

Ore mineralization at the Rabenstein occurrence near Banská Hodruša, Slovakia

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Abstract

The Štiavnica-Hodruša ore field represented one of the most productive medieval sources of silver and gold. Despite, the mineralogy of the ores that sustained the mining in this region for many centuries is not fully known, mainly because the rich ores were exhausted a long time ago. This report describes the minerals present at the occurrence Rabenstein, a system of old shallow mines, where such rich ores were probably exploited. The mineralogical investigation was largely performed on heavy mineral concentrates because the available ore samples are relatively poor. The most common mineral is quartz, being bound to the zone of silicified and altered rocks. The ores comprise disseminated pyrite with galena, sphalerite, and chalcopyrite. The identified Ag-Au minerals include acanthite, gold-silver alloys (electrum), freibergite, pyrrargyrite, polybasite/pearceite, and uytenbogaardtite. Acanthite and uytenbogaardtite replace galena and electrum, respectively, and seem to be a product of late hydrothermal or supergene stage of the ore formation. Perhaps these minerals, notably acanthite, were responsible for the significant enrichment of the ores that attracted the attention of old miners.

Key words: Hodruša, ore mineralization, silver-gold minerals

Introduction

The Štiavnica stratovolcano is a Badenian-Pannonian complex generated by an extensive, mostly andesitic volcanic activity (Konečný and Lexa, 2002). In addition to the most common andesites or the corresponding pyroclastic rocks, there are also rhyolite and basalt bodies and flows known in this area. In the central zone of the Štiavnica stratovolcano, the corresponding magmatic rocks (granodiorite, diorite) are exposed at the present-day surface.

Beside being known as an example of the Tertiary volcanic activity in the Western Carpathians, the region of Banská Štiavnica and Banská Hodruša is famous as one of the most productive medieval sources of silver and gold (Lexa et al., 1999; Bakos and Chovan – eds., 2004). The epithermal precious metals/base-metal deposits and occurrences were just one of the types of the ore mineralizations (see Lexa et al., 1999 for a list and description of the other ones). The source of heat and fluids for this mineralization was a deeply seated siliceous magma chamber. The temporal evolution of the fluids was characterized by a progressive mixing between the magmatic and meteoritic fluids, the latter ones being dominant in the final episodes of the ore formation. The mineralization of the veins belongs to the low-sulfidation type and its age is 12.0–10.5 Ma (Lexa

et al., 1999). Numerous veins were exploited with a general NNW–SSE strike and a dip of 20–50° to E. In the Banská Štiavnica region, the mineralogy and parageneses were studied in detail by Koděra (1959). He described the vertical zonality of the veins which are rich in Ag near the surface, enriched in Pb and Zn in the moderately deeper portions and Cu-rich in the deep parts. The veins in Banská Hodruša were not examined in a comparable detail. They were famous, however, for the spectacular specimens of Ag sulfides and sulfosalts, such as stephanite, polybasite, pyrrargyrite, proustite, and acanthite (Koděra – ed., 1986). The formation conditions of this and other spatially related mineralizations were estimated by Kovalenker et al. (2006) and Koděra et al. (2005).

The Rabenstein occurrence belongs to so-called upper-Hodruša veins, together with the veins Unverzakt-Alžbeta, Finsterort, Brenner, Mikuláš, Všechsvätých, Jozef, Umbruch, and Bärenleuten (Bakos and Chovan – eds., 2004). The Rabenstein veins are located in altered granodiorite, following the tectonic structures parallel to those intruded by a quartz-diorite porphyry (Onačila and Rojkovičová, 1992). In these veins are assumed the oldest mining works in the region, dated to the times before the first written documents (R. Kaňa, personal communication). If true, these ores were probably rich and located in shallow depths, and therefore accessible to old miners and

their technologies. The occurrence is located ~2.3 km NE from the historical village of Banská Hodruša (Tri križe), approximately 720 m a.s.l.

In this work, the mineral composition of the ores at Rabenstein was studied. A combination of bulk analytical techniques, optical microscopy, and electron microprobe analyses allowed to determine the identity of the primary ore minerals. Whether these minerals were the object of interest of the medieval miners is not clear.

Materials and methods

Hand specimens and larger samples (see below) were taken at the Rabenstein occurrence. The mines are situated in a quartz-rich zone with a general NNW–SSE strike. Owing to the slower weathering of the very hard quartz-rich material, this zone forms geomorphologically a conspicuous ridge which extends several meters over the surrounding terrain. The samples were collected mostly outside from the quartz-rich walls. The old mines are still largely accessible and a few samples were taken from underground, mostly from the debris at the floor of the mine works. Visual inspection of the material outside and inside the mines did not show any significant differences.

The samples were prepared in a form of standard polished sections and inspected in reflected polarized

light. It has become clear very soon that the ore minerals are scarce and the standard ore microscopy will yield only limited results. Therefore, in a second sampling campaign, we amassed several larger samples from selected spots in the quartz-rich walls. The geographic coordinates and the localization of these sampling points are listed and shown in Appendix, Table A1 and Fig. A1, respectively. Altogether ~100 kg of material in 5 samples was brought to the laboratory. A small portion from each sample was laid aside and most of the material was crushed to a size of 0.2–0.5 mm. This material was then separated on a shaking table into a light and heavy fraction. The heavy fraction was further purified in heavy liquids (sodium polytungstate). The resulting fraction enriched in ore minerals was then used to produce grain concentrate polished sections. These sections allowed us to determine the mineralogical composition of the samples although we recognize that the paragenetic information was lost.

A small representative portion of each large sample was ground further and digested in an industrial microwave oven MLS Microprep in an aqua regia ($\text{HCl} : \text{HNO}_3 = 1 : 3$) solution. The resulting liquid was analysed for selected elements with atomic absorption spectrometers Analytik Jena Vario 6 (flame AAS) or Perkin-Elmer 4110 ZL Zeeman (graphite furnace AAS) at the University of Freiburg (Germany) for Cu, Mn, As, Sb, Au and Ag.

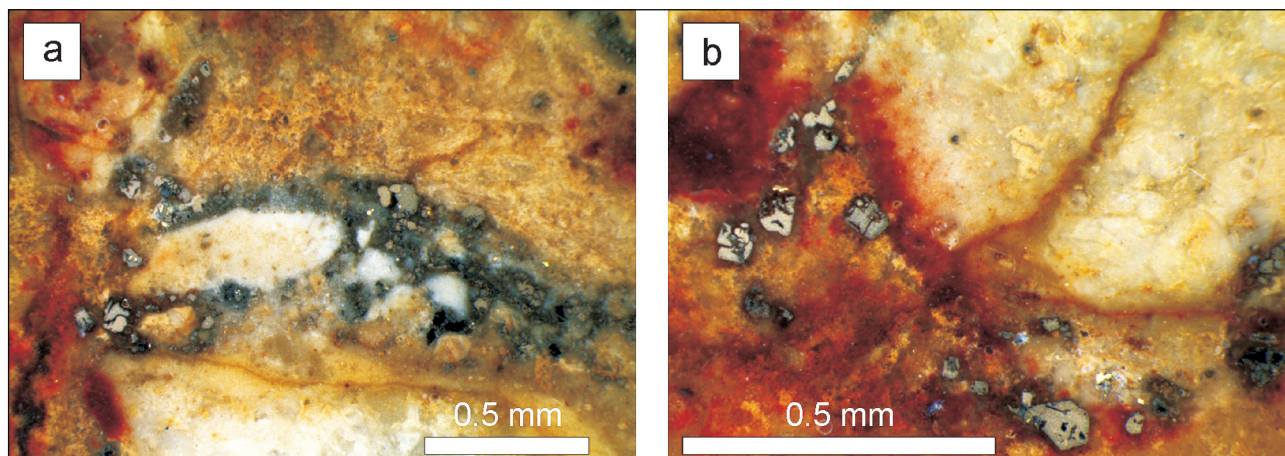


Fig. 1. Photographs of ores with visible sulfides, mostly pyrite with inclusions of galena or sphalerite. The sulfides follow the outlines of fragments of quartz and silicified rocks. The rock fragments (for example, upper portion of the Fig. a), in addition to the pervasive silicification, are also strongly altered.

Tab. 1
AAS analyses of samples from Rabenstein

	Cu	Mn	As	Sb	Au	Ag	Description
Rab-1	538	37 270	683	184	0.17	116.6	secondary Mn minerals
Rab-5	30	1 299	n. d.	n. d.	0.30	25.3	massive quartz
10SK	227	822	223	n. d.	0.29	135.6	massive quartz
11SK	129	7 526	48	n. d.	0.29	185.9	massive quartz
12SK	60	319	293	284	0.70	410.3	massive and vuggy quartz
13SK	30	1 342	125	n. d.	0.35	61.2	vuggy quartz

All values in ppm. n. d. = not detected

Chemical composition of minerals was determined by spot analyses with a Cameca SX 100 electron microprobe at the University of Freiburg (Germany), using these conditions and standards: 20 kV, 40 nA, beam size 5 μm ; arsenopyrite (As, $L\alpha$, 40 s), AuTe_2 (Au, $M\alpha$, 20 s), tetrahedrite (Sb, $L\alpha$, 40 s), galena (Pb, $M\alpha$, 20 s), pyrite (Fe, $K\alpha$, 20 s), greenockite (Cd, $L\alpha$, 40 s), Ag (Ag, $L\alpha$, 20 s), pyrite (S, $K\alpha$, 20 s), sphalerite (Zn, $K\alpha$, 20 s) and tetrahedrite (Cu, $K\alpha$, 20 s). The same instrument was used for semiquantitative analyses with the energy-dispersive system and for the acquisition of the back-scattered electron images.

Results

All samples from the Rabenstein occurrence are dominated by quartz with small and variable amount of other minerals. Clay-rich fragments, representing probably original rocks, later silicified, are common. These fragments are surrounded by quartz, sometimes by thin reddish layers or patches with dispersed hematite (Fig. 1). Some of

the fragments in this matrix consist of white quartz. The ore minerals are found in veinlets and patches of white quartz; locally the sulfides are more abundant and the quartz has greyish colour. The sulfides commonly follow the outlines of the rock or quartz fragments (Fig. 1). However, as many small quartz veinlets intersect each other and the ore minerals are sometimes accumulated in irregular patches, the assignment of a single quartz type to the ore minerals was not possible. Cavities in the vuggy quartz are commonly lined by small euhedral quartz crystals. From a limited set of samples available, it appears that the massive varieties with fragments and quartz veinlets are richer in ore minerals than the vuggy quartz.

The chemical composition of the ores reflects their mineralogical content to some extent. The silver content in the samples varied from 25 to 410 ppm, that of gold from 0.3 to 0.7 ppm (Tab. 1). The concentrations of As, Sb, Cu are generally low and vary erratically from sample to sample. Because quartz is the only mineral that can be recognized in most samples in the field (either outside of the mines or underground), it is difficult to detect any

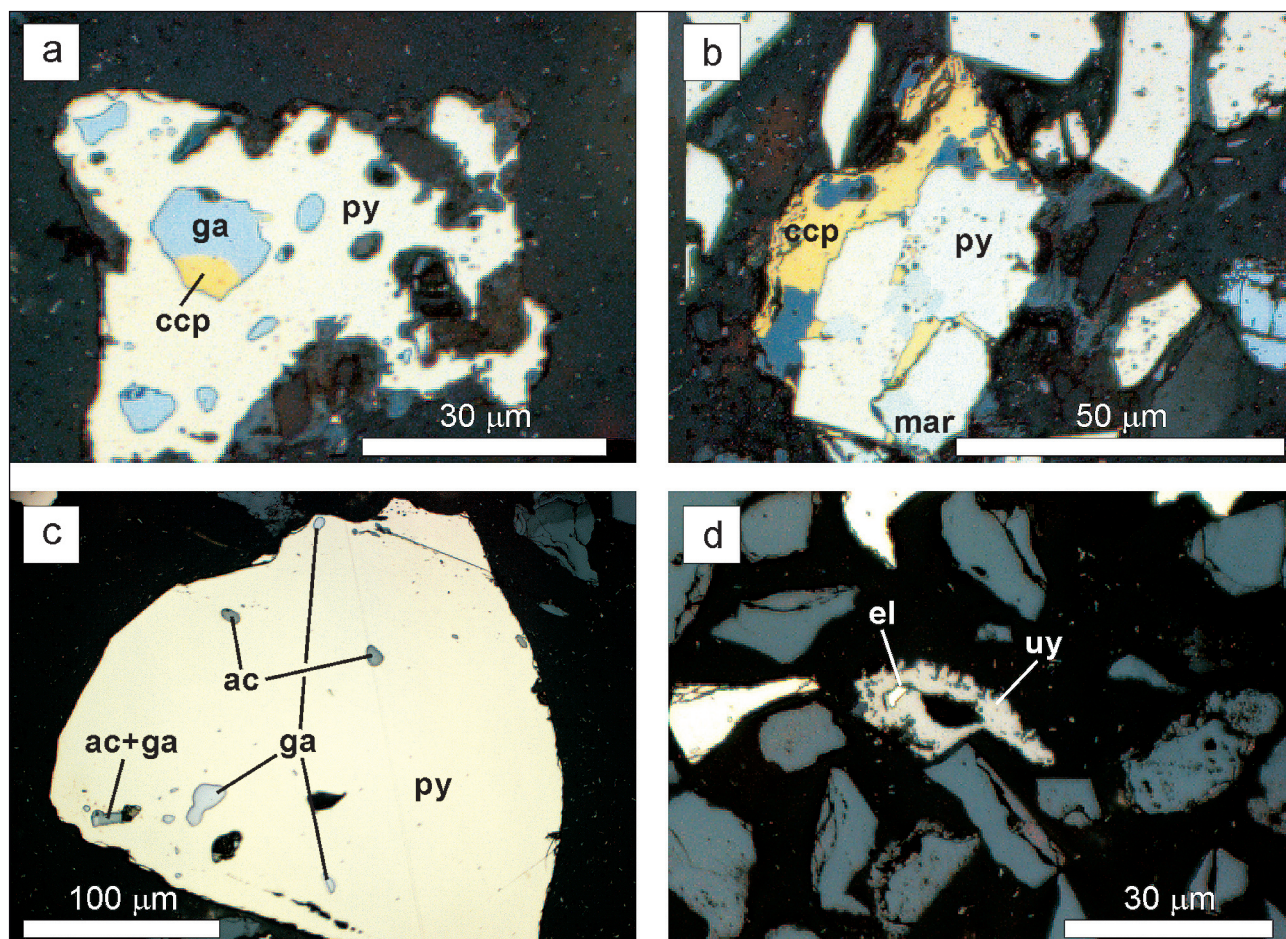


Fig. 2. Images from grain concentrates in plane-polarized reflected light. **a** – A pyrite grain with inclusions of galena and chalcopyrite (11SK, W). **b** – Chalcopyrite penetrates into an aggregate of pyrite and marcasite (marcasite has slight bluish tint in comparison with pyrite) (sample 11SK, grain AF). **c** – A large pyrite grain with galena, acanthite, and galena + acanthite inclusions. Note that the galena in inclusions with acanthite contains no silver (12SK, B). **d** – Uytnebogaardite replacing an electrum grain. A BSE image of the same grain is shown in Fig. 3d (12SK, H).

trends in the chemical or mineralogical composition of the ores without a very detailed sampling which is beyond the scope of this work.

Primary ore minerals of metals other than Au and Ag

Chalcopyrite is an infrequent mineral. It is either found as inclusions in sphalerite, pyrite (Fig. 2a) or galena, or forms small multiminerall grains with Ag minerals. The grain concentrates from some samples contained also larger (200–300 μm) grains of chalcopyrite, exceptionally with tiny galena inclusions, mostly with no other minerals. Chalcopyrite rarely penetrates into fractures in pyrite grains (Fig. 2b). Chemically, the grains do not deviate from the composition CuFeS_2 .

Galena is a common mineral, mostly found in association with pyrite (Fig. 2a). Galena is likely younger than pyrite and appears to preferentially nucleate and grow at the expense of older pyrite crystals. Larger fragments made of galena and sphalerite with no pyrite were found in grain concentrates but not in polished sections of the ores. Chemically, galena from Rabenstein is almost pure PbS (Tab. 2), even if found in direct contact with silver minerals, for example with acanthite (Fig. 2c).

Marcasite was found as infrequent grains in the grain concentrates and ore sections. Its reflectivity and colour are very similar to those of pyrite (Fig. 2b) but the grains show moderate anisotropy. It appears to have crystallized together with pyrite. Chemically, marcasite corresponds well to the formula FeS_2 .

Pyrite is the most common primary sulfide. It forms euhedral to subhedral crystals, up to 2 mm large. These crystals are commonly accumulated in small veinlets or rim fragments of altered rocks or quartz in massive ores (Fig. 1). Pyrite is often accompanied or replaced by galena and sphalerite and contains inclusions of these minerals and chalcopyrite, scarcely also acanthite (Figs. 2a, c). Pyrite at the Rabenstein occurrence is almost devoid of As and elements other than Fe and S are not present (Tab. 2).

Sphalerite is also a common mineral, usually found to replace pyrite. Occasionally, large intergrowths of sphalerite and galena can be also found. Inclusions and blebs of chalcopyrite, from ~50 μm down to "chalcopyrite disease" in sphalerite are common. Sphalerite also hosts rarely inclusions of acanthite. An interesting chemical feature of sphalerite from Rabenstein is a significant concentration of Cd, sometimes exceeding that of Fe (Tab. 2).

Minerals of silver and gold

Acanthite is common and dominant Ag carrier in some grain concentrates but essentially missing in other ones. In reflected light, it is grey with moderate reflectivity. Due to fine-grained nature of many acanthite grains, pleochroism or anisotropy are not observed. No internal reflections were seen. Only once it was found as inclusions in sphalerite, with distinct anisotropy. The absence of polysynthetic twinning in these inclusions suggests that the crystallization temperature was lower than ~170 °C. More commonly, acanthite forms inclusions in pyrite, either with or without galena (Fig. 2c). The last form of occurrence is porous acanthite which appears to replace galena (Figs. 3a, b, c). Such grains are probably fragile and many of them may have been destroyed during crushing of the large samples. Therefore, the contribution to the overall Ag budget may be underestimated; in one grain concentrate (13SK), such acanthite grains are more abundant than any other Ag mineral. Chemically, acanthite corresponds to Ag_2S , with negligible amounts of other elements (Tab. 3).

Freibergite is a relatively rare mineral. In reflected light, it is brownish with moderate to low reflectivity, isotropic, and with no internal reflections. Freibergite was occasionally found as small inclusions and blebs in pyrite together with galena inclusions or as inclusions in sphalerite. Freibergite inclusions in sphalerite were also found directly in the ore sections, not only in grain concentrates. It forms intergrowths with chalcopyrite or pyrargyrite. The chemical composition of this mineral is rather complicated (Tab. 3). The $\text{Ag}/(\text{Ag} + \text{Cu})$ (at/at %) ratio varies from 0.25 to 0.46. The freibergite grains in contact with sphalerite have more Zn than those which associate with other minerals. The $\text{Sb}/(\text{Sb} + \text{As})$ (at/at %) ratio is always more than 0.89.

Gold and silver alloys (electrum) are the most important carriers of Au in the studied samples. In reflected light, this mineral is yellow with very high reflectivity. It is isotropic, with no internal reflections. Electrum forms inclusions in pyrite, rarely at the contact between pyrite and galena and occurs together with other sulfides. In the latter case, electrum associates with chalcopyrite, galena, and polybasite/pearceite. Electrum was found only in grain concentrates and its relationship to the other minerals is difficult to determine. It seems to be replaced by uytenbogaardtite (Figs. 2d, 3d). Chemically, silver always dominates on atomic basis and the composition of electrum varies from $(\text{Au}_{24}\text{Ag}_{76})$ to $(\text{Au}_{46}\text{Ag}_{54})$ (Tab. 3). The small amounts of Fe

Tab. 2
Averaged analyses of galena, pyrite and sphalerite

Mineral	<i>n</i>	Au	Cu	Ag	Fe	Zn	As	Sb	Pb	S	Total
galena	12	0.00	0.05	0.07	0.56	0.05	0.01	0.05	85.46	12.88	99.13
pyrite	8	0.00	0.04	0.02	46.10	0.07	0.10	0.03	0.01 Cd	51.50	97.86
sphalerite	11	n. a.	0.14	n. a.	0.86	65.33	n. a.	n. a.	0.42	31.92	98.66

Note that Cd is reported in the same column for sphalerite as Pb for galena and pyrite. All data are in weight %. *n* = number of analyses averaged, n. a. = not analysed

and S measured may be a contamination from the pyrite host.

Polybasite/pearceite is rare, found only in one grain concentrate (11SK). In reflected light, these minerals are grey with a bluish tint and may be difficult to distinguish from pyrrargyrite, especially in the tiny grains. The reflectivity is moderate. Pleochroism was not observed but anisotropy is easy to see. Internal reflections were mostly not seen and this property distinguished these minerals from pyrrargyrite. The distinction of polybasite and pearceite based on optical properties only is generally complicated and impossible in the small grains in our samples. These minerals can be found in tiny grains together with acanthite, galena, chalcopyrite, uytenbogaardtite, and electrum (Figs. 3e, f). Interestingly, the Sb-dominant members (polybasite) are sharply separated from the As-dominant members (pearceite) when they occur together. This separation was observed several times and appears to document a miscibility gap in this solid solution. The Sb-dominant grains have the Sb/(Sb + As) (at/at %) ratio larger than 0.85, the As-dominant grains have the ratio lower than 0.26. An interesting chemical feature of these minerals is their minor but constant Au content (from 0.12 to 1.49 wt.% Au) (Tab. 3).

Pyrrargyrite is not common. In reflected light, it is bluish, with moderate reflectivity. Pleochroism was not observed and the anisotropy is often masked by abundant and vivid red internal reflections. Pyrrargyrite was found only in grain concentrates as isolated, larger (up to 50 μm) grains or in small multimineral grains, together with chalcopyrite, freibergite, or electrum. The Sb/(Sb + As) (at/at %) ratio varies from 0.87 to 0.97, that is, the proustite component is only minor (Tab. 3).

Uytenbogaardtite is very rare, found only in three grains but in two different grain concentrates (11SK, 12SK). In reflected light, the mineral is brownish (deeper brown than freibergite; Fig. 2d), with moderate reflectivity (between that of sphalerite and hematite). Pleochroism was not observed but anisotropy is relatively strong, easy to observe but without distinct colours. Internal reflections are absent. The textures suggest that uytenbogaardtite replaces electrum, although the number of observations is certainly not sufficient to draw firm paragenetic conclusions. Chemically, in addition to the major Au and Ag, uytenbogaardtite from Rabenstein contains minor concentrations of Cu and Fe (Tab. 3). However, the porous nature of the analysed grains and their small size precluded acquisition of more than a few good analyses; analyses not shown in Tab. 3 were similar to those shown but their totals were higher than 103 %.

Other minerals

A very common mineral that could be observed in hand specimens, ore sections, and grain concentrates, is goethite. Given that the most common primary sulfide is pyrite, the abundance of goethite as the alteration product of pyrite is not surprising. Other than the ubiquitous quartz and the ore minerals, these minerals were found rarely

in the grain concentrates: hematite, Ti oxide, and most likely a secondary Mn oxide (Fig. 3h). The minerals were identified by their optical properties and EDS analyses. The Mn oxide, in addition to abundant Mn, contains also K and Pb, according to an EDS analysis. Such mineral could correspond to a phase from the hollandite group, where the K- and Pb-end-members are cryptomelane and coronadite, respectively (Post, 1999). A fracture in one of the mines was filled by black crumbling material. Chemical analysis of this material showed that it is a Mn oxide with elevated concentration of Ag (117 ppm, Tab. 1). This material is, however, X-ray amorphous. Similar Mn-Fe oxides, X-ray amorphous, enriched in Ag (up to 134 ppm) and Au (up to 15.4 ppm), were found in Pukanec (Bahna and Chovan, 2001). The general features of the primary mineralization in Pukanec are similar to those of the mineralization from Rabenstein; the Pukanec ores have been described as low-sulfidation type of the epithermal Au-Ag mineralization (Bahna and Chovan, 2001).

Discussion

An interesting geochemical feature of the ores at Rabenstein is almost complete absence of As. Most minerals that could potentially accommodate As in their crystal structure (pyrite, freibergite, pyrrargyrite) contain very little of this element. The only mineral where As is present in a significant amount is pearceite. None of the studied minerals shows chemical zoning, as if they were deposited in a single pulse or from a fluid whose composition was kept constant over a longer time.

The study of the grain concentrates provides a good overview of the mineralogy of the remaining ores but little is learned about the paragenetic sequence. The inspection of the hand specimens, where ores are visible, suggests that the ore formation was preceded by brecciation and silicification of the rocks, likely in multiple episodes. Pinkish minerals present in some fragments of the breccias are probably Mn carbonates or silicates; these minerals were not studied in detail. The oldest ore mineral appears to be pyrite, followed by sphalerite and galena. The temporal position of the minerals of silver and gold is very difficult to ascertain because of the small number of observations and the fact that the Ag sulfides form commonly grains with no pyrite, sphalerite, or galena. The few finds of Ag sulfides and electrum as inclusions in pyrite and sphalerite hint that the Ag-Au minerals postdate the most common sulfides. In a final, low-temperature stage, galena was replaced by porous acanthite and electrum by uytenbogaardtite.

The ore mineralization from Rabenstein and other veins in Hodruša was described in a comprehensive study of Onačila and Rojkovičová (1992). They reported the occurrence of pyrite, accompanied by sphalerite, galena, and chalcopyrite. The Ag carriers were pyrrargyrite, stephanite, acanthite, and freibergite; Au was present in the form of gold-silver alloys (electrum). In comparison with this study, they did not identify the minerals of the polybasite/pearceite group and uytenbogaardtite. In turn, we did not encounter stephanite in our samples. Onačila

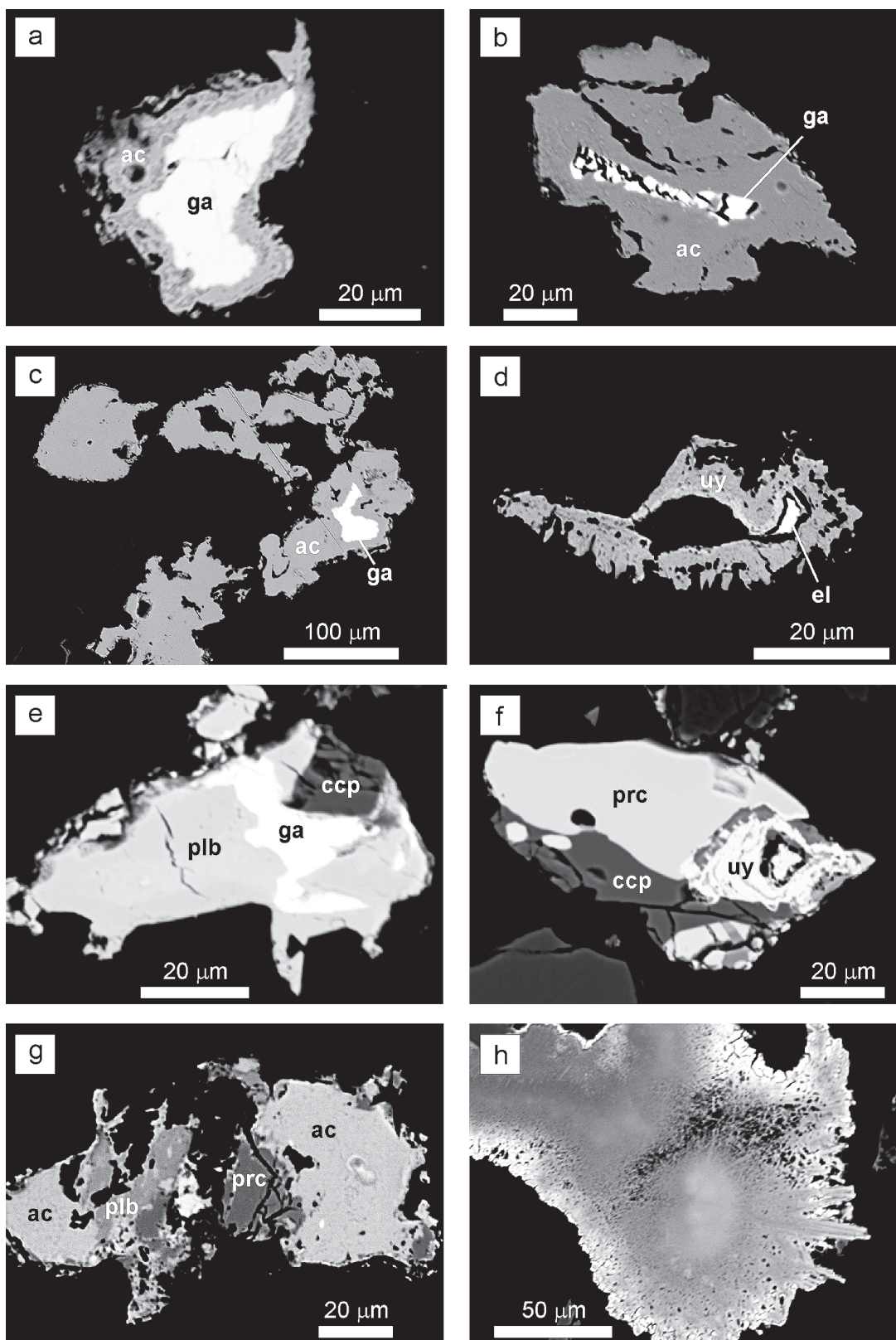


Fig. 3. Back-scattered electron images of grain concentrates. **a, b, c** – acanthite grains which replace galena (a: sample 12SK, grain F; b: 13SK, B; c: 13SK, C); **d** – uyttenbogaardite as a likely alteration product of electrum (12SK, H); **e** – an intergrowth of polybasite, galena and chalcopyrite (11SK, S); **f** – a grain made of pearceite, chalcopyrite and uyttenbogaardite (11SK, T'); **g** – a complex intergrowth of acanthite, polybasite and pearceite (11SK, N2); **h** – Mn oxide with elevated concentration of K and Pb (13SK, H).

Tab. 3
Selected individual analyses of Ag-Au sulfides and Ag-Au alloys

Mineral	Sample (grain)	Au	Cu	Ag	Fe	Zn	As	Sb	Pb	S	Total
Ag-Au	11SK(B)	35.94	0.13	62.49	0.14	0.00	0.00	0.02	0.03	0.03	98.80
Ag-Au	11SK(D1)	58.30	0.00	40.88	1.15	0.06	0.00	0.03	0.00	0.10	100.51
Ag-Au	11SK(Q3)	49.84	0.00	49.48	0.34	0.02	0.01	0.02	0.01	0.08	99.80
Ag-Au	13SK(E2)	57.76	0.00	41.08	0.48	0.00	0.01	0.00	0.00	0.04	99.37
Ag-Au	13SK(E2)	53.71	0.01	45.44	0.73	0.07	0.00	0.02	0.00	0.04	100.02
Ag-Au	13SK(E4)	51.25	0.05	47.87	0.18	0.00	0.01	0.00	0.00	0.02	99.37
Ag-Au	13SK(E3)	60.85	0.03	38.64	0.24	0.00	0.01	0.00	0.00	0.02	99.80
Ag-Au	12SK(O)	56.35	0.12	43.98	0.60	0.00	0.01	0.00	0.01	0.06	101.14
Ag-Au	12SK(D)	58.49	0.01	41.48	0.33	0.01	0.00	0.00	0.05	0.02	100.40
Ag-Au	12SK(H)	60.31	0.00	39.29	0.63	0.00	0.00	0.01	0.02	0.04	100.30
Ag-Au	12SK(Y)	58.29	0.00	41.65	0.25	0.03	0.01	0.00	0.03	0.03	100.31
ac	11SK(X)	0.01	0.19	85.60	0.20	0.69	0.00	0.00	0.00	13.80	100.49
ac	11SK(Y)	0.01	0.00	85.55	0.34	0.02	0.01	0.03	0.03	13.68	99.68
ac	11SK(O)	0.12	0.71	85.62	1.16	0.00	0.00	0.00	0.00	12.54	100.15
ac	11SK(N2)	0.00	0.17	85.10	0.22	0.18	0.01	0.00	0.00	12.75	98.44
ac	11SK(F)	0.02	0.30	85.29	0.21	0.03	0.00	0.02	0.00	12.24	98.11
ac	11SK(T)	0.02	0.17	85.72	0.47	0.16	0.02	0.00	0.00	13.18	99.74
ac	13SK(A)	0.01	0.38	84.23	0.47	0.10	0.06	0.18	0.04	11.88	97.35
ac	12SK(E)	0.01	0.04	86.49	0.59	0.01	0.01	0.02	0.00	13.61	100.80
ac	12SK(F)	0.06	1.74	84.69	1.07	0.04	0.10	0.17	0.04	13.01	100.92
frg	Rabe12	0.00	18.50	26.84	3.10	4.94	1.75	24.23	0.00	21.45	100.80
frg	Rabe13	0.09	21.53	19.41	2.47	6.26	0.98	25.34	0.00	22.42	98.50
frg	Rabe13	0.00	20.76	23.11	3.36	4.05	0.87	26.17	0.02	21.28	99.60
frg	11SK(U)	0.01	20.41	23.99	2.27	4.82	1.11	25.19	0.00	21.47	99.26
frg	11SK(A)	0.00	23.21	20.16	3.55	3.10	1.21	25.81	0.00	21.89	98.93
frg	11SK(A)	0.00	23.50	19.06	3.74	2.72	1.11	26.06	0.00	22.26	98.44
frg	11SK(V)	0.04	26.91	15.42	5.26	1.56	1.61	25.95	0.00	22.19	98.94
prg	11SK(A)	0.01	0.32	60.90	0.09	0.16	0.58	20.96	0.03	16.34	99.37
prg	11SK(A)	0.00	0.27	61.20	0.10	0.28	0.71	20.43	0.00	16.23	99.24
prg	11SK(L)	0.00	0.04	61.13	0.26	0.14	0.62	20.86	0.00	16.41	99.47
prg	11SK(L)	0.00	0.08	60.55	0.41	0.00	0.53	21.34	0.00	17.09	99.99
prg	11SK(R)	0.00	0.24	59.85	0.36	0.00	1.28	21.07	0.60	16.64	100.04
prg	11SK(Q)	0.00	0.12	59.97	0.37	0.04	0.63	21.80	0.00	16.20	99.14
prg	11SK(L3)	0.04	0.02	61.26	0.07	0.28	0.83	20.45	0.00	16.30	99.24
prg	11SK(AG)	0.04	0.00	62.33	0.12	0.11	1.38	19.21	0.00	16.28	99.47
prg	12SK(C)	0.00	0.09	61.28	0.24	0.00	0.51	21.54	0.00	16.61	100.27
prg	12SK(L)	0.00	0.06	61.22	0.32	0.00	0.56	21.37	0.00	16.83	100.36
prg	12SK(E)	0.00	0.03	61.81	0.42	0.01	1.83	19.55	0.00	16.72	100.37
uy	11SK(T')	27.59	0.85	55.65	0.30	0.12	0.04	1.09	0.92	12.09	98.63
uy	12SK(O)	24.39	0.03	64.24	1.70	0.16	0.07	1.15	0.00	8.61	100.33
p/p	11SK(B)	1.49	3.50	72.50	0.14	0.02	4.74	2.80	0.00	14.76	99.95
p/p	11SK(B)	0.70	4.59	72.91	0.68	0.00	5.70	0.65	0.00	14.59	99.81
p/p	11SK(N)	0.44	3.92	72.40	0.07	0.00	0.19	9.90	0.00	14.64	101.55
p/p	11SK(N2)	0.12	5.83	72.25	0.15	0.25	6.03	0.00	0.00	14.25	98.88
p/p	11SK(N2)	0.74	4.37	69.75	0.23	0.22	0.23	9.81	0.00	13.72	99.06
p/p	11SK(F)	0.17	6.55	72.23	0.28	0.02	6.02	0.18	0.00	13.73	99.18
p/p	11SK(F)	0.19	5.88	71.12	0.26	0.08	0.85	8.36	0.00	12.76	99.48
p/p	11SK(T')	0.35	4.00	73.35	0.19	0.11	5.10	1.92	0.00	14.60	99.62
p/p	11SK(S)	0.33	2.18	72.93	0.19	0.00	1.15	8.47	0.00	13.26	98.51

All data in weight %. Mineral abbreviations: el = electrum, ac = acanthite, frg = freibergite, uy = uytenbogaardtite, prg = pyrrargyrite, p/p = polybasite/pearceite

and Rojkovičová (1992) observed that the Ag-Au minerals are a product of the youngest mineralization episode. Pyrargyrite and stephanite penetrate into quartz and both may be replaced by acanthite. Freibergite associates with sphalerite or pyrite. In general, these two sets of observations (ours and that of Onačila and Rojkovičová, 1992) converge to similar conclusions, although the dispersed nature of the mineralization at Rabenstein would probably require a more exhaustive study to clarify the small discrepancies. Given that Rabenstein was just a small locality in the Hodruša ore field, such study will probably not be carried out soon.

Uytenbogaardtite was not previously known from the ores of the Štiavnica-Hodruša ore field but has been mentioned from the Kremnica ore field (the Teich vein; Košuth, 1992). In its first description, uytenbogaardtite was found in three deposits in close association with electrum, acanthite, quartz, and other minerals (Barton et al., 1978). All three deposits are low-temperature Ag-Au accumulations where uytenbogaardtite belongs to either late hydrothermal or supergene stage of formation. The deposits contain common quartz, adularia, kaolinite, Ca-Mn carbonates, pyrite, galena, sphalerite, and Ag sulfosalts. Locally, a cementation zone enriched in acanthite is developed. Barton et al. (1978) reported that electrum blebs are invariably rimmed by 5–10 µm zone of uytenbogaardtite. Furthermore, uytenbogaardtite was found in Pongkor deposit (west Java; Warmada et al., 2003), in the Shila-Paula district (southern Peru; Chauvet et al., 2006), and Ulakhan deposit (northeastern Russia; Savva and Palyanova, 2007). All these deposits are Ag-Au epithermal deposits with initial silicification and precipitation of Mn minerals and subsequent formation of pyrite, galena, sphalerite, chalcopyrite, and later Ag sulfides and electrum. Uytenbogaardtite and, to a smaller extent, acanthite, were described as products of the final, low-temperature stages, sometimes designated as alteration stages. A thermodynamic modeling supports the idea that these minerals can be produced at low temperatures (as low as 25 °C), even if the fluids are relatively oxidizing (Palyanova and Savva, 2008).

All these deposits are noticeably similar to the Štiavnica-Hodruša ore field. The significant difference is that the above-mentioned deposits are still actively mined, although some of the occurrences in southern Peru were exploited already by Incas (Chauvet et al., 2006). One may speculate that, in analogy to these active deposits, the object of mining at the Rabenstein occurrence were late hydrothermal or supergene accumulations of Ag-Au sulfides, mostly acanthite. The earlier Ag sulfides seem to be finely dispersed in the ores and were probably difficult to use in the early medieval times. However, these are only speculations that cannot be supported by our results because the rich ores are long gone.

Freiburg) and the microprobe analysis would not be obtained without the help of H. Müller-Sigmund (Univ. Freiburg). Parts of this work were produced within the Diploma thesis of R. Michallik and the Bachelor thesis of S. Kopf (Univ. Freiburg).

References

- BAHNA, B. & CHO VAN, M., 2001: Low-sulfidation type of epithermal Au-Ag mineralization near Pukanec (Central Slovakia Neogene Volcanic fields). In: *Geolines*, 13, pp. 11 – 17.
- BAKOS, F. & CHO VAN, M. (eds.), 2004: Gold in Slovakia. *Bratislava, Slovenský skauting*, 298 p.
- BARTON, M. D., KIEFT, C., BURKE, E. A. J. & OEN, I. S., 1978: Uytenbogaardtite, a new silver-gold sulfide. In: *Canad. Mineralogist (Ottawa)*, 16, pp. 651 – 657.
- CHAUVET, A., BAILLY, L., ANDRE, A. S., MONIE, P., CASSARD, D., TAJADA, F. L., VARGAS, J. R. & TUDURI, J., 2006: Internal vein texture and vein evolution of the epithermal Shila-Paula district, southern Peru. In: *Mineralium Depos.*, 41, pp. 387 – 410.
- KODĚRA, M., 1959: Doterajšie výsledky výskumu paragenetických pomerov rudných žíl v štiavnicko-hodrušskom rudnom obvode. In: *Acta geol. geogr. Univ. Comen.*, 2, s. 7 – 17.
- KODĚRA, M. (ed.), 1986: Topografická mineralógia Slovenska, 1. diel. *Bratislava, Veda, Vyd. Slov. Akad. Vied*.
- KODĚRA, P., LEXA, J., RANKIN, A. H. & FALICK, A. E., 2005: Epithermal gold veins in a caldera setting: Banská Hodruša, Slovakia. In: *Mineralium Depos.*, 39, pp. 921 – 943.
- KOŠUTH, M., 1992: Príspevok k technologickej mineralógii striebra ložiska Kremnica – Šturec. In: *Zbor. Striebrné minerálne asociácie v Československu. Dům Techniky, Ústí nad Labem – Donovaly*.
- KOVALENKER, V. A., NAUMOV, V. B., PROKOFEV, V. Yu., JELEŇ, S. & HÁBER, M., 2006: Compositions of magmatic melts and evolution of mineral-forming fluids in the Banská Štiavnica epithermal Au-Ag-Pb-Zn deposit, Slovakia: A study of inclusions in minerals. In: *Geochemistry International*, 44, pp. 118 – 136.
- KONEČNÝ, V. & LEXA, J., 2002: Evolution of the horst-graben structure in the central Slovakia volcanic field. In: *Geolines*, 13, pp. 78 – 80.
- LEXA, J., ŠTOHL, J. & KONEČNÝ, V., 1999: The Banská Štiavnica ore district: Relationship between metallogenetic processes and the geological evolution of a stratovolcano. In: *Mineralium Depos.*, 34, pp. 639 – 654.
- ONAČILA, D. & ROJKOVIČOVÁ, L., 1992: Zlato-strieborná mineralizácia žíl v hodrušskom rudnom poli. In: *Miner. Slov. (Bratislava)*, 24, s. 245 – 256.
- PALYANOVA, G. A. & SAVVA, N. E., 2008: Some sulfides of gold and silver: Composition, mineral assemblage, and conditions of formation. In: *Theoretical Foundations of Chemical Engineering*, 42, 5, pp. 749 – 761.
- POST, J. E., 1999: Manganese oxide minerals: Crystal structures and economic and environmental significance. In: *Proc. National Acad. Sci. USA*, 96, pp. 3 447 – 3 454.
- SAVVA, N. E. & PALYANOVA, G. A., 2007: Genesis of gold and silver sulfides at the Ulakhan deposit (northeastern Russia). In: *Russ. geol. geophys.*, 48, 10, pp. 799 – 810.
- WARMADA, I. W., LEHMANN, B. & SIMANDJUNTAK, M., 2003: Polymetallic sulfides and sulfosalts of the Pongkor epithermal gold-silver deposit, West Java, Indonesia. In: *Canad. Mineralogist (Ottawa)*, 41, pp. 185 – 200.

Acknowledgements. I thank P. Koděra for the review of the manuscript, M. Chovan and D. Ozdín for the editorial handling, and R. Kaňa (Slovenská Banská, Hodruša) for showing us the locality Rabenstein. All sections were prepared by M. Schrage (Univ.

Rukopis doručený 16. 2. 2009
Rukopis akceptovaný 30. 6. 2009
Revidovaná verzia doručená 16. 4. 2009

Appendix

Localization of the large samples from which the heavy (ore) minerals were separated and identified. The smaller (hand) specimens were collected in the immediate vicinity of the old mines at Rabenstein.

Tab. A1

The coordinates and details about the large samples. The last entry (for Tri križe) shows the coordinates for the square of this name in the village of Banská Hodruša as a control.

Sample	Latitude (°)	Longitude (°)	Notes
Rab-1			collected underground, see Fig. A1
Rab-5	48.472 15	18.841 83	collected outside, from a vertical wall created probably by the mining activities
10SK			collected underground, see Fig. A1
11SK	48.472 12	18.841 50	collected 2–3 meters from the mine entrance where the coordinates were measured
12SK	48.472 03	18.841 37	collected 2–3 meters from the mine entrance where the coordinates were measured
13SK	48.472 10	18.841 20	collected 2–3 meters from the mine entrance where the coordinates were measured
Tri križe	48.461 77	18.819 80	control coordinates

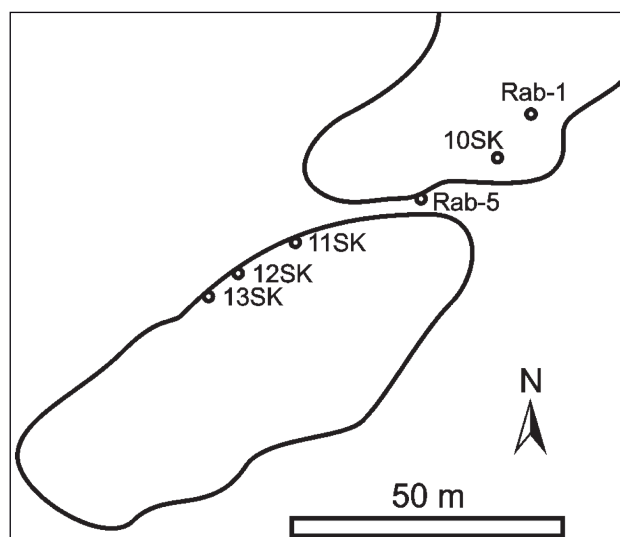


Fig. A1. A sketch of the locality Rabenstein with the sampling points for the large samples. The lines show the approximate limits of the quartz-rich material which forms a distinct geomorphological feature in this area. The geographic coordinates for the samples are given in Table A1.

Rudná mineralizácia na výskyte Rabenstein pri Banskej Hodruši

Štiavnicko-hodrušský rudný obvod patril v stredoveku k významným oblastiam ťažby zlato-strieborných rúd. Napriek tomu mineralógia rúd, ktoré po stáročia zabezpečovali jedinečné postavenie hodrušských ložísk, je preskúmaná nedostatočne. Nedostatok poznatkov o tejto mineralizácii je podmienený najmä tým, že bohaté rudy dolované počas stredoveku boli už dávno vyťažené. Tento príspevok opisuje minerály na rudnom výskyte Rabenstein (Havraní kameň) v blízkosti Banskej Hodruše (obec Hodruša-Hámre). Na Rabensteine nachádzame ešte aj dnes početné zachované a prístupné dobývky, ktoré boli razené plytko pod povrchom. Predpokladáme, že predmetom ťažby tu boli aspoň v počiatočných fázach bohaté Ag-Au rudy, a preto sme sa pokúsili stanoviť ich mineralogické zloženie.

Rudné minerály sa nachádzajú v silne prekremenenej zóne. V hojnom kremeň, pravdepodobne niekoľkých generácií, sú uzatvorené úlomky alterovaných hornín. Lokálne je kremeň sfarbený jemnozrnným hematitom do červena. Ružové nerudné minerály boli len opticky identifikované ako uhličitany, pravdepodobne s obsahom Mn. Tieto minerály neboli bližšie určené. V odobraných kusových vzorkách boli rudné minerály také zriedkavé, že ich štúdium v odrazenom polarizovanom svetle prinieslo len veľmi sporé poznatky. Preto sme použili väčšie vzorky (jedna vzorka až 40 kg), ktoré boli podrvené, a rudné minerály sa oddelili od nerudných minerálov viacerými metódami. V nábrusoch aj koncentrátoch ťažkých minerálov sa identifikoval hojný pyrit s častým galenitom, sfaleritom a chalkopyritom. Ojedinele sa spolu s pyritom vyskytuje markazit. Chemické zloženie týchto minerálov stanovené pomocou elektrónového mikroanalýzátora

je jednoduché. Pyrit, galenit a chalkopyrit zodpovedajú nominálnemu zloženiu FeS_2 , PbS a CuFeS_2 . Sfalerit obsahuje priemerne 0,86 hm. % Fe a 0,46 hm. % Cd. V niektorých analyzovaných zrnkách však prevláda Cd nad Fe.

Spomedzi minerálov ušľachtilých kovov sa kombináciou odrazovej mikroskopie a analýzy elektrónovým mikroanalýzátorom identifikovali akantit, freibergit, pyrargyrit, polybazit/pearceit, uytenbogaardtit a zliatiny zlata a striebra. Akantit sa našiel ako inklúzie v pyrite, vzácné v sfalerite. Zliatiny zlata a striebra sa vyskytujú ako inklúzie v pyrite, v jednom prípade sa zaznamenali aj na kontakte medzi pyritom a galenitom. Ostatné Ag-Au minerály navzájom prerastajú v drobných zrnkách, v ktorých nie je prítomný pyrit. Keďže sme tieto minerály zistili takmer výhradne v ťažkých koncentrátoch, stanovenie ich veku vo vzťahu k nerudným minerálom alebo hojnejším sulfidom je veľmi ťažké alebo nemožné. Porézne zrnká akantitu zatláčajú galenit a uytenbogaardtit zatláča Ag-Au zliatiny. Pomer $\text{Ag}/(\text{Ag} + \text{Cu})$ (at/at %) vo freibergite je 0,25 až 0,46. Zrnká freibergitu, ktoré sa stýkajú so sfaleritom, obsahujú viac Zn ako tie zrnká, ktoré v kontakte so sfaleritom nie sú. Pomer $\text{Sb}/(\text{Sb} + \text{As})$ (at/at %) vo freibergite je viac ako 0,89 a v pyrargyrite viac ako 0,87. Pearceit, ktorý je vo vzorkách veľmi vzácný, je jediný minerál v študovaných rudách, ktorý má zvýšený obsah As. Zliatiny Ag-Au obsahujú vždy viac striebra ako zlata a ich zloženie sa pohybuje medzi $(\text{Au}_{24}\text{Ag}_{76})$ a $(\text{Au}_{46}\text{Ag}_{54})$.

Je možné, že hlavnou rudou Ag na Rabensteine bol porézny akantit, ktorý je pomerne hojný v niektorých ťažkých koncentrátoch. Či to však bolo skutočne tak, zostáva otvorenou otázkou.