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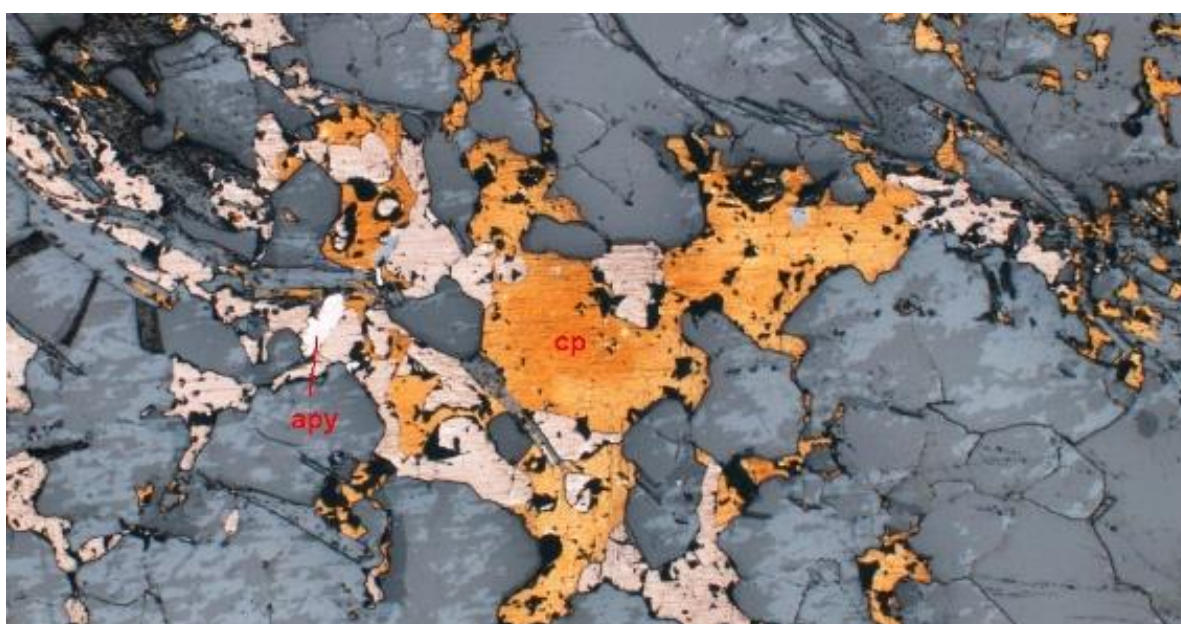
FORECASTING AND ASSESSING EUROPE'S
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WP7 Historic Mine Sites revisited

Case Study

The Krobica and Gierczyn Sn deposits (SW Poland)

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1 Geology and mine history

The Krobica and Gierczyn tin deposits are located in the Lower Palaeozoic Stara Kamienica Schist Belt on the northern part of the Variscan Karkonosze Granite Massif, which are a part of the Karkonosze-Izera-Lausitz Block in the West Sudetes (NE part of the Bohemian Massif).

A tin ore occurs along a 15 km schist belt in two main zones, northern and southern, in which there are also several smaller mineralized zones. Tin mineralization is hosted by quartz-mica schists, which are fine-grained rocks, light grey (often with a greenish shade), with clearly visible foliation and lamination. The cassiterite-sulphide mineralized zones run latitudinally and strike from 37.5 to 57.5 degrees towards N. The thickness and grade of the main ore zones are characterized by high variability in the interval from 0.04 to 8.07 m and from 0.0001 % to 16.78% Sn, respectively.

Ore mineralization in quartz-mica schists has a vein-impregnation character and it is represented mainly by cassiterite, pyrrhotite, chalcopyrite, sphalerite, arsenopyrite, ilmenite and rutile. The cassiterite is macroscopically indistinguishable, whereas microscopically occurs as a small (max. 300 μm , usually up to 100 μm diameter) hypautomorphic or rarely automorphic grains forming grape-like concentration and it mostly occurs in association with quartz, chlorite and garnet (less often with sulphides, muscovite, chloritoid and biotite). Metal sulphides present in the mineralized zones are usually easy to identify macroscopically, however they are not restricted to the zones mineralized with tin – they form an individual mineral association. The sulphides occur within schist laminas or quartz clusters and they are mainly represented by pyrrhotite, chalcopyrite, arsenopyrite, sphalerite, galena, and pyrite and less common bismuthinite. In total, over a dozen ore minerals co-occurring with cassiterite mineralization were identified. This mineral association refers to quartz-chlorite-sulphide tin deposit formation.

Latest geochemical – mineralogical investigations of tin deposits in the Stara Kamienica schist belt in Poland (including Krobica and Gierczyn deposits and perspective areas) indicate elevated concentrations of critical elements (In, Bi, Ga, Co, Nb, Pt, Pd and Re) as well as some associated elements (Cu, Zn and Pb). Moreover, EMPA studies (Cameca SX-100) enabled quantitative and qualitative identification of trace elements admixtures in ore minerals (mostly sulphides).

The Krobica and Gierczyn tin deposits were a subject of intermittent exploitation from the 16th through the 20th centuries. After WWII prospective works indicted resources amount to 5.5 million tons of ore with an average content of about 0.5% Sn, while reserves in this area were estimated at approximately 20 million tons of ore containing approximately 100,000 tons of metallic tin. Nowadays, the resources of these deposits are classified as off-balance sheet.



2 Field work

A several field works between June 2019 and January 2020 concerning Sn deposits near Krobica and Gierczyn areas (Sudetes, SW Poland) has been carried out including field revision of natural rock outcrops, remains of historical mining sites and work on archival drilling cores.

At one day in December 2019, at the field work we cooperated with a delegation from Czech Geological Survey. Common work of Polish and Czech Geological Surveys is justified by a fact that Sn mineralization zone continues across Polish-Czech border and both geological surveys are making geological research and investigation on it. Our cooperation took place in a Polish part of the Stara Kamienica schist belt (which hosts a cassiterite-sulphide mineralization) near Krobica and Gierczyn tin deposits. This one-day field work was filled with discussion and an exchange of information and data about Polish and Czech parts of this Sn mineralization area (Fig. 8). We presented a characteristic part of the archival drilling cores from the Krobica and Gierczyn tin deposits and by using portable XRF analyzer (Olympus Delta) we pointed the intervals with highest Sn mineralization which is invisible to the naked eye. Later on we took part in a trip inside the historical tin mines of St. Johannes and St. Leopold where we could see the internal geological structures of the Stara Kamienica schist belt and get to know the mining history of this area. Finally we got inside the operating quarry of schists in Orłowice, where we were looking for signs of the sulphide mineralization which accompanying tin mineralization.



Figure 1: Geologists from PGI-NRI and Czech Geological Survey during one day meeting examined cores from the historic Krobica tin mine in Sudetes (NE part of Bohemian Massif).



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Figure 2: Rock examinations by used of portable XRF inside the historical tin mine of St. Leopold in Krobica (Sudetes, NE part of Bohemian Massif).

3 Statistics and results of lab work/analysis

Overall, 28 samples from a 12 archival boreholes has been bought from the National Treasury, from which we made about 20 thin section preparations. We carried out microprobe Cameca SX-100 analyzes on 8 thin section preparations and geochemical analyzes (using ICP-MS, WD-XRF and GF AAS methods) of 22 samples. Also a 232 analyzes on archival boreholes using portable XRF analyzer has been made.

Geochemical analyzes of 22 samples revealed average Sn content (arithmetic mean) of 3032.82 ppm. Average content of accompanying elements in studied samples was detected as follows: Ba – 354.4 ppm, Zn – 146.6 ppm, Cu – 321.2 ppm, Zr – 115.2 ppm, Rb – 123.7 ppm, Pt – 93.2 ppm, V – 83.8 ppm, Ni – 76.2 ppm, Co – 35.6 ppm, As – 203.5 ppm, Bi – 55.7 ppm and REE's: Ce – 60.3 ppm, La – 29.6 ppm, Nd – 27.0 ppm, Y – 27.4 ppm. Other elements are in a trace level below 30 ppm.

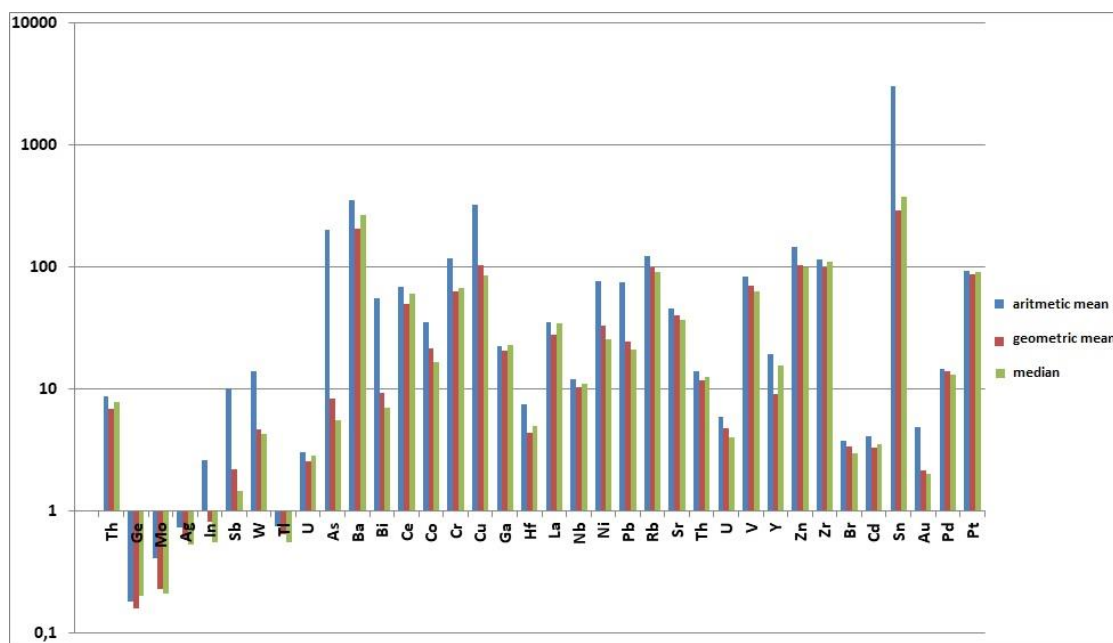


Figure 3: Logarithmic graph of the comparison of statistical parameters of the content of selected elements in samples from the tin mineralization area of the Stara Kamienica range.

Measurements with the portable XRF spectrometer by Olympus were made on 20 archival boreholes located within the documented tin ore deposits of Krobica and Gierczyn and the prospective areas of tin ore deposits - the Czerniawa Zdrój area and tin and cobalt ore – Przecznicza area. A total of 232 measurements were made in 0.5 m intervals. Sn content was recorded in 19 out of 20 boreholes, the highest average amount of which is 5359.36 ppm (+/- 71.93 ppm) while Co contents were recorded only in 3 boreholes with the highest average amount of 157.65 ppm (+/- 34.0 ppm). The average concentrations of accompanying elements are as follows:

- Ti: maximum average (arithmetic mean) is 5189.8 ppm (+/-63.3 ppm, n=12);
- V: max. mean = 226.7 ppm (+/-13.4 ppm, n=6);
- Cr: max. mean = 173.2 ppm (+/-8.8 ppm, n=6);
- Fe: max. mean = 132613.0 ppm (+/-750.3 ppm, n=4);
- Ni: max. mean = 71.6 ppm (+/-7.3 ppm, n=20);
- Cu: max. mean = 423.6 ppm (+/-6.6 ppm, n=7);
- Zn: max. mean = 1406.8 ppm (+/-7.8 ppm, n=7);
- As: max. mean = 807.3 ppm (+/-5.0 ppm, n=20);
- Pb: max. mean = 135.4 ppm (+/-2.0 ppm, n=7).

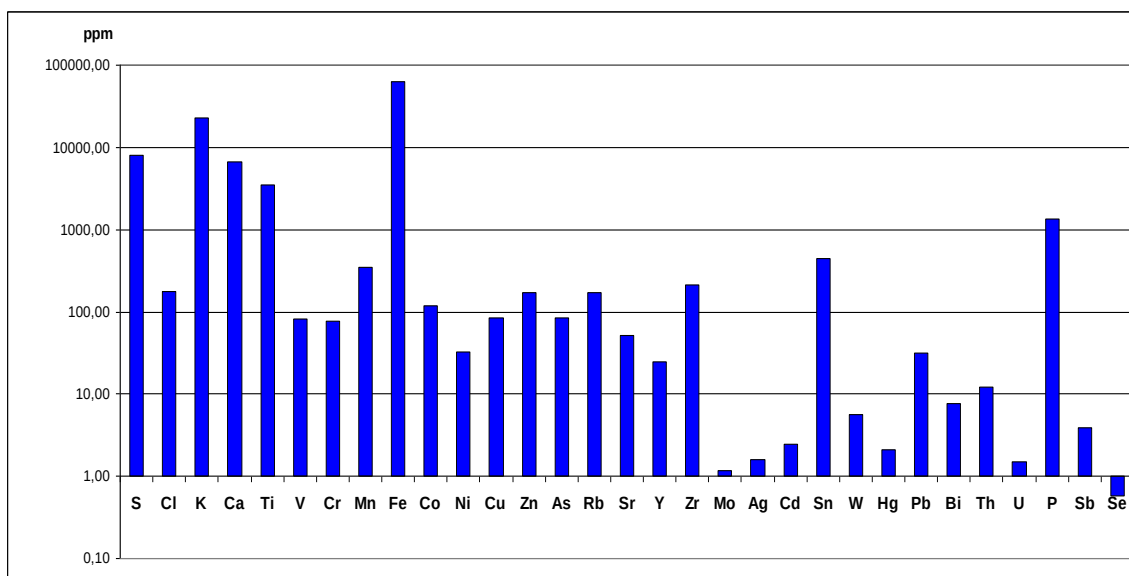


Figure 4: Average content of individual elements from all 20 analyzed boreholes from the Stara Kamienica schist belt analyzed with the Olympus portable XRF spectrometer.

Microprobe analyzes using Cameca SX-100 were carried out on 8 thin section preparations. Analyzes were focused on cassiterite, sulphides and REE-bearing minerals to define their chemical compositions and distribution of associated elements at trace levels (including CRM's). As a partial result we enclose below examples of different mineral analyzes.

There are two generations of cassiterite: 1st one is older and it is called as "spongy" cassiterite because of its porous form, while 2nd one (called "grape like" because its form) is younger and often replaces 1st generation cassiterite. Point 1 and 2 represents 1st generation cassiterite while points 2 and 3 represent 2nd generation. Chemical compositions of cassiterite show that they are almost barren. Only difference is that 1st generation cassiterite has a trace amount of W.



Table 1: Results of EPMA studies of cassiterite from the historical tin mines in Krobica and Gierczyn (values in weight %.)

Mineral	point #	Sb	Al	Nb	Sn	Th	W	Fe	Mn	Cr	V	Ce	Ti	O	Total
cassiterite	1	0.03	0	0	78.327	0.004	0.043	0.05	0.008	0.004	0.004	0.016	0	21.158	99.642
	2	0.027	0	0	78.17	0.001	0.062	0.029	0	0.029	0.03	0	0.009	21.139	99.495
	3	0.019	0.009	0	78.692	0.001	0	0.022	0	0.004	0.019	0.004	0.028	21.265	100.064
	4	0.032	0.008	0.002	78.617	0	0	0.015	0.004	0.004	0	0	0	21.218	99.901

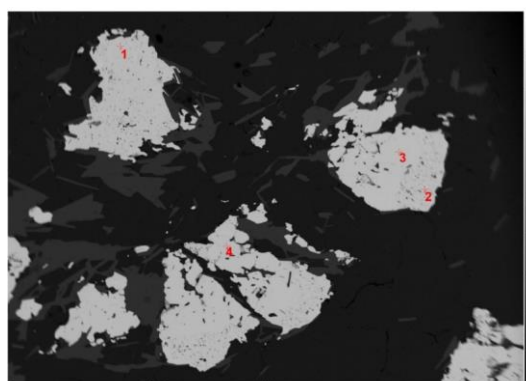


Figure 5: Example of occurrence form of cassiterite in studied samples.

Moreover, sulphides were also subject of detailed EPMA studies. Figure 46 shows an example of sulphide aggregate made of pyrite (py, points 1-6), pyrrhotite (po, point 7) and arsenopyrite (apy, points 8, 9). Results show significant enrichment of Co and less in Zn and Cd in pyrite. There is also some elevated concentration of Co in pyrrhotite and the highest in arsenopyrite (even more than 1.2 wt %).

Another example of sulphide aggregate made of sphalerite (sp, points 1 and 2), pyrrhotite (po, points 3 and 4) and chalcopyrite (cp, points 5 and 6) is shown in figure 47. Measurements shows that there is high content of Cd and less of In in sphalerites. In addition, there is some enrichment of Ni and Co in pyrrhotite. Some trace concentrations of In, Zn and Co is noticeable in chalcopyrite.



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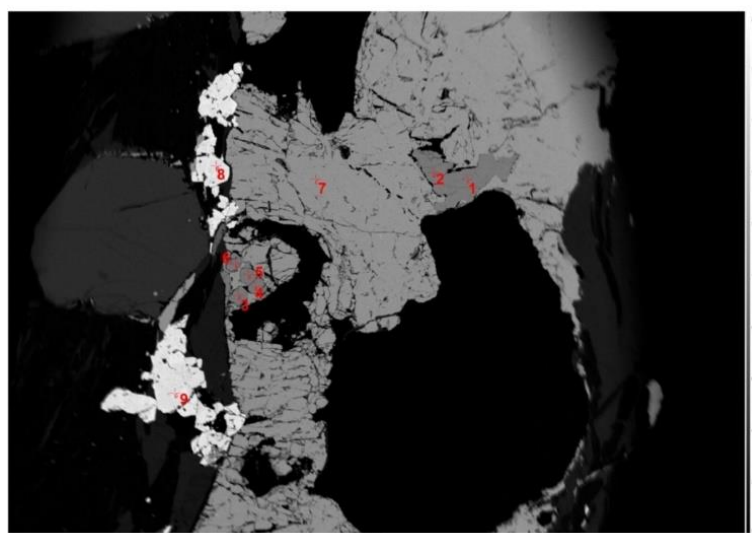


Figure 6: Example of occurrence form of sulphides in studied samples.

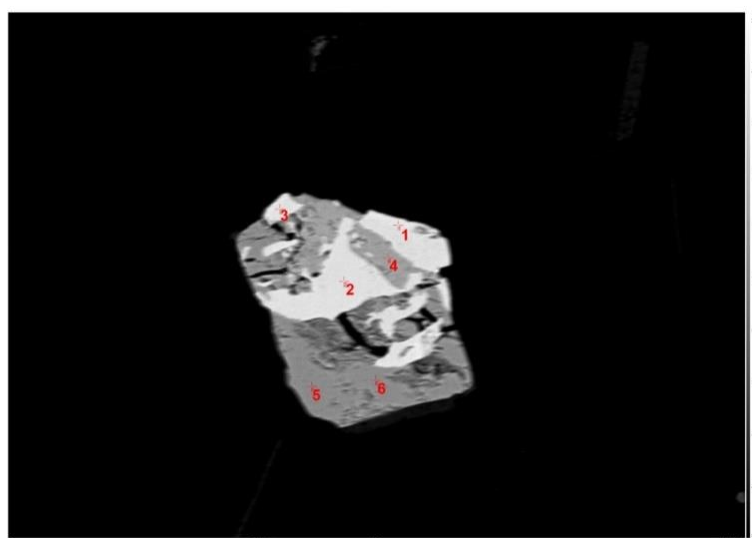


Figure 7: Sulphides aggregate in studied samples

During EMPA a high amount of bismuth minerals in studied samples was revealed. Figure 8 displays a mutual overgrowth of native bismuth (Bi, points 1 and 2) and bismuthinite (bis, points 3 and 4). Analyzes showed a trace amounts of Cd, Ag, Zn, Cu, Ni, Fe and Au in bismuth minerals.

In addition, some less frequent occurring sulphide minerals were recognized and measured: cobaltite (Co max 34.7 wt. %), costibite (Co max 24.5 wt. %), gersdorffite (Ni max 26.63 wt. %,



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Co max 11.22 wt. %), hessite (Te max 41.3 wt. %, Ag max 61.3 wt. %), unnamed indium-bearing mineral previously called “sakuraiite” (In max 19.1 % wag., Cd max 0.65 % wag.) and ullmannite (Sb max 53.0 wt. %, Bi max 23.38 wt. %).

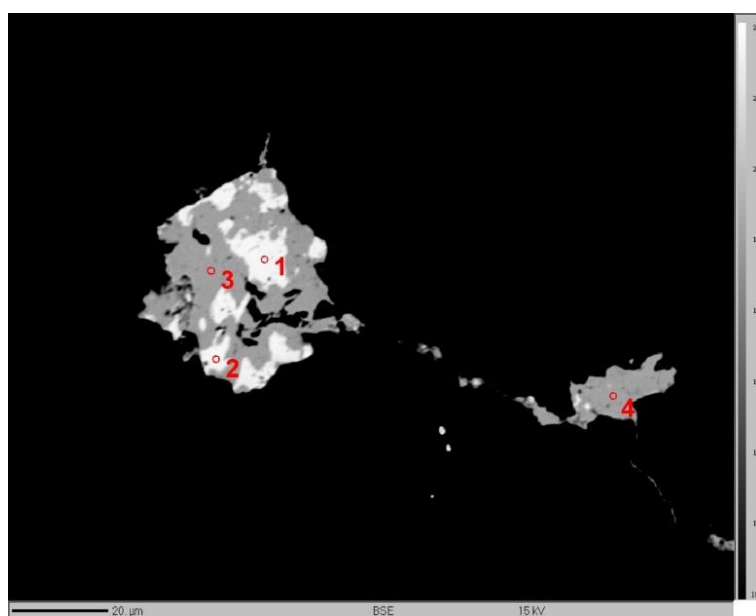


Figure 8: Native bismuth and bismuthinite overgrowth.

Table 2: Results of EPMA studies of pyrite and arsenopyrite from the historical tin mines in Krobica and Gierczyn (values in weight %)

mineral	point #	Si	S	Te	Ca	In	Cd	Ag	Sb	Cl	Bi	Zn	Se	As	Cu	Ni	Co	Fe	Mg	Au	Mo	Ba	Pd	Pt	Total
pyrite	1	0.006	52.224	0.029	0.002	0	0.029	0.033	0.026	0.01	0	0.086	0	0	0.079	0.06	0.093	46.696	0.005	0.055	0.015	0	0	0	99.448
	2	0.028	52.738	0.003	0.007	0	0.002	0	0.022	0.019	0	0.021	0	0.001	0	0.04	0.109	46.81	0.003	0	0	0.037	0.005	0	99.844
	3	0.02	53.1	0	0	0	0.017	0.024	0	0.016	0	0.032	0	0	0.074	0.03	0.107	46.746	0	0	0	0.07	0	0.007	100.241
	4	0.008	52.614	0.003	0.003	0.003	0.042	0	0.009	0.019	0	0.03	0	0	0.019	0.04	0.107	46.571	0.005	0.066	0.01	0.094	0.029	0.001	99.672
	5	0.015	52.915	0.016	0.002	0.01	0.02	0	0.021	0.013	0	0.073	0	0	0.016	0.081	0.135	46.738	0.007	0.082	0	0	0.002	0	100.147
	6	0.004	52.812	0	0	0	0.013	0.027	0	0	0	0	0	0	0.043	0.045	0.072	46.855	0.011	0.005	0	0.033	0	0	99.92
	7	0.032	39.216	0.011	0.007	0	0.048	0	0.029	0.001	0	0.052	0	0	0.074	0.041	0.129	59.798	0.017	0	0	0	0.009	0.018	99.491
arsenopyrite	8	0.035	20.983	0	0	0.005	0.022	0.013	0.118	0.013	0	0.004	0.021	42.675	0.033	0.042	0.536	34.504	0.028	0.051	0.116	0	0.024	0	99.244
	9	0.033	18.784	0	0	0	0	0.027	0.077	0.01	0.072	0.045	0.054	45.493	0.044	0.058	1.254	33.449	0.046	0.062	0	0.081	0	0	99.589



Table 3: Results of EPMA studies of sphalerite, pyrrhotite and chalcopyrite from the historical tin mines in Krobica and Gierczyn (values in weight %)

mineral	point #	Si	Al	S	Te	Ca	In	Cd	Ag	Sb	Cl	Pb	Zn	Cu	Ni	Co	Fe	Mg	Au	Mo	Ba	Pd	Pt	Total
sphalerite	1	0.037	0.011	32.733	0	0.005	0.057	0.631	0.005	0.006	0.01	0.018	58.61	0.06	0	0.06	7.663	0.014	0	0	0	0.019	0.014	99.954
	2	0.021	0.007	32.806	0	0.004	0.076	0.688	0.006	0.025	0.007	0	59.029	0.124	0.046	0.041	7.381	0.009	0.113	0	0	0.029	0.043	100.455
pyrrhotite	3	0.017	0.004	39.044	0	0.002	0	0.028	0	0	0	0.004	0	0.034	0.091	0.179	60.349	0	0.032	0.002	0	0.002	0.03	99.822
	4	0.013	0	39.225	0.017	0	0	0	0.013	0	0	0	0.041	0.005	0.112	0.173	60.492	0.003	0.021	0	0.034	0	0	100.148
chalcopyrite	5	0.005	0	34.553	0	0.014	0.03	0.006	0	0.013	0.02	0	0.085	34.574	0.012	0.047	30.486	0.01	0	0.024	0.089	0	0	99.969
	6	0.051	0.022	34.666	0	0	0.029	0.003	0.013	0.003	0.01	0	0.033	34.181	0	0.062	29.525	0	0	0	0.055	0.017	0.001	98.671

Table 4: Results of EPMA studies of bismuth minerals from the historical tin mines in Krobica and Gierczyn (values in weight %)

Mineral	point #	Si	Al	S	Ca	Cd	Ag	Sb	Sn	Bi	Zn	Se	Cu	Ni	Co	Fe	Mg	Au	Mo	Total
Native Bismuth	1	0.053	0	0.011	0.015	0.088	0.062	0.081	0	99.301	0.022	0	0.044	0.029	0	0.156	0.003	0.012	0.028	99.904
	2	0.047	0.01	0.033	0.03	0.063	0.101	0	0.01	98.582	0.089	0	0.1	0.017	0.002	0.327	0.009	0	0.053	99.473
bismuthinite	3	0.045	0	19.312	0.004	0.063	0.037	0.03	0	79.856	0.097	0.001	0.191	0.054	0	0.105	0.01	0.067	0	99.873

3.1 REE-bearing minerals

A number of REE-bearing minerals were recognized: allanite, monazite, uraninite, xenotime, plumbogummite, zircon and Fluorine-carbon phases which have no specific identification because lack of carbon analyzes. The sizes of the identified REE minerals are usually small - most of them do not exceed 80 µm in diameter, and occasionally larger grains have been observed (e.g. allanite with a diameter of about 200 µm). Also common are aggregates of fine REE minerals (mainly REE Fluorine-carbon phases) with diameters up to 100 µm. In minerals - REE carriers, mainly light rare earth elements (LREE) were identified, i.e. lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd) and dysprosium (Dy) and yttrium (Y) classified as heavy rare earths (HREE).



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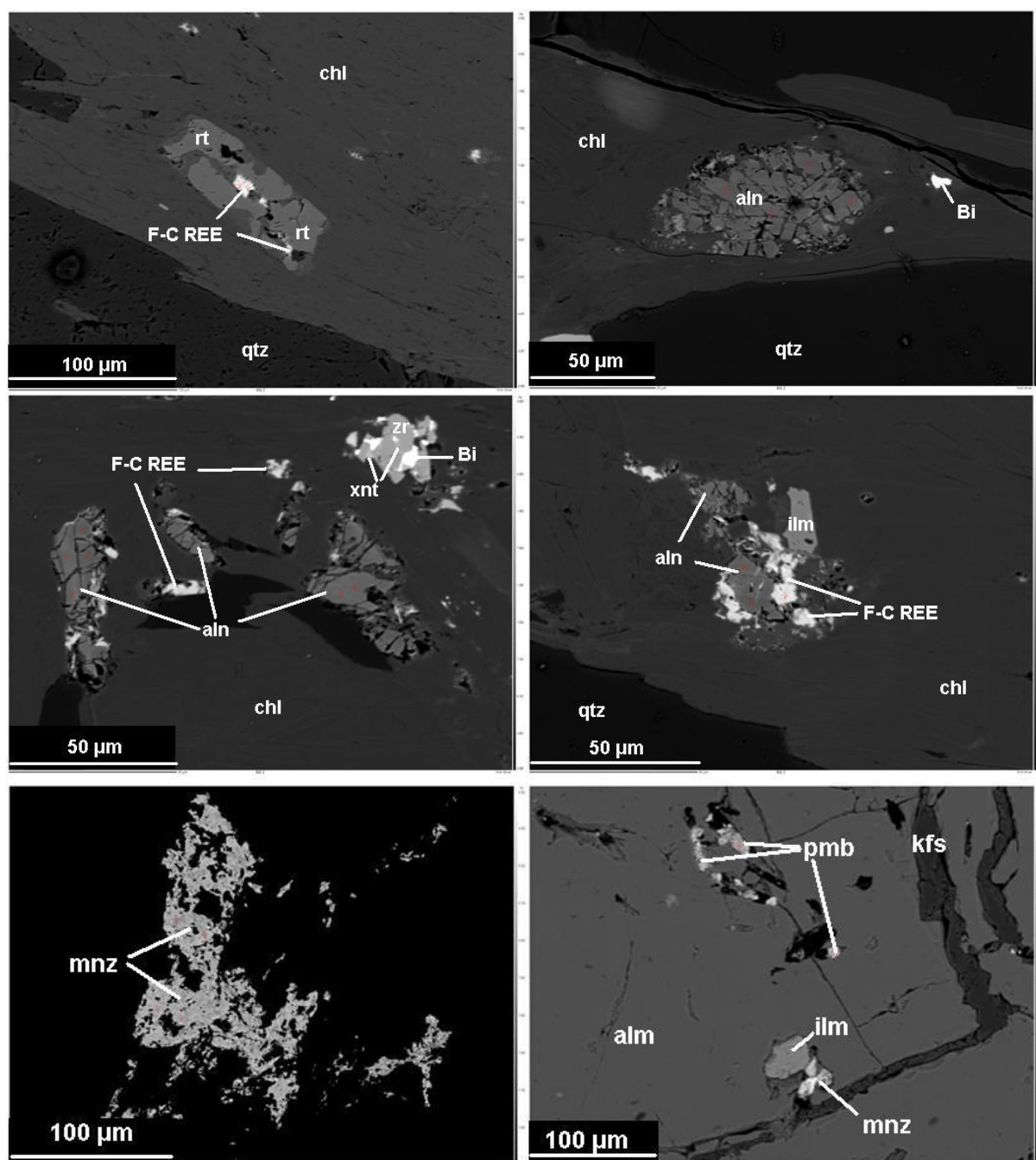


Figure 9: Different REE-bearing minerals in the studied samples. Abbreviations: rt – rutile, chl – chlorite, qtz – quartz, F-C REE - Fluorine-carbon phases, Bi – native bismuth, aln – allanite, xnt – xenotime, zr – zircon, ilm – ilmenite, mnz – monazite, kfs - K-feldspar, pmb – plumbogummite.



4 Conclusions

In the examined samples with cassiterite - sulphide mineralization from the area of the historical mining and documented tin ore deposits in Krobica and Gierczyn in the Western Sudetes, the presence of over 50 main and trace elements was identified.

Geochemical investigations with application of ICP-QMS, ICP-OES, WD-XRF and GFAAS methods as well as EMPA studies revealed elevated concentrations of critical elements: In (arithmetic mean = 0.92 ppm), Bi (in the range from <0.05 to 1740 ppm), Ga (arithmetic mean = 20.2 ppm), Co (arithmetic mean = 37.8 ppm), Nb (arithmetic mean = 12.8 ppm), Pt (arithmetic mean = 56 ppb) and Re (arithmetic mean = 0.48 ppm) as well as associated elements (Cu, Zn and Pb). Some of these critical elements show a strong positive correlation with tin or base metals distribution (e.g. In, Bi or Ga).

Based on detailed microscopic and microprobe (EMPA) studies carriers of trace elements in sulphides associated with cassiterite ores were identified:

- in chalcopyrite: Bi (max 2.2 wt.%), Ni (max. 0.59 wt.%), Co (max. 0.4 wt.%), Au (max. 0.15 wt.%), Zn (max. 0.11 wt.%); in sphalerite: Cd (max. 0.67 wt.%), Ag (max. 0.289 wt.%) and Co (max. 0.137 wt.%); in pyrrhotite: Ni (max 0.65 wt.%), Co (max 0.29 wt.%), Au (max 0.14 wt.%); in pyrite: Ni (max. 0.661 wt.%), Co (max. 0.35 wt.%);
- in arsenopyrite: Bi (max. 9.13 wt.%), Ni (max. 0.809 wt.%) and Co (max. 0.210 wt.%)
- in bismuthinite: Te (max. 0.39 wt.%), Ni (max. 0.83 wt.%), Co (max. 0.63 wt.%) and also Au (max. 8.23 wt.%).

A number of less frequent occurring metal sulphides were identified: cobaltite (Co max 34.7 wt. %), costibite (Co max 24.5 wt. %), gersdorffite (Ni max 26.63 wt. %, Co max 11.22 wt. %), hessite (Te max 41.3 wt. %, Ag max 61.3 wt. %), unnamed indium-bearing mineral previously called "sakuraiite" (In max 19.1 % wag., Cd max 0.65 % wag.) and ullmannite (Sb max 53.0 wt. %, Bi max 23.38 wt. %).