



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

WP7 Historic Mine Sites revisited

Case Study

The Radzimowice Au-Cu-As deposit (Sudetes, SW Poland)

Authors: Stanislaw Mikulski and Rafal Małek (PGI-NRI)



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731166





FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

Disclaimer

The contents of this document are the copyright of the FRAME consortium and shall not be copied in whole, in part, or otherwise reproduced (whether by photographic, reprographic or any other method), and the contents thereof shall not be divulged to any other person or organization without prior written permission. Such consent is hereby automatically given to all members who have entered into the FRAME Consortium Agreement, dated 01.07.2018, and to the European Commission to use and disseminate this information.

This information and content of this report is the sole responsibility of the FRAME consortium members and does not necessarily represent the views expressed by the European Commission or its services. Whilst the information contained in the documents and webpages of the project is believed to be accurate, the author(s) or any other participant in the FRAME consortium makes no warranty of any kind with regard to this material.



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

Table of Contents

1	Introduction	4
2	Geology.....	4
3	Mine History	4
4	Field work	5
5	Results of lab work/analysis	7
6	Conclusions	13



1 Introduction

The Radzimowice Au-Cu-As deposit from the Kaczawa Mts. is situated in the Western Sudetes (SW Poland) that constitute the NE part of the Bohemian Massif and is considered as a continuation of the Saxothuringian Zone of the European Variscides.

The main gold-bearing ore mineralization is found in the major sixth quartz-sulfide veins that cut the Zeleznik rhyolite intrusion built of intrusive rocks of sub-alkaline and alkaline suites of Upper Carboniferous post-collisional arc setting and Paleozoic sedimentary rocks of flysch-like character. These veins strike E-W and dip about 60-85° N or S. The quartz-sulfide-carbonate veins range from 0.06-1.4 m in thickness. They are typically 300 to 350 m long, with the exception of the Miner consolation vein, which measures about 2 km in length, and is up to 1.4 m thick.

2 Geology

The mineralization of the Radzimowice deposit is considered as related to alkaline magmatism and is characterized by superposition of low-sulphidation epithermal mineralization on higher-temperature and deeper-seated mesothermal / porphyry style. A several stages of ore mineralization in quartz $\pm$ carbonates veins are recognized: pyrite-arsenopyrite stage (with refractory gold), base metal sulfides stage (with electrum), Bi-Te-Au-Ag minerals stage, and sulfosalts stage. However, in major quartz veins are prevailing only two generation of sulfides: Co-arsenopyrite and pyrite that occur in the outer part of veins and base metal sulfides associated with carbonates in central part of veins. Base metals sulphides representing by chalcopyrite, galena, sphalerite and fahlore are very often cemented earlier sulphides that were subject of strong cataclasis. They may form massive aggregates showing variable size, or veins and disseminations present within a gangue dominated by crystalline white quartz with carbonates. At least three or four quartz and carbonates generation is possible to recognize. Barren parts of veins are built mainly by quartz that in the central and cataclased zones may contain calcite, ankerite, dolomite, siderite and/or barite of younger successions.

3 Mine History

The Radzimowice deposit had a long history of exploitation that was subject of many stops or intensive mining since 13th century to 1957. The richest Au-bearing ores had an average gold grade of 17 and 19 g/t, respectively. The arsenic content ranged from 1.0 to 20.0 %, copper from 0.8 to 8.2 %, and silver from 40 to 400 g/t. It is estimated that total productions from the



Radzimowice deposit in 19-20th centuries was from ca. 0.5 Mt of metal ores and ca. 4.2 tons of gold. An average grade of metal ores was from 5 to 8 ppm of Au.

4 Field work

In 2019 and 2020 during two days were carried out field works within the abandoned mine sites at the Radzimowice Au-Cu-As deposit. Field investigation were focused on rock collecting, especially focus on ore sampling from wastes. In this are a few a variable size mine wastes occur that contain barren rocks as well as remnants of metallic ores (Fig. 50). Besides, the subject of field works was rock exposures, weathering zones of mineralization outcrops, as well as abandoned traces of former mine workings. Remnants of old excavations to the east of the known veins were also visited, indicating the possibility of ore mineralization extending beyond the former mining area.

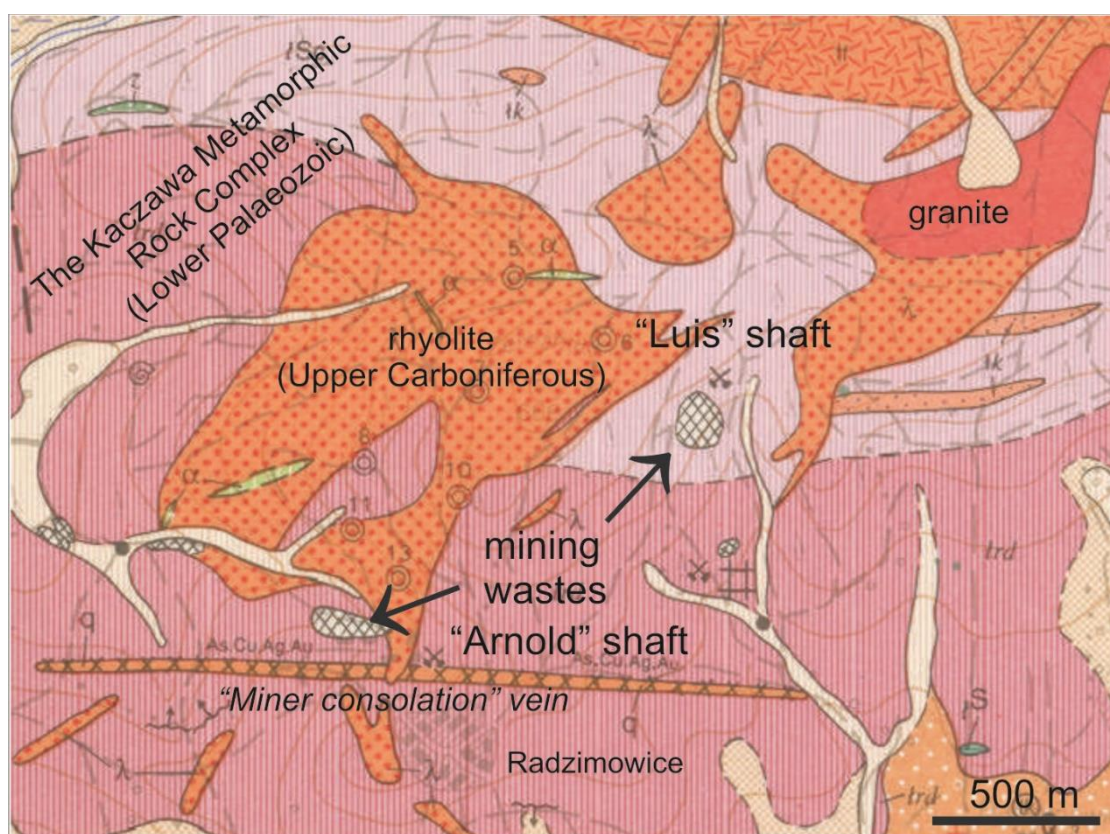


Figure 1: Fragment of the geological map (after Cwojdzinski and Kozdroj, 1994) of the abandoned Au-Cu-As Radzimowice deposit with location of mining wastes being subject of WP7 works.



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS



Figure 2: Post-mining heaps covered with trees in the area of the Luis shaft in Radzimowice, which was the subject of studies within WP7.

In the area of Radzimowice, two heaps of post-mining waste (Fig. 35) was subject of geochemical and mineralogical investigation. In the study from 1992, the resources of some elements occurring in the considering wastes were estimated. The heap near the Luis shaft has a volume of approximately 60,000.0 m³, and the second heap located near the Arnold shaft is smaller and has 27,500.0 m³. Table 7, below presents the estimated metal resources for both post-mining heaps.



Table 1: Estimated resources of selected elements in two main post-mining heaps in the area of the Radzimowice historic As-Cu-Au mine (after Seifert and Siemiątkowski, 1992).

As [Mg]	Cu [Mg]	Pb [Mg]	Zn [Mg]	Mn [Mg]	Sb [Mg]	Sn [Mg]	Bi [Mg]	Cd [Mg]	Ag [Mg]	Au [kg]
1309.9	134.0	103.1	25.9	42.1	9.2	2.2	4.5	0.3	1.5	51.0

In the current research during field work was used portable XRF spectrometer for initial X-ray rock examination. In total almost 100 measurements in selected hand specimen ore samples were made on the both mining wastes. Measurements showed elevated concentrations of noble and trace elements. Among them enrichments indicate the following traces: Au (from 10 to 150000 ppm), Ag (10 - 680000 ppm), Bi (25 to 11500 ppm) Co (up to 7500 ppm), Sb (up to 34000 ppm), Te (10-250 ppm). The obtained results confirmed previous published data about trace elements concentration within the abandoned gold-bearing polymetallic sulphide mines in Radzimowice. According to previous investigation the presence of Co is connected with its own minerals (mainly cobaltite, and minor linnaeite) and with its high admixture in Co-arsenopyrite (up to ca. 6.5 atom. %).

5 Results of lab work/analysis

In the Polish Geological Survey the geochemical and mineralogical studies for the purpose of gold and other minerals carrier of trace elements were carried out. There were selected 10 hand specimen samples from two biggest post-mining heaps. The studied samples consist of mineralized rocks (porphyries, variable composition metamorphic schists – e.g. quartz-sericite-graphite, quartz-albite) and of sulphide-bearing quartz-carbonate veins. Among sulphide minerals dominate arsenopyrite and pyrite which are cataclased and overprinted mainly by chalcopyrite associated with subordinate galena and sphalerite. Five samples were selected for detailed geochemical and mineralogical investigation. The geochemical results of ICP-MS, WD-XRF and GF AAS measurements are presented in table 8.

The content of trace elements were determined in pressed powder samples (As, Ba, Bi, Br, Cd, Ce, Co, Cr, Cu, Ga, Hf, La, Mo, Nb, Ni, Pb, Rb, Sn, Sr, Th, U, V, Y, Zn, and Zr). Analyses were performed by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF) method using a Philips PW-2400 spectrometer. The content of trace elements (Ag, In, Re, Sb, Se, Te, Tl, and W)



were determined by means of the inductively coupled plasma mass spectrometry (ICP-MS). Au, Pd, and Pt were measured using a Perkin Elmer model 4100 ZL spectrometer by graphite furnace atomic absorption spectrometry (GF AAS) method).

The conducted geochemical studies of 5 mineralized rock samples collected from the historical mine waste in Radzimowice confirmed increased concentrations of such strategic elements as cobalt, bismuth and antimony in the gold-bearing sulphide ores. The maximum concentrations determined in a single sample were for: cobalt - 3559 ppm, bismuth - 818 ppm, antimony 228 ppm, and tungsten – 1901 ppm. The appearance of tellurium (up to 122.4 ppm) and indium (up to 42 ppm) are also noticeable (Table 5). In the tested samples, the content of gold ranged from 80 to 7010 ppb, while the content of copper ranging from 178 ppm to 10.1% and of arsenic from 221ppm to 29.1%. The contents of Au, Co, Te, and In are highly related to the appearance of Cu and Zn sulphides ((correlation coefficient, $r > 0.97$ for $n=5$ samples; Fig. 19) and their own mineral phases in samples. In turn, the presence of bismuth correlates with the appearance of selenium ($r = 0.83$ for $n=5$ samples), tungsten ($r = 0.66$), uranium ($r = 0.61$) and arsenic ($r = 0.55$), (Fig. 20). The arithmetic means of the contents of some elements were as follows: As = 10.42% ($n=5$), Cu = 2.87%, Co = 0.11%, Zn = 0.06%, Bi = 0.04%, Sb = 160 ppm, Se = 43 ppm, Te = 30 ppm, In = 11.5 ppm, Ag = 3.2 ppm and Au = 2.51ppm.

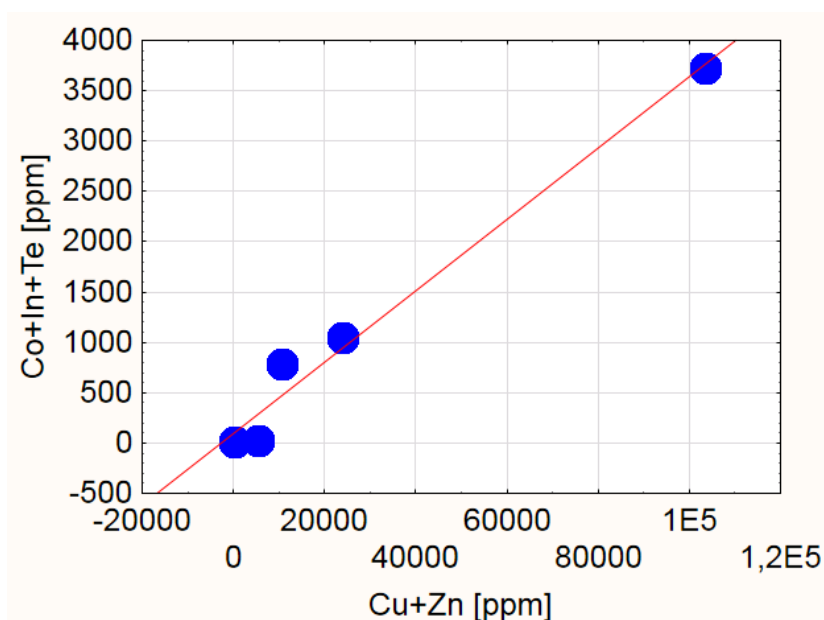


Figure 3: Bivariate plot of trace elements (ppm) in bulk-rock samples of auriferous sulfide ores from the historic Radzimowice As-Cu-Au deposit. Cu + Zn vs. Co + In + Te



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

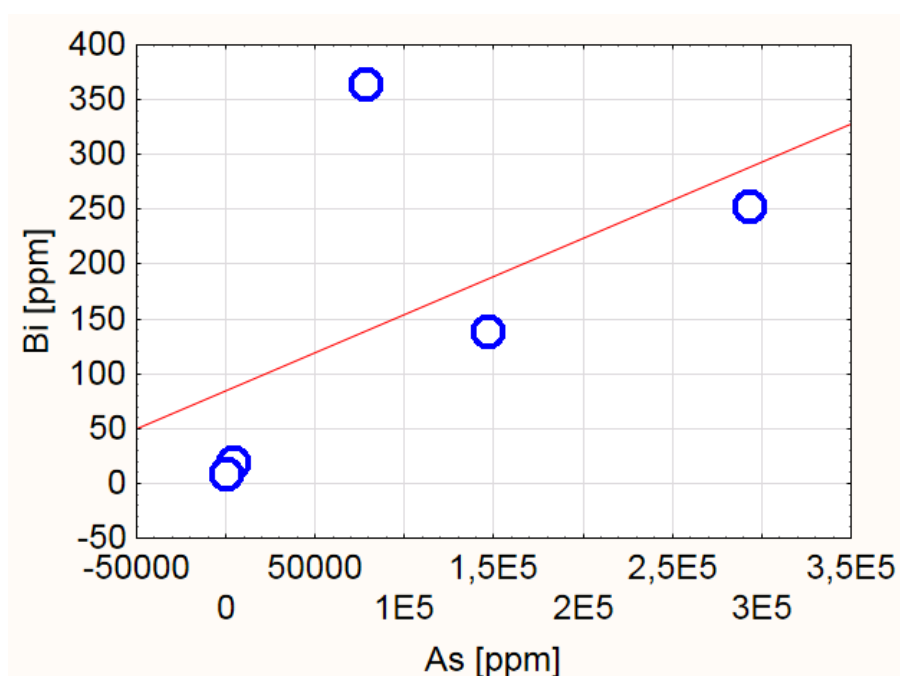


Figure 4: Bivariate plot of trace elements (ppm) in bulk-rock samples of auriferous sulfide ores from the historic Radzimowice As-Cu-Au deposit. Bi vs. As



Table 2: Results of geochemical investigation (ICP-MS, WD-XRF and GFAAS) of 5 samples from mining waste at Radzimowice historic As-Au-Cu mine in Sudetes (NE Bohemian Massif, Poland)

Sample description	Lab no.	As	Ba	Bi	Ce	Co	Cr	Cu	Ga	Hf	La	Mo	Nb	Ni	Pb	Rb	Sr	Th	U
		ppm [WD-XRF]										mg/kg [ICP-MS]							
quartz vein with massive Au-bearing sulfide ore (R1)	15/20/1	146184	22	648	<5	3559	83	10101	<3	<3	20	<2	<2	98	131	<3	22	<3	23
dacite with pyrite-arsenopyrite veinlet (R2)	15/20/2	4017	318	16	327	7	16	178	20	6	31	<2	11	4	734	227	29	15	5
rhyolite with Cu sulfides in quartz-carbonate veinlet (R3)	15/20/3	221	1346	36	66	22	<5	5293	5	<3	40	<2	8	4	25	171	171	9	6
Cu-As-Au ore (R4)	15/20/4	77821	86	666	<5	777	43	10476	<3	<3	9	<2	<2	168	254	23	23	<3	17
Au-As-Cu ore (R5)	15/20/5	293101	347	818	<5	1024	117	23570	<3	<3	69	<2	<2	69	58	46	32	<3	41
Sample description	Lab no.	V	Y	Zn	Zr	Br	Cd	Sn	Se	Ag	In	Sb	Te	W	Re	Tl	Au	Pd	Pt
		ppm [WD-XRF]										μg/kg [GFAAS]							
quartz vein with massive Au-bearing sulfide ore (R1)	15/20/1	<5	<3	2414	<2	518	36	80	60	1	41.7	184	122	13.7	<0.0	0.26	701	8	95
dacite with pyrite-arsenopyrite veinlet (R2)	15/20/2	23	<3	153	95	17	6	62	2	7	0.34	219	0.9	6.1	<0.0	1.93	80	7	105
rhyolite with Cu sulfides in quartz-carbonate veinlet (R3)	15/20/3	15	<3	80	71	6	7	10	7	4	3.67	8.1	<0.5	36.4	<0.0	1.74	105	8	104
Cu-As-Au ore (R4)	15/20/4	8	<3	265	<2	285	19	21	61	1	5.18	162	2.7	766.9	<0.0	0.31	166	11	90
Au-As-Cu ore (R5)	15/20/5	19	<3	352	<2	965	19	17	83	1	6.76	227	22.7	1901	<0.0	0.8	369	13	136



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

Selected polished section were also subject of further microscopic investigation in reflected light (NIKON ECLIPSE LV100 POL) and then on electron microscope (LEO-1430 (ZEISS) with EDS detector). Most interesting ore minerals with inserts of rare minerals were next analyzed on electron microprobe (EMPA) with use of CAMECA SX-100. Several rare minerals and gold were recognized. Gold was found as fine-microscopic grains in quartz or as inserts in fractured sulphides (Fig. 21). However, most of gold occurs as a submicroscopic form (so-called refractory gold) within sulphides - arsenopyrite and pyrite, mainly in 3 grain classes (0.2-0.063 mm).

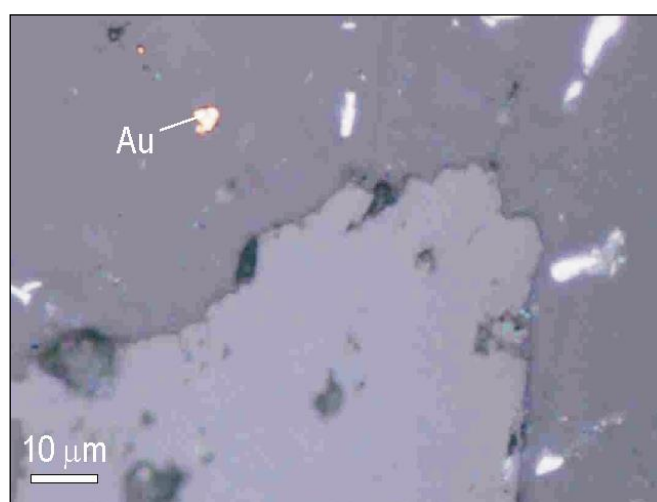


Figure 5: Native gold grain in strongly weathered ore sample collected from the mining waste near Luis shaft in Radzimowice. Reflected light.

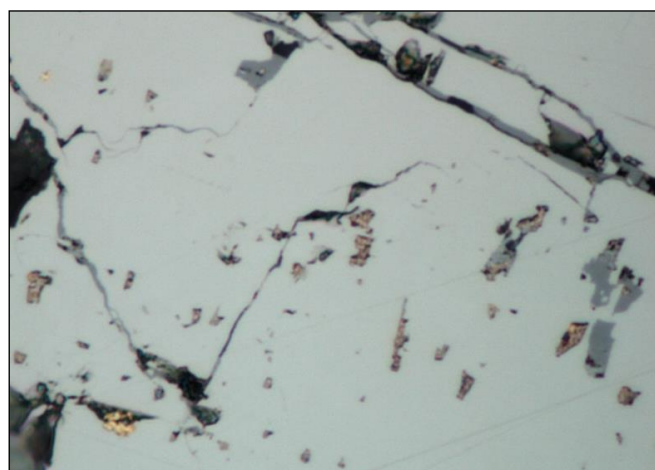


Figure 6: Native bismuth, galena (grey), gold (yellow) and hessite inserts and micro-veinlets hosted by arsenopyrite (white) in ore sample from the mining waste near Luis shaft in Radzimowice. Reflected light. Microphotograph size 80x100 μm.



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

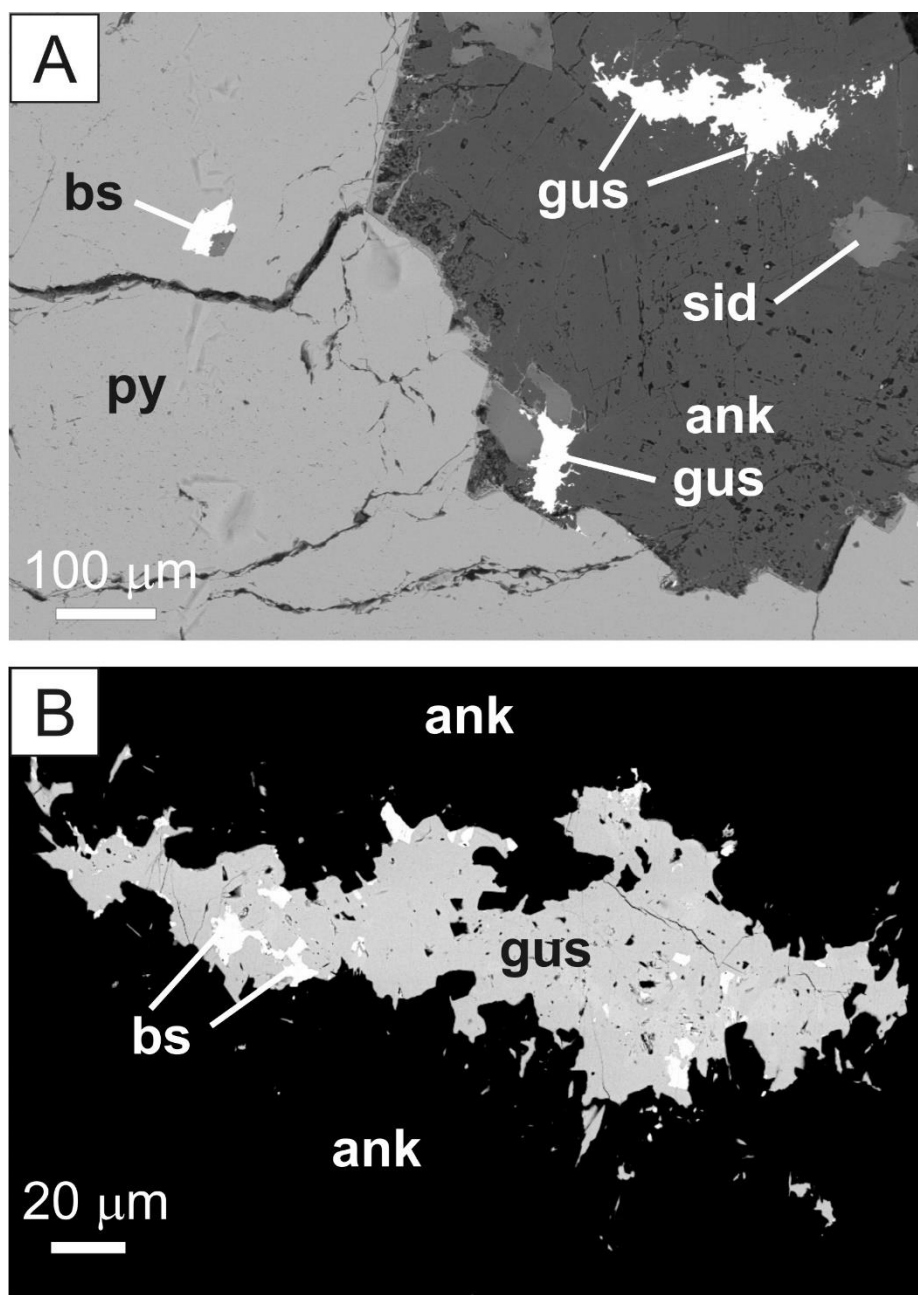


Figure 7: Backscattered Electron image of Bi minerals with carbonates and pyrite. R4 sample from mining waste near the Luis shaft in Radzimowice. Symbol explanation: ank – ankerite, sid – siderite, bs – bismuthinite, gus – minerals from the Gustavite group (Ag-Pb-Bi sulphur salts).



In the richest ore samples a number of minerals such as Co-bearing arsenopyrite, with chalcopyrite, pyrite and base metal sulphides occurred in association with rare mineral assemblages (carriers of critical elements – Bi, Sb, Co and Te) of native bismuth, bismuthinite, gold, electrum, hessite, gustavite, tellurides and sulphotellurides and carbonate minerals (Figs. 22, 23A,B). Gustavite group are represented by minerals of the Ag (Cu) - Pb-Bi (Sb) - S series. Gustavite ($\text{AgPbBi}_3\text{S}_6$) - has been identified within granular chalcopyrite-arsenopyrite-pyrite-magnetite aggregates bonded with ankerite. Gustavite microcrystals are up to about 150 μm in length. EPMA indicated that gustavite composition is very close to its theoretical composition (9–12 wt.% Ag/Cu, 18–28 wt.% Pb, 48–57 wt.% Bi, 8–15 wt.% S). Gustavite has also been found with electrum and variable Ag, Pb, Cu and Bi sulphur salts in the form of lamellar microcrystals (20–30 μm) in pyrite and hydrated Fe oxides replacing pyrite. Along with gustavite it was found, among others treasurite ($\text{Ag}_7\text{Pb}_6\text{Bi}_{15}\text{S}_{32}$).

6 Conclusions

The considering Radzimowice historic As-Au-Cu deposit and its surroundings have a high potential for new Au, Ag and polymetallic metallic resources as well as for CRM. Geochemical (ICP-MS, WD-XRF and GF AAS) and mineralogical research (SEM and EPMA) carried out as part of the current project showed an increased content of critical elements such as Bi, Te, Co and Sb and additionally Au and Ag. Minor resources of these elements are found in two post-mining heaps. Moreover, on the basis of earlier VLF geophysical surveys, there is a high probability of prolongation of previously operated veins, both along dip and strike. The results of VLF results were also confirmed by the shallow drills made in 2010. It was found that there may be new ore veins in the area of the former deposit.

The As-Au-Cu deposit in Radzimowice was genetically classified as a transition between the porphyry and epithermal deposits. Apart from mineralization in the veins, this deposit also contains sulphide impregnation within porphyries (mainly rhyolite and dacite), and in andesite and lamprophyre dykes. The first stage of a high-temperature ore mineralization with Cu-As-Fe sulphides was next overprinted by a low-temperature mineralization with Pb-Zn-Fe-Sb sulphides. Base metal sulphides are also accompanied by rare minerals containing trace elements. In rich sulphide ores, high concentrations of critical elements such as Bi, Te and Co are often present. The Radzimowice deposit constitutes probably the upper part of the larger porphyry system that developed in Upper Carboniferous to lower Permian. Therefore, the entire area is promising for the presence of Cu-Au porphyry deposits and gold and silver polymetallic epithermal deposits at greater depths or under shallow cover in the surrounding areas.



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

References

- Cwojdzinski S., Kozdrój W., 1994. Detailed Geological map of Poland. Wojcieszów sheet. Wyd. Geol. Warszawa.
- Seifert K., Siemiątkowski J. 1992. Quality assessment of selected heaps to determine their suitability and disposal. Region: Radzimowice. National Geological Archive. Warsaw PGI-NRI. (in Polish).