyrite and pyrrhotite, or both minerals. Sometimes they are intergrown with arsenopyrite or tetrahedrite.

Even perfunctory microscopic studies revealed the presence of minerals resembling native bismuth and bismuthinite, as well as heterogeneous mineral concentrations differing from the mentioned minerals in their optical features. Detailed studies showed that these concentrations contained the following minerals: 1. native bismuth, 2. bismuthinite, 3. a mineral with the formula $\text{Bi}_2\text{S}_2\text{Se}$, and 4. bismuth antimonite ($\text{Sb}_{1.75}\text{Bi}_{0.25}\text{S}_3$).

The optical features of these minerals, determined approximately by the comparative method, are given in Table 1, along with the data for laitakarite, horobetsuite, guanajuatite, bismuthinite and antimonite (after Uytendogaardt, Burke 1971).

Compared with the dominant pyrrhotite and chalcopyrite, the minerals in question appear in insignificant amounts. Their intergrowths are irregular, and the boundaries between the individual mineral phases are not well-defined.

The composition of minerals was determined with an ARL SEMQ electron microprobe operated at a voltage of 20 kV and a sample current of about 10 nA, using the following X-ray lines, synthetic compounds and pure element standards:

Table 1
Optical features of bismuth minerals from Gierczyn and data according to Uytendogaardt, Burke (1971)

Mineral	Reflectance	Colour	Bireflectance	Anisotropy
Native Bi Bismuthinite $\text{Bi}_2\text{S}_2\text{Se}$ Bi- antimonite	$\text{Bi} > \text{R} > \text{Cp}$ $\text{R} < \text{Cp}$	pale orange creamy white grey, bluish tint grey	distinct weak weak weak	strong strong strong strong
Guanajuatite*	about 55%	creamy white	air:distinct oil:strong	strong
Laitakarite* Horobetsuite*	about 55% 546 nm: 25.8—29.6	white very pale brown to pale blue	weak not distinct	moderate
Bismuthinite*	546 nm: 37.8 < 50.2	white	weak to distinct	very strong
Antimonite*	546 nm: 31.4 (Rp) 40.9 (Rm) 46.8 (Rg)	white to greyish white	distinct	strong

* After Uytendogaardt, Burke (1971).

SK_α , FeK_α (FeS_2), CuK_α , ZnK_α , AsK_α , SeK_α , CdL_α , SbL_α , SnL_α , AuL_α , TeL_α , PbM_α (PbS), BiL_α . Corrections were made for absorption, fluorescence and atomic number difference effects (Tab. 2).

Native bismuth (Phot. 1), with the optical properties given in Table 1, was found in several places in association with bismuthinite, $\text{Bi}_2\text{S}_2\text{Se}$ mineral and chalcopyrite. In one case it was accompanied by arsenopyrite. In two samples native Bi formed inclusions in pyrrhotite. The grains of native bismuth are small, up to several dozen microns in size, and irregular. Microprobe analysis revealed a notable content of gold at one point, rising above 1% (Tab. 2). Copper content in the native bismuth under study runs up to 2 wt.% (Phot. 1).

Bismuthinite occurs in paragenesis with native bismuth, forming intergrowths with the $\text{Bi}_2\text{S}_2\text{Se}$ mineral. Its content is somewhat higher than that of native bismuth. It is conceivable that bismuthinite coexists with bismuth antimonite, but it is difficult to distinguish these minerals on the basis of optical features alone. Bismuthinite shows a fairly high (up to 5.4%) admixture of antimony and an increased content of Zn and As.

The $\text{Bi}_2\text{S}_2\text{Se}$ mineral was detected in one samples (Phot. 1), and its presence was confirmed by electron microprobe analysis. Its optical properties (Tab. 1) are not typical enough to identify it in other samples with confidence. The analysis showed about 75% Bi, about 13% Se and about 12% S. Like bismuthinite, it contains some Cu, Fe, As and Pb.

The chemical composition of the mineral in question indicates that it is a sulphate having in places a fairly high content of selenium. Compared with guanajuatite, it shows certain similarity in optical features but differs in chemical composition. Based on the microprobe analysis (Tab. 2) and certain resemblance of optical features (Tab. 1), the discussed mineral can be said to show the closest similarity to laitakarite ($\text{Bi, Pb}_4\text{Se}_2\text{S}$ (Pringle, Thorpe 1980), but again it differs in chemical composition.

Minerals	Sample	S	Fe	Cu	Zn	As	Se	Sb	Au	Pb	Bi	Cd	Σ	Phot	
Native Bi	B3-3 2a 1	≤0.40	0.36	1.73	≤0.28	≤0.40	≤0.40	≤0.19	1.20	≤0.30	98.50	≤0.20	101.79	Phot. 1	
															From Gierczyn
Bismuthinite Bi ₂ S ₃	B3-3 2 9 5 2	19.72	≤0.18	≤0.18	0.40	0.33	≤0.28	0.53	2.24	≤0.30	77.05	≤0.21	99.36	Phot. 1	
															0.81
															20.35
															18.72
Bi ₂ S ₂ Se	B3-3 3	11.67	0.30	0.25	≤0.20	1.38	12.27	≤0.20	≤0.50	0.50	74.81	≤0.21	101.19	Phot. 1	
															2.02
Bi-antimonite Sb _{1.75} Bi _{0.25} S ₃ *	49 5	26.10	0.03	0.22				58.34	≤0.38		13.20	1.20	99.06	Phot. 2	
															3.00
Guanajuatite Bi ₂ (Se, S) ₂ *	6	25.10		0.01				1.77	≤0.38		0.23	0.04	100.52	Phot. 2	
															3.00
Laitakarite (Bi, Pb) ₄ Se ₂ S**		3.0					24.13			7.0	72.5				
															2.5
Horobetsuite (Bi, Sb) ₂ S ₃ *		21.57	tr.				17.5	21.49		8.5	72.5				
															23.00
							16.5	32.30			56.93				
											44.80				

Sought for but not detected: Sn ≤ 0.30, Te ≤ 0.22

* Analyses after data from "Mineraly" (1960).

** Analyse after Pringle, Thorpe (1980).

tion (Pb content — 0.7%). The unquestionable determination of this mineral requires confirmation with other methods and a greater number of samples.

Bismuth antimonite (Phot. 2) was detected in one sample. It occurs in a concentration of minerals differing in reflectance and slightly in colour. It forms grey-bluish groundmass in which are embedded lighter spots and streaks. Bismuth antimonite displays strong anisotropy. Chemical analysis has shown that the dominant elements in its composition are antimony (up to 58%), bismuth (18%) and sulphur (about 25%). Sb content is much lower than the percentage of this element in antimonite. The isomorphous series Bi₂S₃—Sb₂S₃ has been described in the mineralogical literature, but the end member rich in Sb is horobetsuite (Springer 1969), which contains up to 32% Sb (Minerały 1960). According to the cited author, no member of this series was found till 1971 (Springer, Laflamme 1971), in which Sb content would be intermediate between horobetsuite and antimonite, i.e. in the range from about 21% (cf. Table 2) to about 71% (theoret. Sb—71.38). It is feasible that the mineral studied is the missing member of the isomorphous series in question.

DISCUSSION

The above short description of minerals containing Bi supplied certain data on native bismuth and bismuthinite — the minerals discussed in other papers, and some preliminary information on minerals or mineral varieties unreported so far from Gierczyn. Because of the incomplete data and the small amount of material available for investigations, the unequivocal identification of these minerals has not yet been possible. It will be possible after additional, mainly X-ray, determinations. However, basing on the studies carried out to-date, it can be stated that the minerals in question are a sulphide enriched in Se, showing close similarity to laitakarite, and a sulphide that seems to be a member of the mixed series of Bi and Sb sulphides, placed between antimonite and horobetsuite.

Minerals with antimony entering into their composition have been reported from the area of Gierczyn. Tetrahedrite was found by several investigators, and boulangerite was also determined (Kowalski *et al.* 1978, Wiszniewska 1984).

The minerals discussed occur in association with sulphides, and their intergrowths indicate that they formed contemporaneously, or nearly so, with chalcopyrite, sphalerite, pyrrhotite and pyrite. In the mineral succession (cf. Mochacka 1985), they are younger than cassiterite of the first generation and older than cassiterite of the second generation.

The minerals studied form a group characterized by heterogeneous chemical composition and heterogeneous optical features. The present studies are insufficient to identify them with confidence, but they suggest the presence of isomorphous series. A feature deserving note is the increased content of gold in the bismuth minerals under study.

Translated by Hanna Kisielewska

REFERENCES

- JASKÓLSKI S., MOCHACKA K., 1958: Złoże cyny w Gierczyniu w Górach Izerskich na Dolnym Śląsku i próba wyjaśnienia jego genezy. *Arch. Miner.* 22, 1.
 KOWALSKI W., KARWOWSKI Ł., ŚMIETAŃSKA I., DO VAN PHI., 1978: Mineralizacja kruszcowa kamienicznego pasma łupkowego w Górach Izerskich. *Prace. Nauk. Uniw. Śląskiego w Katowicach*, 243. *Geologia* 3. Katowice.
 [Minerały] Минералы: 1960.

- MOCHNACKA K. (in press): Struktury i tekstury rud ze złoży cyny w Gierczynie (Sudety-Polska) oraz próba ich genetycznej interpretacji. *Miner. Pol.* 16, 1.
- PRINGLE G. J., THORPE R. I., 1980: Bohdanowiczite, junote and laitakarite from the Kidd Creek Mine, Timmis, Ontario. *Canad. Mineral.* 18.
- STEHR H., 1933: Ein Beitrag zur Kenntniss d. Zinn-Kobalt Lagerstätten von Giehren — Querbach im Izergebirge. Bergmannische Meldearbeit. Clausthal.
- SPECZIK S., WISZNIEWSKA J., 1984: Some comments about stratiform tin deposits in the Stara Kamienica Chain (Southwestern Poland). *Mineralium Deposita* 19.
- SPRINGER G., 1969: Naturally occurring composition in the solid solution series Bi_2S_3 — Sb_2S_3 . *Miner. Mag.* 37.
- SPRINGER G., LAFLAMME I. H. G., 1971: The System Bi_2S_3 — Sb_2S_3 . *Canad. Miner.* 10, 5.
- UYTENBOGAARDT W., BURKE E. A. J. 1971: Tables for microscopic identification of ore minerals. Amsterdam, London, New York.
- WISZNIEWSKA J., 1983: Origin of tin mineralization in the Izera Schists in Kamienickie Range (Sudetes). *Arch. Miner.* 38, 2.
- WISZNIEWSKA J. 1984: Geneza okruszczenia łupków izerskich Pasma Kamienickiego. *Arch. Miner.* 40, 1.

Henryk KUCHA, Ksenia MOCHNACKA

WYNIKI WSTĘPNYCH BADAŃ MINERAŁÓW BIZMUTU ZE ZŁOŻA CYNŹY W GIERCZYNI (DOLNY ŚLĄSK, POLSKA)

Streszczenie

W próbkach pochodzących ze stref cynonośnych nieczynnej obecnie kopalni cyny w Gierczynie znaleziono nie stwierdzone dotąd minerały bizmutu. Oprócz opisywanych we wcześniejszej literaturze: bizmutu rodzimego, bizmutynu, galenobizmutynu, galeny Bi-nośnej, kosality oraz wzmiance o ochrach bizmutowych stwierdzono obecność antymonitu bizmutowego $\text{Sb}_{1,75}\text{Bi}_{0,25}\text{S}_3$ oraz minerału $\text{Bi}_2\text{S}_2\text{Se}$. Określono porównawczo ich cechy optyczne oraz skład chemiczny metodą MAR. Na uwagę zasługuje występująca w nich podwyższona zawartość złota, które stwierdzono w ilościach niekiedy ponad 2%. Spośród minerałów kruszcowych minerałom bizmutu towarzyszą: pirotyn, chalkopiryt, niekiedy arsenopiryt, piryt, sfaleryt, tetraedryt i kasyteryt.

OBJAŚNIENIA FOTOGRAFII

Plansza I

- Fot. 1. Mikrofotografia skupienia mineralnego zbudowanego z bizmutu rodzimego (1, 2a), chalkopiryty, bizmutynu (2), minerału o wzorze $\text{Bi}_2\text{S}_2\text{Se}$ (3) i selenku bizmutu (obszar o najwyższej zawartości Se) w otoczeniu kwarcu
REI — obraz elektronowy, Se, Bi, Cu i S — skanningowe obrazy rozmieszczenia wymienionych pierwiastków, odcinek na fotografii oznacza 30 μm

Plansza II

- Fot. 2. Mikrofotografia $\text{Sb}_{1,75}\text{Bi}_{0,25}\text{S}_3$ otoczonego przez przerosty pirotynu i chalkopiryty
REI — obraz elektronowy, Sb, S, Cu i Bi — obrazy skanningowe rozmieszczenia wymienionych pierwiastków, odcinek na fotografii oznacza 30 μm

Henryk KUCHA, Ksenia MOCHNACKA

ИТОГИ ПРЕДВАРИТЕЛЬНЫХ ИССЛЕДОВАНИЙ МИНЕРАЛОВ ВИСМУТА ИЗ ОЛОВЯННОГО МЕСТОРОЖДЕНИЯ В ГЕРЧИНЕ (НИЖНЯЯ СИЛЕЗИЯ, ПОЛЬША)

Резюме

В образцах, отобранных из оловоносных зон бездействующего в настоящее время рудника олова в Герчине найдены невыявленные до сих пор минералы висмута. Кроме, описываемых раньше в литературе, самородного висмута, висмутитина, галеновисмутитина, Bi-носного галенита, козалита, а также заметке о висмутовых охрах, обнаружено присутствие висмутового антимонита $\text{Sb}_{1,75}\text{Bi}_{0,25}\text{S}_3$, а также минерала $\text{Bi}_2\text{S}_2\text{Se}$. Определены сравнительно их оптические свойства, а микронзонным анализом их химический состав. Заслуживает внимания повышенное содержание в них золота, которое обнаружено в количестве иногда свыше 2%. Среди рудных минералов минералам висмута сопутствуют: пирротин, халькопирит, иногда арсенопирит, пирит, сфалерит, тетраэдрит и касситерит.

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Таблица I

- Фото 1. Микрофотография минерального скопления, сложенного самородным висмутом (1, 2a), халькопиритом, висмутитом (2), минералом формулы $\text{Bi}_2\text{S}_2\text{Se}$ (3) и селенидом висмута (область максимального содержания Se) в окружении кварца
REI — электронное изображение; Se, Bi, Cu и S — сканированные изображения распределения указанных элементов, отрезок на фотографии обозначает 30 μm

Таблица II

- Фото 2. Микрофотография $\text{Sb}_{1,75}\text{Bi}_{0,25}\text{S}_3$, окаймленного срастающимися пирротинном и халькопиритом
REI — электронное изображение; Sb, S, Cu и Bi — сканированные изображения распределения указанных элементов, отрезок на фотографии обозначает 30 μm

EXPLANATIONS OF PLATES

Plate I

- Phot. 1. Microphotograph of mineral assemblage consisted of native bismuth (1, 2a), chalcopyrite, bismuthinite (2), $\text{Bi}_2\text{S}_2\text{Se}$ (3), surrounded by quartz and Bi-selenide (area with the highest Se content).
REI — reflected electrons image, Se, Bi, Cu and S — scanning pictures of these elements. Scale bar — 30 μm

Plate II

- Phot. 2. Microphotograph of $\text{Sb}_{1,75}\text{Bi}_{0,25}\text{S}_3$ surrounded by a mixture of pyrrhotite with chalcopyrite
REI — reflected electrons image, Sb, S, Cu and Bi — scanning pictures of these elements, Scale bar — 30 μm



