

THE RUDABÁNYA-MARTONYI MINERALISATION: POSSIBLE GEOCHEMICAL RECONSTRUCTION

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Abstract: About a new aspect of the Rudabánya-Martonyi ore forming processes in light of ground follow-up geochemical investigations. Geochemical anomalies identified by the national geochemical surveys are being investigated in detail in order to define the type, origin and extent of these anomalies. In 2007–2008, surroundings of sample No. 2603 with anomalously high precious and heavy metal content (e.g. silver, mercury, lead and antimony) collected in the Szalonna area was studied in detail. We have compiled possible genetic model of Rudabánya-Martonyi mineralisation. To our mind the metals derived in Campilian–Anisian (Gutensteinian) formations redeposited from Lower Triassic sediments. The source of barium is the evaporite. The formation of mineralisation was separated in three geochemical stages; we haven't enough data for finer partition. The anomaly associated with the denudation of the abandoned Martonyi ore mining waste dumps was identified and geochemically characterised. Results show that the identified element association is different from that found in sample No. 2603. Field evidence suggests that significant amount of communal wastes has been deposited in the Martonyi Creek catchment. This may explain the geochemical outlier found in the national survey. At the same time, the Martonyi mineralization has been delineated in the south and east.

Keywords: geochemical anomalies, metals, hydrochemistry, iron ores, copper ores, barite deposits, lead-zinc deposits, sulfidation, desulfurization

1. PREVIOUS INVESTIGATIONS

We had controlled the outlier value measured on Szalonna-karst from anomalous samples of national geochemical survey (Ódor et al. 1997, Fügedi et al. 2007). We have detected higher content of mercury, lead and antimony than geochemical background values of region and the content of silver, zinc and arsenic was very close to the top border of background values in the sample No. 2603 with anomalous concentrations of Hg, Mn, Pb, Sb collected for characterization of Hungarian mountainous areas.

It appeared from element content that the reason of anomaly could be the erosion of the margin of the known Martonyi mineralisation area, but the extreme elements (Hg, Pb, Sb) of sample No. 2603 were considerably different from anomalous element contents (Mn, Pb, As, Ni, Zn) of the samples collected from the similar mineralized formations of the Rudabánya-Mts. (Fügedi et al. 2007, Fügedi 2008). For the control of our hypothesis we have compiled a possible

geochemical model of the Rudabánya-Martonyi mineralisation on the score of the literary data (Pantó 1956; Csalagovits 1973; Hadobás 1987; Szentpétery & Less 2006), and we have tried to define the territory and type of anomaly with collecting supplementary samples close to non-disturbed area by the antropogenic impact of the abandoned mine.

2. GEOGRAPHIC POSITION OF RUDABÁNYA-MARTONYI MINERALISATION

We regard the complex mineralisation known in a geological sense Rudabánya-Mts. as "Rudabánya-Martonyi mineralisation" in this article. The mineralisation has two mineral groups: carbonatic iron ores and sulphidic base metal ores.

The Martonyi area is located approx 40 km north from Miskolc and approx 10 km northeast from Rudabánya (Fig. 1). There is a known, genetically conformable mineralisation approx 2 km east-northeast from this area in an open pit opened

between the Kis- and Nagy-Rendek Valleys. The upper, limonitic part (brown iron ore) was exhausted and the mine was closed in 1951. The recently registered reserves (siderite+ankerite+brown iron ore) are 200,000 t.

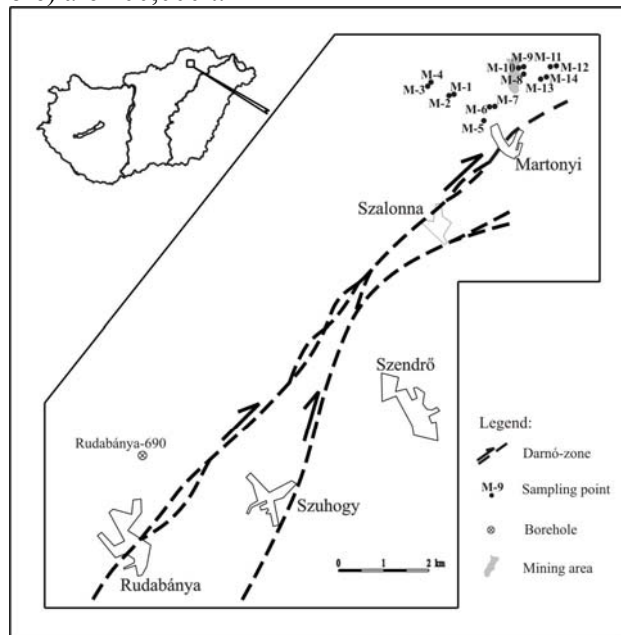


Figure 1. The location of the studied area.

3. GEOLOGICAL-GEOCHEMICAL MODEL OF RUDABÁNYA–MARTONYI MINERALISATION

3.1. Geological description

The Permian evaporitic beds are the oldest formation of this zone, underlaying of Seisian aged sandstone and red-stripped marl, the Campilian blueish gray–winered stripped marl and grey laminated marl, laminated limestone and dolomite and the Anisian aged Gutenstein-type dolomite (Pantó 1956).

The matrix of the Lower Triassic sandstone contains variable amount of sedimentary iron carbonate, which “highly increases at certain sides” (Pantó 1956). Amount of zinc and lead is anomalous high in the Lower and Middle Triassic sediments (Kupi et al. 2009). Because the notable higher metal contents of the sediments, and the inventory of the elements which form the mineralisation (i.e. Fe, Cu, Zn), the andezito-bazaltic character of the former denudation area is presumed.

We agree the opinion of Csalogovits (1973), which has affirmed, that neither for set up of the mineralization, nor for the moving fluids, no magmatic activity was necessary (i.e. the ones presumed by Pantó 1956). Inasmuch, we do not accept the hypothesis of a single ore forming stage

for different ore types, as it was proposed by the above mentioned authors. Existing of baritic mantle of mineralised blocks isn't explained with the one-phase model; it means that the Ba was mobilised after the main stage of mineralisation. Mobilisation of iron and base metals or rather barium demands very different chemical environment: the base metals and iron can mobilise in sulphatic water but the barium in such environment stays insoluble. That's why Csalogovits took the evaporitic beds over the impermeable Campilian marls but they were and are under them.

Lower and Middle Triassic sediments were deposited in a more or less confined gulf overlaying on the evaporitic beds. The section doesn't vary from sequence at Bódva facies (Less et al. 1988, Szentpétery & Less 2006) area: the original color of rocks is grey, which shows the anoxic environment. Therefore, we presume that the main part of iron and non-ferrous metals were as sulfids in the source sediment.

Tectonic movements permit the washout of sediments and the mixing of the different chemical types of water.

3.2. Mineralisation

By tectonic movements the impermeable marls between the two permeable formations were crushed. The some hundred m large blocks of rigid dolomite were pressed in the plastic, laminated marl (as it was observed in mining works). In the Martonyi mine not only iron impregnated blocks, but metamorphic Steinalm limestone and fine grained dolomite blocks were described (Pantó 1956, p. 470.). These exist in the Darnó Zone, too (Less et al. 1988).

The water coming from higher part of margin of the basin could form the ascending water movement in the middle of the depression. This movement's zone has three geochemical stages:

1. In the first stage the chemical character of pervious Lower Triassic formations (reductive, sulphidic) has been different drastically from the character of leaching water (oxidative hydrocarbonatic type). Therefore a redox-front was formed from the basin's margin to the centre as the (mainly biogenic) sulphidic minerals of sediment were oxidized. The cations became dissolved in the more and more sulphidic and more acid water and they remained dissolved as long as ascending water reached the marl and replaced dolomite blocks. In this slightly reductive environment the acid water bit by bit released carbonatic minerals and the ions of the metals were precipitated on the place of this

minerals — one part of iron as iron-carbonate the base metals mainly as sulphates.

The great part of sulphate content came from evaporites. It has importance from mineralization's point of view because barium couldn't mobilise as long as water had been sulphatic.

2. In the second stage the ascensional water remained hydrogen-carbonatic. The barium was dissolved in this stage. When this solution reached the zone of mineralization (with high sulphur content), the barium precipitated as barite. This is the reason that the margin of mineralised blocks is baritic.

3. After cessing of the intensive leaching, by repeated mobilisations, crystallizations and dehydratations, the sulphide ore may be formed. For this reason, we are able to present some general considerations:

The originally sulphatic part of iron became carbonatic when the oxidizable sulphid minerals run out at the source area (the supply of sulphur ended).

The successive levels of iron, respectively the lead-silver, and — on the top — the copper, and the zinc bearing ones (Földessy et al. 2008) were formed replacing the carbonatic host rocks.

3.3. Tectonic features

The known occurrences of Rudabánya–Martonyi mineralization are confined to Darno tectonic zone. The western border of mineralisation at Martonyi is a huge tectonic line with NNE–SSW strike. Here the ore-bearing Lower Triassic schist is touching with ore-free Middle Triassic limestone. The most rich ore bodies were attached to an overlying shale horizon close to the tectonic lines (Pantó 1956).

In Rudabánya, the main structural lines have the same orientation, but following the mineralization, the tectonic zone remains still active. Thus, the ore bodies were broken and moved, mainly horizontally (after the pattern of the stripped fault mirrors) and subsequently, in vertical plane, displacing the ore blocks with barite bearing margins (Pantó 1956).

Inasmuch as the main tectonic (and mineralisation) directions have NNE-SSW strike-directions regarding to Darno Zone in ore mining both in Rudabánya and Martonyi, we presume that the tectonic crushing needed for mineralisation has formed in this structural zone too. If we accepted the existence of this main structural zone beginning in the Paleogene (Fodor et al. 2005) then the beginning of mineralization couldn't happen earlier. Ore bearing rocks surely existed in the beginning of

Miocene: on the NW margin of open pit Rudabánya mine in the section of borehole Rudabánya–690 between 175.8–218.7 m there are ore bearing rock-pieces in an Early Miocene coarse debris (over the Szécsény (Putnok) Schlier Formation and under the partly uncertain aged Bretka (?) Formation).

The age of last phase of mineralization is Pliocene regarding to newest data (Földessy, oral communication).

3.4. The characteristic elements

The main elements of Rudabánya–Martonyi ore deposit are the following: Fe, Mg, Pb, Zn, Cu, Ba; while the accessory elements are Cd, Ag, Tl, Ge, Sb, Hg, As, Au, V. For such elements which were not analysed in our laboratory, we used the published analytical data (Pantó, 1956).

The spatial distribution of these elements shows a zonal structure sterile limestone → dolomite → ankerite → sideritic ore.

3.5. Genetical considerations

Rudabánya-Martonyi type ore could forming places where sediments, coming from anoxic basic rocks overlying the evaporitic lagunar sediments, containing many base and ferrous metals were deposited. Carbonatic beds were deposited over the clastic formation. In border of the basin, carbonatic rocks (or clastics with carbonate matrix) should situate, namely mineralisation demands oxygene bearing, hydrocarbonatic water. The connection between these sedimentary rocks was realized by tectonic movements; the condition of the existing of ascensional water is the relative basin position. The Rudabánya-Martonyi mineralization may be formed in the Paleogene stage of the activity of Darno Zone. It reached its actual place and position during the Lower or Middle Miocene.

It is true, that the stratigraphic and tectonic position of anomalic sample No. 2603 accompie all of elements of secondary dispersion area of Rudabánya-Martonyi mineralization, but its location excludes any relation with the former Martonyi mine and dump.

4. GEOCHEMICAL INVESTIGATION IN SURROUNDING OF SZALONNA AND MARTONYI

4.1. Fieldworks

We had investigated the vicinity of sample No. 2603 with field survey. There are some moderately

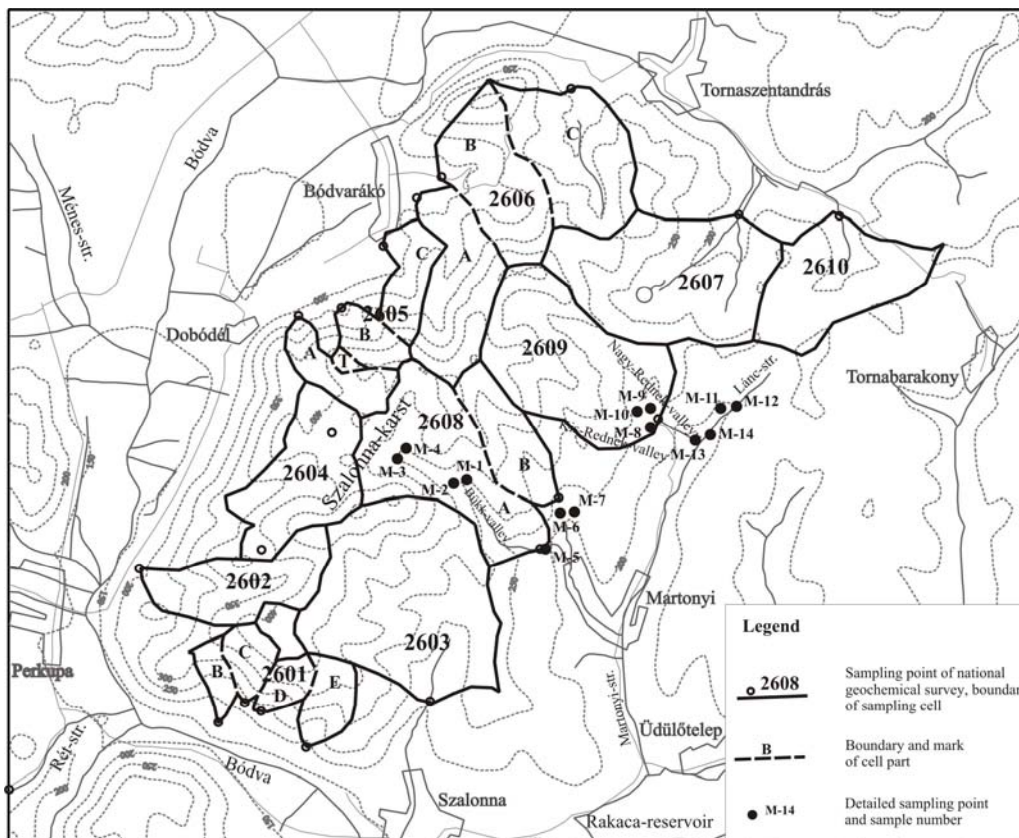


Figure 2. Map of Martonyi sampling area

disturbing anthropogenic impacts (mainly communal waste) westward from Martonyi. Because in the right affluents of the valley, no stream sediment were observed, we had collected 13 samples (Fig. 2) partly under the former mine, partly from the territory between the mine and the place of sample No. 2603, without notable anthropogenic impact.

4.2. Laboratory investigations

Trace and main elements (Table 1-2.) were analyzed in the Laboratory of Geological Institute of Hungary with ICP-AES method.

4.3. Data processing

The exceeding and anomalic data were separated cutting off the histogram at the local minimum; therefore the numeric investigation of homogeneity (Dixon-Messey criteria) wasn't necessary. Because the distribution of most of the elements is quite irregular, the common movement of elements was tried to know by principal component analysis.

The geological processes change the geological environment towards its own state of equilibre. Because the geological processes run still slow, these equilibria practically never will be

accomplished. Thus, most of formations show the fingerprints of some processes (Fügedi et al. 2006). Among them, the action of most of geological factors may be described with those of the principal components.

The principal component analysis was used for variables with normal distribution. The significance levels are invalid if the variables hadn't normal distribution, and they give false results if the distributions are different or asymmetric. Distribution of all variables should transform to symmetric and the same type, for eliminating a part of these failures. The best method is to replace the original concentrations with their ranks. In this case all of derived variables will have discrete uniform distribution and we can follow our processing on rank correlations instead of Pearson's linear correlation method. Unfortunately the test with SPSS PC+ software used by us we can fulfill only on the base of Spearman's rank correlation coefficients (i. e. linear correlations of ranks). Therefore, though the results of analysis of principal components are realistic but the given significance levels are informative. The statistically correct methods were the test based on the Kendall's rank correlation method but the mistake of our method isn't too high.

Table 1–2. Element concentrations (mg/kg) in the samples from the Martonyi area

Sample No.	Li	Mn	Mo	Ni	P	Pb	S	Sr	Ti	V	Zn
MART–1	6,54	1029	0,577	22,5	803	47,4	550	19,2	63,0	15,7	92,4
MART–2	5,35	859	0,548	21,9	795	36,2	335	19,4	81,0	19,8	91,0
MART–3	87,01	930	<0,2	19,8	749	33,4	343	18,4	105	22,2	87,6
MART–4	4,31	819	<0,2	18,1	657	31,2	1215	14,2	61,1	17,8	72,5
MART–5	8,48	1000	0,456	21,2	719	33,3	195	37,5	59,3	24,0	90,4
MART–6	8,91	1130	<0,2	33,2	607	47,3	468	13,2	61,1	42,1	116
MART–7	4,28	1530	1,58	31,3	333	47,4	939	46,7	47,0	25,3	98,7
MART–8	16,4	1998	0,465	37,2	866	51,4	656	34,5	72,0	30,7	117
MART–9	11,3	2845	0,433	30,1	646	184	940	70,2	52,0	22,9	201
MART–10	14,2	898	0,835	26,6	612	32,8	259	57,3	96,0	29,4	77,9
MART–11	18,7	1105	1,12	48,1	587	31,6	436	31,1	322	32,4	84,1
MART–12	16,0	429	1,57	41,3	899	29,6	428	21,5	23,2	28,0	75,2
MART–14	14,2	5078	1,37	58,0	907	38,3	551	33,7	17,0	29,9	115

Sample No.	As	Ba	Cd	Co	Cr	Cu	K	Na	Al	Ca	Fe	Mg
MART–1	8,03	205	0,174	9,36	17,8	147	3233	398	7,56	21,0	22,1	1,96
MART–2	8,19	161	0,242	10,9	19,2	109	3232	419	8,57	8,25	21,5	1,96
MART–3	8,82	199	0,112	12,0	20,2	50,5	3270	316	10,4	7,37	22,1	1,81
MART–4	5,94	200	0,173	13,0	17,1	53,7	2455	276	6,97	6,02	21,6	1,06
MART–5	10,7	156	0,231	12,1	23,2	30,6	2600	162	8,36	41,3	23,8	6,23
MART–6	16,7	172	0,333	15,2	34,2	52,2	2207	154	14,4	7,22	29,2	2,88
MART–7	20,0	144	0,434	18,5	25,3	43,9	1807	247	7,02	19,2	32,6	4,69
MART–8	17,3	1003	0,433	14,9	31,8	98,5	4073	381	16,3	12,4	33,0	3,79
MART–9	36,2	2785	0,621	12,1	23,0	324	2330	206	10,1	68,3	54,8	9,88
MART–10	10,0	158	0,434	9,03	27,7	30,7	3662	257	15,1	88,2	21,1	47,5
MART–11	10,6	204	0,528	12,0	32,4	23,9	3055	612	17,0	4,24	22,0	2,68
MART–12	11,8	203	0,259	6,74	295	40,7	1350	172	13,4	3,14	28,8	2,91
MART–14	14,9	322	0,731	15,2	103	40,1	815	183	11,4	5,93	33,6	2,90

The analyses are performed in the Laboratory of Geological Institute of Hungary.

4.4. Results of statistic tests

Comparison of the new data with the background values on mountainous areas of Hungary (Fügedi et al. 2007) shows that concentration of many elements is far over rate of areal background. For interpretation of this phenomena we have to take into account the fact that the background values were determined from cca 4 km² catchment areas, while the new taken samples characterize only about 1 km²; thus, the variability

will higher when the represented territory is smaller (Fügedi et al. 2006).

The expected values in stream sediment samples which come from some km² catchment areas only on a few cases show the features of the bedrock on a territory with exceptionally homogenous geological construction (Fügedi et al. 2007). On the neighboring aquiferes with carbonate and silicate bedrocks the background is practically not different, i.e. it is homogenous in each region. Contrarily geochemical background values of

regions can be rather different because of differences in the overlying young, soil forming materials (loess and rhyolitic tuff).

It is clear, that among our samples, a few anomalous values appear for Mn, Ni, Cu, As, and Ba, each for two samples. These contents do not cover neither the theoretical anomalies, nor the values of the *anomalous* sample No. 2603. Here, the anomalous concentrations appear in different element-pairs.

Variance explained by principal components isn't too high considering small number of samples. Only the first two components (component1: 33,5%, component2: 20%) have practical significance: they explain more than half of total variability.

The representative elements of the 1st and 2nd principal component:

* component1: As, Cd, Fe, Ni, Mn, Cr (all with positive component score coefficients, in descending order);

* component2: Cu, Pb, S, Zn (with positive coefficients, in descending order); Al, Li, Cr (with negative coefficients, in descending order of absolute values).

A marking of geological processes' intensity is deducible from territorial distribution of principal component scores.

4.5. Interpretation of results

All great (higher than 0.6) positive scores of the first principal component (samples 6–9. and 14.) appear southward and southeastward from former mine, mainly in the lower stage of the watercourses. It means that the negative values (samples 1–4.) come down westward from the mine (under the ruins of the monastery). Samples with second principal component score higher than 0.9 (samples 1., 4., 7., 9.), were collected from the upper stages of small sidevalleys. The samples with negative second principal component come from the lower stages of the valleys where the waterflow is very slow.

Elements determining first principal component — Fe, Mn, Cr, Ni, As, V, Cd (Zn) — squarely are elements of the limonite colloid precipitated in the intergrain space at oxidative circumstances:

* The Mn, Cr, Ni, V are classic siderophile elements

* The As accumulated mostly on the oxihydroxids of iron on the surface or near the surface (Csalagovits, 1999)

* The Zn (and Cd) can step into place of iron with isomorphous replacement.

The positive values of the first principal component are indeed in the samples with the highest iron content.

In the second principal component two groups of elements appear. The first one is formed by the positive values of the Pb, Cu, Zn, and S. They are the elements that represent the undestroyed sulphides. In the second group, negative values of elements such as Li, Cr and Al take place. The Li and Al are coming from clay minerals; however the K is missing and the Cr is a stranger apparition in this group. It shows that the little number of samples can make disturbance in interpretation of second principal component. Considering these uncertainties it seems to be acceptable, that the second principal component is positive on the step sectors of watercourse, because the sulphide minerals dissolve more slowly and the clay minerals are leached off. The second principal component is strongly negative in the channels of permanent watercourses and on these segments in which the water flows frequently.

A possible conclusion is following from the fact that the weathering sends many sulphide minerals in alluvium, that the Martonyi mineralisation is surrounded by spacious, geochemically easy detectable dispersion halo. This fact is confirmed by the distribution of concentration for Cu: all values which are higher than background (samples 1–4., 6., 8. and 9.) are situated in the valley-system of Bükk-, Kis-Rednek-, and Nagy-Rednek-valleys. On the other hand, we have not anomalous Cu-concentrations in the catchment area of Lánç-valley, up to mouth of Nagy-Rednek-valley. This dispersion halo is weak; therefore the sedimentation plays most important role as geochemical feature of ablation area in forming of principal components.

However, features of the mineralisation are traceable even if not in the first and second principal components. Such type of feature is the extreme (higher than 0.1%) Ba-content of samples 8 and 9. It is very likely on the basis our experiences got in Mátra Mts. that the main part of this high amount of Ba is in barite; barite is the typical gangue mineral of Rudabánya-Martonyi mineralisation. The main mass of barite is located on the segment of valleys, which are favourable for depositing the heavy minerals (so called „placer lenses”), because barite is chemically stable on surficial environment. Definitely the fourth principal component, which has only Ba as considerable, positive element, indicates these places. (The third principal component, which has similar weight as fourth one, shows probably the episodic, complex salt precipitations.)

We didn't find anomalous sample with element-set and principal component similar to sample 2603. The rates of elements (mainly the raport of Hg to other ore forming elements) in that sample are very different from rates of elements in samples collected in Rudabánya Mts. and its surroundings.

5. CONCLUSIONS

1. The Martonyi mineralisation is surrounded by geochemically well developed secunder dispersion area, in wich the Cu, as the second useful element of the Rudabánya-Martonyi mineralization is well contoured. However, the classical sulphocalcophile elements (Pb, Zn, Cd) do not form such characteristics. Here the barite appears too, as classic gangue mineral of the mineralization.

2. Because the anomalies are quite slightly, the factual concentration of elements are strongly influenced by sedimentation in waterflows and, indeed by the meteorologic factors. Therefore, only by the more dense sampling — one sample for 100 m — is able to draw the real contours of anomalies.

3. We made sure on the field that the inhabitants dumped many wastes on the catchment area of Martonyi-rivulet and probable this is the reason of anomaly detected in the course of previous survey (Fügedi et al. 2007). Therefore this cell No. 2603 was excluded from results of geochemical survey of Hungarian mountainous areas.

4. The boundary of the dispersion area at south and at east from the Martonyi mineralization can be draw between Martonyi and Perkupa.

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