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Ph.D. THESIS SUMMARY

Mineralogical-geochemical study and genesis of a rare and accompanying elements occurrence within the tin-bearing deposit mineralization of the Stara Kamienica schist belt in the Sudetes

The Stara Kamienica schist belt in the Western Sudetes is a part of the Karkonosze-Izera metamorphic massif (northern cover of the Karkonosze granite) and mainly consists of quartz-chlorite-mica schists within which a tin (cassiterite) with associated sulphide mineralization has been recognized. In the second half of the 20th century, two deposits (Krobica and Gierczyn) and several prospective areas (Krobica Zachód – Czerniawa and Przecznica) have been designated. A tin-bearing area of the Stara Kamienica belt was the subject of numerous geochemical-mineralogical studies. However, there are no comprehensive studies on the qualitative and quantitative determination of accompanying and rare elements occurring accessorially in the ore, often in trace amounts. By the term 'accompanying elements' the author understands accessory elements present in tin ores, which are represented mainly by metal suplhides such as zinc, lead or copper, occurring locally in elevated concentrations. On the other hand, the term 'rare elements' refers to the elements that coexist in ores, which usually don't form their own mineral phases but occurs as an admixtures in chemical compositions of the other ore minerals.

The doctoral dissertation aims to determine the qualitative and quantitative elements accompanying tin mineralization in the Stara Kamienica belt and rare elements contained in ore minerals in trace amounts. In addition, mineralogical observations obtained by the author and micro-area investigations provide evidence for the complex, hydrothermal genesis of cassiterite-sulphide mineralization within Stara Kamienica schists. A 22 selected intervals of archival drilling cores from the Krobica, Gierczyn, Przecznica and Krobica Zachód-Czerniawa deposit areas, samples from the historic mines of St. Johaness and St. Leopold in Krobica and samples from former mining waste were tested to achieve the assumed goal.

The following research scheme has been adopted:

- at first, archival geological studies and documentation of the Stara Kamienica schist belt tin mineralization were examined to designate interesting boreholes and certain intervals of drilling cores with cassiterite-sulphide mineralization;

- sampling and analysis using portable XRF spectrometer Olympus Delta Premium of selected drilling cores intervals, historic mines of St. Johaness and St. Leopold and nearby mining waste piles were done;

- 64 samples containing cassiterite and sulphide mineralization were selected for geochemical studies using the WD-XRF, ICP-MS and GF-AAS methods;

- 61 microscope slides (polished thin section) were prepared, which were examined using a polarized microscope and some of them also using LEO-1430 scanning electron microscope (SEM) and CAMECA SX-100 electron microprobe (EMP);

- a total of 1,672 point analyses of the chemical composition of both rock-forming and ore minerals were performed using a WDS spectrometer associated with the electron microprobe on a selected thin section slides;

- dating was carried out using the CHIME method on 36 hydrothermal uraninite, monazite and xenotime grains located in thin section preparations from the Stara Kamienica schist belt;

- obtained results were analysed statistically using descriptive statistics, linear correlation and factor analysis along with a graphic results presentation (charts, histograms);

- geological interpretation of the obtained results was made.

Among the main elements analysed (in the oxide form) by the WD-XRF method, the highest contents were obtained for SiO_2 (the arithmetic mean was 61,80 wt. %, n=57) as well Al_2O_3 and Fe_2O_3 with arithmetic mean respectively 13,34 and 14,45 wt. %. Among the other analysed elements, the highest arithmetic mean was found for Sn (1571,9 ppm, n=64), which confirms the presence of tin mineralization in studied samples from the Stara Kamienica schist belt. The obtained results of geochemical analyses of the content of individual elements and the comparison to their average content in the earth's crust led to the indication of As (mean 381,3 ppm), Cu (mean 338,8 ppm), Pb (mean 180,5 ppm) and Zn (mean 382,5, n=64) as elements accompanying with tin. An additional criterion assumed by the author was their arithmetic mean higher than 100 ppm in the studied samples. On the other hand, the author considered rare elements in the samples from the Stara Kamienica belt as those which in geochemical studies showed average contents several times higher than the average content in the earth's crust, but not exceeding 100 ppm, that are Bi, Co, Br, Cd, Ag, In, Sb and Pt. The performed model of factor analysis grouped the examined elements showing mutual geochemical connections. On this basis, it can be assumed that the elements within a given group coexist with each other, and their minerals-carriers create associations and/or paragenesis.

The results of the observation of rock-forming and ore minerals largely coincide with the work of previous researchers of the Stara Kamienica schist belt and its mineralization. Microscopic, and mainly micro-area studies, allowed to identify several ore minerals and their generations, including those that had not been previously described in Stara Kamienica shists. A number of minerals responsible for the occurrence of the rare and accompanying elements were identified: pyrrhotite (carrier of trace admixtures of Co), chalcopyrite (carrier of Cu and trace admixtures of Zn, Co, In and As), arsenopyrite (carrier of As and trace admixtures of Co and Sb), pyrite (carrier of trace admixtures of Co), sphalerite (carrier of Zn and trace admixtures of Cd, Co, In and Ag), galena (carrier of Pb and trace admixtures of Bi and Ag), native bismuth and bismuthinite (carriers of Bi and trace admixtures of Sb, Pb, Co and Ag), Au-Ag electrum (carrier of Ag and trace admixtures of Co), cobaltite (carrier of Co, As and trace admixtures of Sb), costibite (carrier of Co, Sb and trace admixtures of Zn, As and Cd), cosalite (carrier of Pb and trace admixtures of Sb, Ag, Cd and Co), gersdorffite (carrier of As and trace admixtures of Co and Sb), safflorite (carrier of Co and As and trace admixtures of Sb), ullmannite (carrier of Sb and trace admixtures of Bi, Zn, Ag, Co and Cd), unnamed Zn-In-Cu-Fe sulphide (carrier of Zn, Cu, In and trace admixtures of Cd and Co), hedleyite (carrier of Bi and trace admixtures of Sb, Cd and Ag), hessite (carrier of Ag and trace admixtures of Sb, Cu and Bi), ikunolite (carrier of Bi and trace admixtures of Pb, Ag and Co), mimetite (carrier of Pb, As and trace admixtures of Cu, Zn and Co). Several REE carrier minerals were also identified, such as allanite, monazite, REE fluorocarbonates, xenotime, plumbogummite and uraninite.

The results of the author's research correspond well with the analysis of other researchers and additionally provide several new data that may constitute arguments in the discussion on the genesis of cassiterite and sulphide mineralization of the Stara Kamienica belt. Among the minerals dated by the CHIME method, ages of uraninites and xenotimes have shown the most accurate results. Most analyses indicated ages in the range of about 345-360 million years and slightly less in the ranges of about 360-375 and 299-310 million years. The obtained age ranges indicate the intrusion of the Karkonosze granitoid as a genetic source of fluids responsible for the precipitation of cassiterite and sulphide mineralization.

The author of the dissertation, based on his observations and mineralogical research, supports the theory of the multi-stage development of intrusive-metamorphic processes related to pre- and Variscan plutonic activity of the Karkonosze granitoid and the accompanying multiple hydrothermal events. In addition, based on the observation of mineral paragenesis, the results obtained by previous researchers and comparisons with other world tin deposits, the author believes that the temperatures of the earlier hydrothermal solutions responsible for the crystallization of first-generation cassiterite and sulphides fluctuated within 500-300°C (+/- 50°C), while the later solutions responsible for the precipitation of the younger cassiterite and ore minerals of the next generations were characterized by a temperature in the range of 300-100°C.