Acta Mineralogica-Petrographica, Szeged, XXXVI, 5–15, 1995

SILVER MINERALS FROM RUDABÁNYA (N-HUNGARY)

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ABSTRACT

Numerous silver minerals were found recently in the primary and in the secondary oxidation zone of the hydrothermal-metasomatic iron ore deposit at Rudabánya, Northern-Hungary.

In the baritized zone bound to the carbonatic ore - primary in the galena-rich orebodies - silver, acanthite, proustite, pyrargyrite and xanthoconite? were found. The limonitic and siliceous limonitic ores of the oxidation zone contains acanthite, moschellandsbergite, bromargyrite, chlorargyrite and iodargyrite. These minerals are the resultant products of the recrystallization of the silver-bearing phases of the baritized zone, i.e. of secondary origin. This paper is on the description of the minerals referred to above.

INTRODUCTION

The professional literature refers to only one silver mineral, pyrargyrite from Rudabánya. This is surprising, having regard to the fact that Rudabánya was famed for its medieval silver mining. According to PODÁNYI (1956), the mineral under mining was silver-bearing galena. The earlier examinations proved that silver was present almost in every ore type as a trace element (KOCH, GRASSELLY and DONÁTH, 1956; PANTÓ, 1956; CSALAGOVITS, 1973). From the examinations of Csalagovits it turned out however, that the richest in silver is the baritized zone. It was also proved that silver enrichments are always bound to lead, therefore to galena. The only described silver mineral, pyrargyrite was observed by KOCH (1966), by ore microscope in a galena specimen from the primary zone. According to his description it occurs at the boundary of galena and barite as narrow strips.

RESULTS OF THE EXAMINATIONS

Primary silver minerals

Silver

It was found several times in the Polyánka and Vilmos areas of the deposit. In case of the specimen from Polyánka, the correct place of occurrence is not known, because it was found on the waste dump. The carbonatic ore consist of calcite, siderite and quartz grains, according to the microprobe analysis.

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The microprobe analyses and the SEM examinations were made by AMRAY 1803 I equipment with connected energy dispersive sensor at the Dept. of Metallurgy, University of Miskolc. Accelerating voltage: 20 kV, test current 10^{-10}, SiLi detector, W cathode, EDAX-EDS system, analyses by supplied softwares.

Disseminated pyrite and galena were also observed in the carbonatic ore. Silver occurred as shining white scales in fissures of the ore. At the edge of the grains thorn-like crystals were observed by SEM. According to analyses the grains are formed by xenomorphous silver and acanthite in its gaps and on the edges (*Fig. 1.*). Acanthite was often observed as acicular aggregates and as silver-form grains in cases alteration had completed. The greatest silver grains which size of 20 µm. Based on the EDX studies it contains no other element. It also occurs in the cavities of the galena-bearing barite of a Vilmos area as 1-3 mm hair-like aggregates and tufted bunches (*Fig. 2.*). On the surfaces of these aggregates acanthite appears as acicular crystals. This mineral association is supposedly of secondary origin.

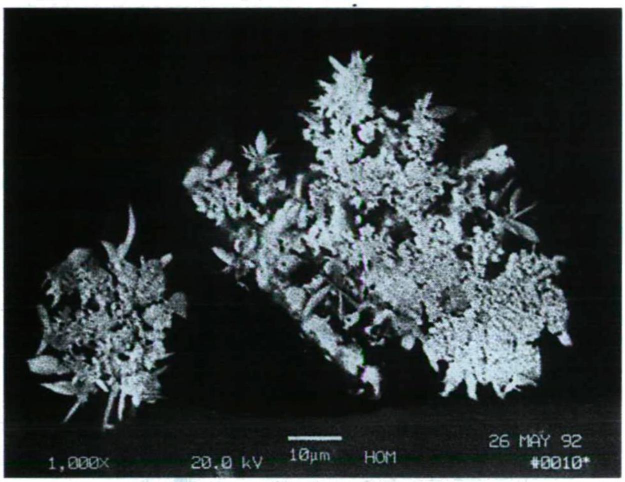

Fig. 1. Silver, grained appearance with acicular acanthite. Rudabánya-Polyánka. Back-scattered electron image. (Herman Ottó Museum (HOM) collection)

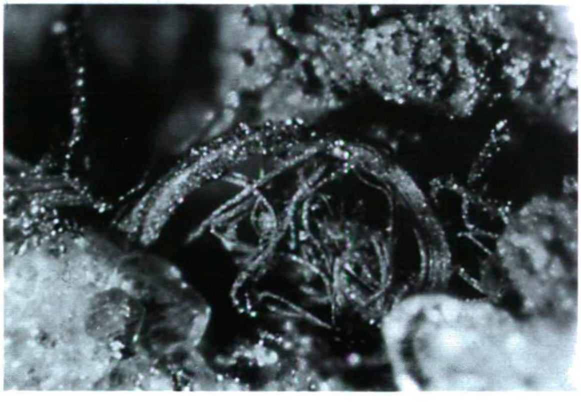

Fig. 2. Silver, hair-like aggregates. Rudabánya-Vilmos. Width of the picture: 5 mm. (S. Klaj collection).

Acanthite

As a widely distributed silver mineral acanthite was observed in the primary and the secondary zone as well in numerous openings, always in small quantities. When occurring in the primary zone it is always bound to galena (Polyánka, Andrássy-I, Andrássy-II, and Vilmos areas). Its 2-40 mm grains are enclosed in galena, and it was also observed on the edge of galena accompanied by pyrite and sphalerite. Thus, the prime material of the medieval mining may have been acanthite-bearing galena. Apart from this primary acanthite occurrence, a second generation acanthite formed from silver is also known from Rudabánya. Acicular acanthite crystals were observed on and among the silver grains and the tufted bunches as well. In several cases, the entire grain altered into acanthite. The microprobe analyses of the acanthite is entirely corresponds to those of other localities. Acanthite frame crystals of similar appearance (*Fig. 3.*) are well known from the professional literature (WALENTA, 1984). Its formation can be credited to the alteration of silver.

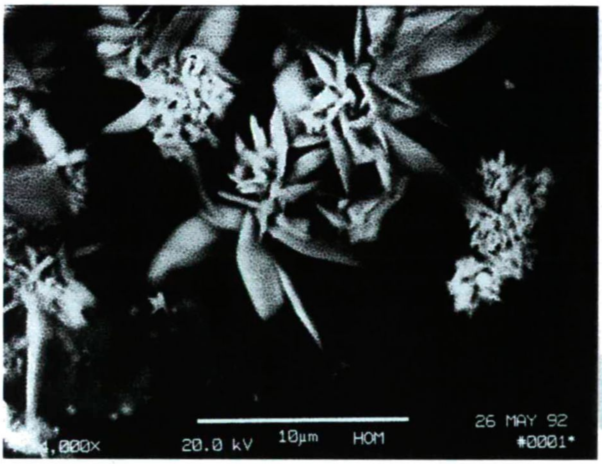

Fig. 3. Acanthite, acicular crystals. Rudabánya-Polyánka. Back-scattered electron image.(HOM collection).

Proustite

It is found in the galena-bearing ore of the Andrássy-I, Andrássy-II and Vilmos areas mostly as xenomorphous grains. It occurs in the galena-bearing ore of the spar edge accompanied by galena, sphalerite, tetrahedrite, pyrargyrite, barite, calcite. It is found as some mm rufous patches. Its presence was proved by ore microscopic studies during which its strong inner reflection was detected, and by microprobe analyses, either (Table 1). Its composition, derived from the analysis is $Ag_{3,58}$ $AsS_{3,44}$, thus showing somewhat less As compared to the theoretical composition. Small crystals of poustite were also found in cavities, which are of short, columnar habit, reaching 1-2 mm (*Fig. 4.*), with faces of (1120, 0112). This is the only locality of idiomorphous proustite in Rudabánya so far.

TABLE 1

Chemical composition of proustite from Rudabánya-Vilmos (Wt%)

Ag	66,8	67,5
As	13,4	13,2
S	19,8	19,3
	100,0	100,0

Analyst: Á. KOVÁCS

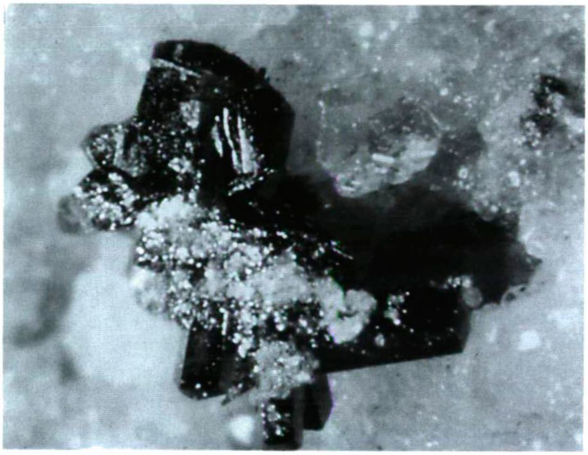

Fig. 4. Proustite, stubby columnar crystals. Rudabánya-Vilmos. Width of the picture: 4 mm. (S. Klaj collection).

Pyragyrite

It was often observed together with proustite in the galena-bearing ore of the Vilmos area. Its colour is dark red, showing dark red inner reflection in ore microscope, and occurs as 30-80 μm grains and also disseminated in sphalerite and barite (*Fig. 5.*). It was also found in columnar crystals reaching 1-2 mm in small cavities. The microprobe analyses assured its presence (Table 2) as its chemical composition corresponds to those of the literature (ANTHONY et al., 1990), the Ag content higher, and the sulphur content is lower, than the reference, however.

TABLE 2

Chemical composition of pyragyrite from Rudabánya-Vilmos (Wt%)

Ag	62,8	65,5
Sb	23,3	19,8
S	13,9	14,7
	100,0	100,0

Analyst: Á. KOVÁCS

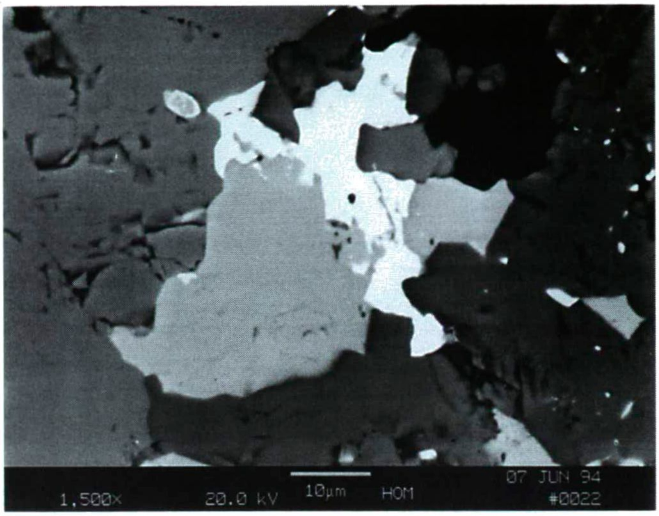

Fig. 5. Pyrargyrite (light grey), anhedral appearance with barite (white), galena (grey) and calcite (dark grey). Rudabánya-Vilmos. Back-scattered electron image. (HOM collection).

Xanthoconite?

A dark yellow mineral containing Ag, As, S elements according to the EDX studies was rarely found in the silver mineral rich ore of the Vilmos area. It was very rarely observed as short crystals reaching 1 mm. Its lustre was bright, the scratch was lemon-yellow. The extremely small sample quantity was not enough for an X-ray powder study, therefore its presence is not proved yet.

Secondary silver minerals

Acanthite

As referred above, the acicular acanthite on the surface of the silver precipitations in siderite and barite in the Polyánka and Vilmos areas are supposed to be secondary phase. The acanthite described in this paragraph however, is surely of secondary origin. In the Andrássy-I area, near the surface, the galena-rich baritized zone was exposed to strong weathering processes, changing the originally massive ore into hollow texture and making the primary ore minerals dissolve and precipitate again in different appearance and phase. These processes formed the thin tabular crystals of barite, the 2-3 mm rhombohedras of calcite and the short crystals of quartz. As a typical oxidation zone mineral, anglesite was also found as tabular and columnar crystals, smaller than 1 mm. Similarly, the sulphides were observed as small crystals or thin crystalline crusts instead of the original massive appearance. Finally, resembling to galena, appearing as tin-like crusts, coatings and branchy aggregates, a bright grey silver and sulphur-bearing phase also observed, which is considered to be acanthite, judging by its appearance, composition and genetics (*Fig. 6.*).

It occurred as a member of an intriguing mineral assembly in the Adolf area. In the secondary ore, along occasionally 0,5 m thick siliceous veins, a diverse mineral assemblage rich in various elements (Pb, Fe, Cu, Sb, Hg, Ag, S, As, Cl, Br, I) and minerals was found. In this material cinnabar aggregates reaching 1-2 mm were found, which are of zonal structure according to the microprobe studies, with concentric precipitations of an Ag, S containing phase considered to be acanthite.

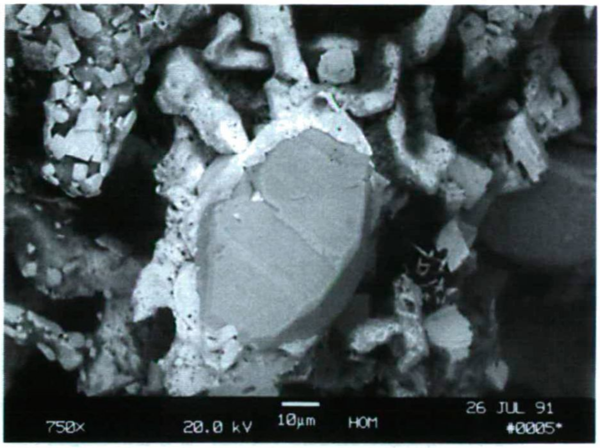

Fig. 6. Acanthite, crusts on calcite. Rudabánya-Andrássy I. Scanning electron micrograph. (HOM collection)

Moschellandsbergite

In the siliceous limonitic ore of the Adolf area referred to above silver coloured 1 mm grains were observed in the environs of cinnabar enrichments. The grains are mostly of xenomorphous appearance, but rarely occur as idiomorphous crystals with smooth edges, mainly of dodecahedral habit. Its 4-8 mm hexahedral crystals and crystal aggregates were also observed in thin sections. The grains and crystals are commonly found as pathes black with tennantite and their surfaces encrusted by malachite. The crystals are often accompanied by mercury drops. Thus, moschellandsbegite is likely to be considered to have formed from the Hg, content of the tennantite and the high Ag content of the formation. The results of the microprobe studies show a right correspondence to those in the literature (ANTHONY et al., 1990) is seen (Table 3). The strongest reflections of moschellandsbergite have appeared on the X-ray powder diffraction image (Table 4).

TABLE 3

Chemical composition of moschellandsbergite from Rudabánya-Adolf (Wt%)

Hg	68,8	70,2
Ag	31,2	29,8
	100,0	100,0

Analyst: Á. KOVÁCS

TABLE 4

X-ray powder diffraction data of bromargyrite and chlorargyrite from Rudabánya-Adolf

bromargyrite, chlorargyrite Rudabánya-Adolf		bromargyrite JCPDS 6-438		chlorargyrite, bromian JCPDS 14-255	
d(Å)	int (obs)	d(Å)	int	d(Å)	int
2.866	100	2.886	100		
2.826	69			2.810	100
2.029	76	2.041	55		
2.005	41			1.989	60
1.662	25	1.667	16		
1.625	17			1.623	30
1.256	15			1.258	40

Made in Dept. of Mineralogy, Landesmuseum Joanneum (Graz)

Chlorargyrite

Chlorargyrite is a member of the mineral assemblage of the siliceous limonitic ore type of the Adolf area with other silver halides. It was found in the small cavities of the ore, as clear, greenish-yellow or light magenta mostly octahedral crystals and amorphous aggregates. The crystals change colour exposed to light and turn grey and black. Oriented intergrowths are common (*Fig. 7*), fine grained aggregates and crust-like coatings were also found. Based on the EDX images the chlorargyrite of Rudabánya sometimes contains bromium (*Fig. 8a*). The four strongest reflections of chlorargyrite have appeared on the X-ray powder diffraction image that corresponds to the chlorargyrite, bromian of the JCPDS standards, though (Table 5). Its accessory minerals are dominantly quartz, cuprite, cerussite, malachite, barite, goethite, calcite, rarely sulphur, mercury, and according to X-ray and microprobe studies pale yellow powder-like bindheimite. The matrix of the ore also consists of hematite ans cinnabar.

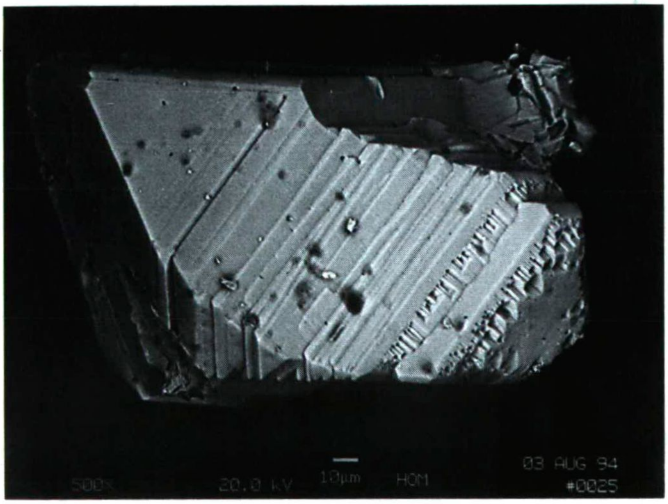

Fig. 7. Chlorargyrite, epitaxial octahedral crystals. Rudabánya-Adolf. Scanning electron micrograph. (HOM collection)

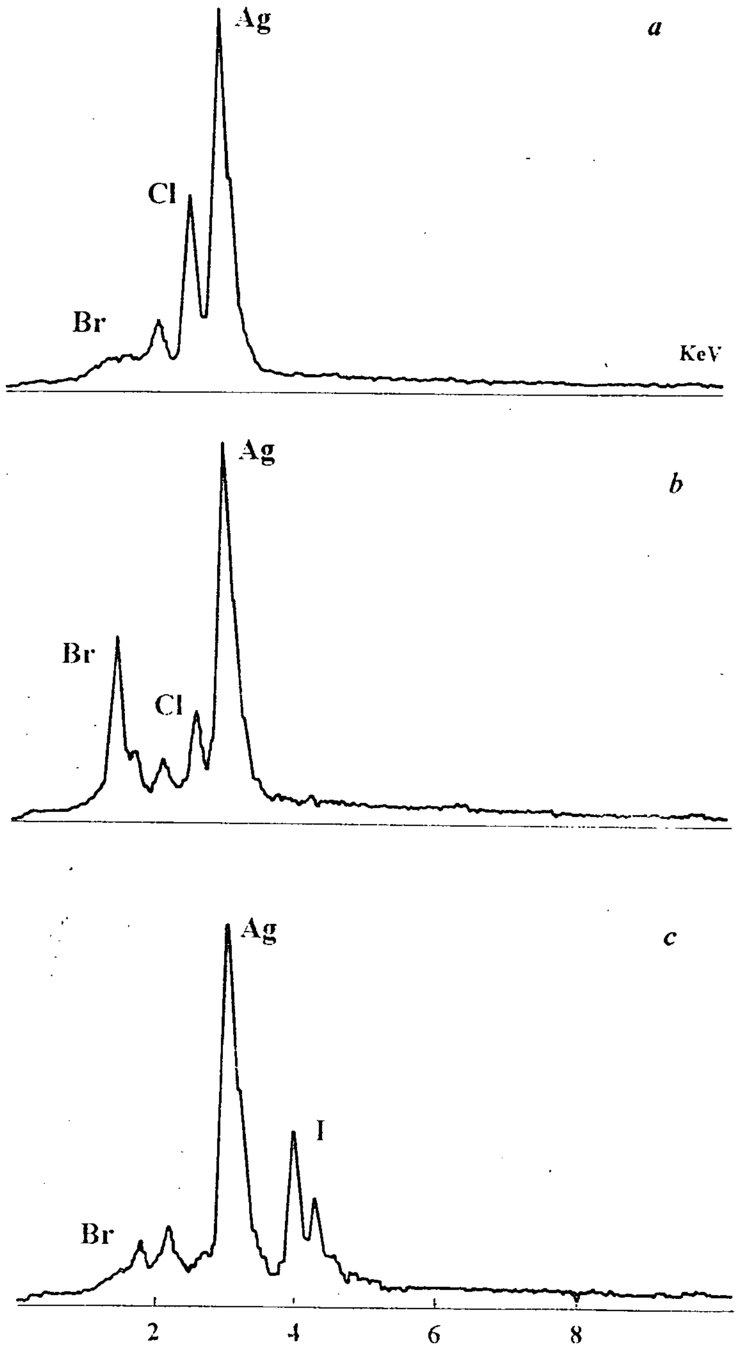

Fig. 8. Energy dispersive X-ray spectrum of chlorargyrite, bromargyrite and iodargyrite from Rudabánya-Adolf.

TABLE 5

X-ray powder diffraction data of moschellandsbergite from Rudabánya-Adolf.

moschellandsbergite			moschellandsbergite	
Rudabánya-Adolf			JCPDS 11-0067	
d(Å)	int (obs)		d(Å)	int
			4.080	10
			3.530	10
3.34	15	Q		
2.89	10		2.880	30
2.68	12		2.670	40
2.41	31	Q		
2.36	100		2.360	100
2.270	8	Q		
2.239	6		2.240	30
2.137	6		2.130	30
1.966	8		1.965	40
1.831	4		1.828	20
1.669	9		1.667	40
			1.629	10
1.586	2		1.583	10
1.541	3		1.547	20
1.481	5		1.478	30
1.449	5		1.447	40
1.417	6		1.419	40
1.376	7	Q		
1.366	15		1.365	70
1.341	13		1.341	20

Made in ALUTERV-FKI (Budapest)
Q= quartz

A different chlorargyrite occurrence in the oxidation zone is also known. The X-ray powder diffraction and chemical studies revealed the presence of pale green, massive paratacamite in the fissures of limonitic ore on a rock specimen the accurate place of occurrence of which is not known (SZAKÁLL, 1992). During the SEM examinations chlorargyrite dendrite aggregates were observed on the surfaces of the tabular paratacamite crystals.

Bromargyrite

Accompanying chlorargyrite, bromargyrite occurs as clear or greyish-white aggregates, crusts and rarely cubooctahedral crystals, reaching 1 mm (*Fig. 9.*). According to EDX studies chlorargyrite always contains more or less bromium, but phases containing dominantly bromium also occur (*Fig. 8b*). By the microprobe studies made on sections of crystal aggregates it was pointed out that the crystals had grew in several stages, with formation gaps between each generation. These studies did not show any order in the chlorine and bromium content, i.e. the bromium distribution image on wich among chlorargyrite reflexions of three highest peaks of bromargyrite are seen (Table 5).

Iodargyrite

In the cavities of the silicious limonitic ore containing chlorargyrite, bromargyrite, yellow, hexagonal tabular crystals greater than 1 mm with very intense lustre can be observed very rarely. The colour of the crystals does not change exposed to light. The forms of the hexagonal base and prism are present on the crystals (*Fig.10*). Crystal growth phenomena can be seen on the base faces. Even rarer, its short, columnar crystals, reaching 0,5 mm were observed.

By EDX studies, I, (Br) and Ag are the only compounds of the crystals (*Fig. 8c*). Having regard to the chemical composition and the physical characteristic, the crystal morphology and the paragenesis, these crystals are considered to be iodargyrite.

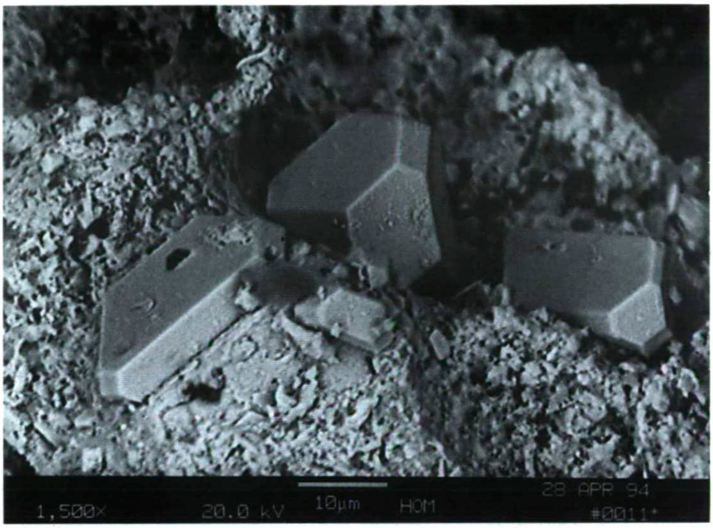

Fig. 9. Bromargyrite, cubooctahedral crystals. Rudabánya-Adolf. Scanning electron micrograph. (HOM collection)

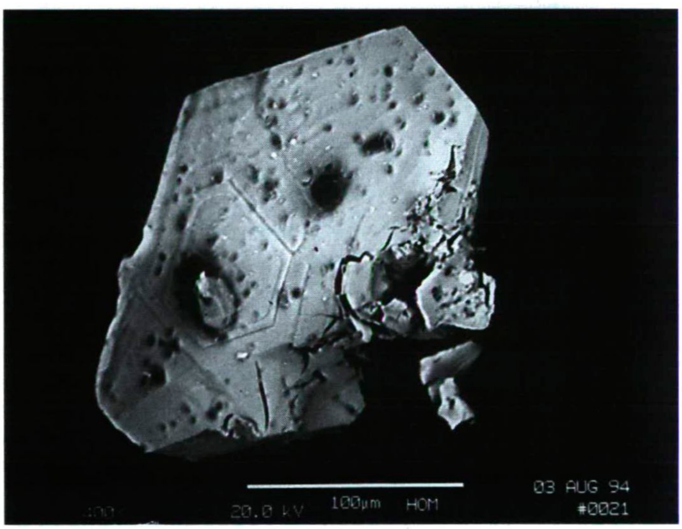

Fig. 10. Iodargyrite, tabular crystal. Rudabánya-Adolf. Scanning electron micrograph. (HOM collection)

Unidentified silver sulfhalides

AgHgSCl mineral (RB-01)

A mineral occurring in clear or yellowish, elongated, columnar crystals smaller than 1 mm with diamond lustre is found very rarely in Ag halide paragenesis (Adolf area). According to the EDX analysis, Ag, Hg, S, Cl are present in the crystals. Unfortunately, structure examinations were not made on the sample, because of its extremely small quantity.

AgHgSBr mineral (RB-02)

On the southern side of the Andrássy-I area in lower Villanytető openings, the below paragenesis was observed in barite veins. Galena, sphalerite, tennantite, heteromorphite? occur as primary minerals forming patches and veins in the barite mass. The weathering of these minerals resulted in the formation of the secondary cerussite, bindheimite, goethite, cinnabar, hematite, malachite and rarest a greenish-yellow powder-like mineral, the surface of which turns dark grey when exposed to light. This phase contains Ag,Hg,S,Br according to the EDX analyses.

Further examinations are still made on these interesting samples.

ACKNOWLEDGEMENTS

We thank ISTVÁN SAJÓ (ALUTERV-FKI, Budapest) and WALTER POSTL (Landesmuseum Joanneum, Graz) for the X-ray diffraction studies. We are grateful to MIKLÓS GÁL (Komló), SÁNDOR KLAJ (Pécs), CSABA PAPP (Pécs) and GYŐZŐ VÁRHEGYI (Budapest) for providing us with some of the samples examined.

The helpful cooperation of GÁBOR HERNYÁK (Rudabánya), retired chief geologist, during the groundwork through years is also gratefully ackowledged

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Manuscript received 21. Aug. 1994.