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CONTENT AND DISTRIBUTION OF SOME ELEMENTS IN THE MAJOR MINERALS FROM THE TORANICA Pb-Zn DEPOSIT (NE MACEDONIA)

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A b s t r a c t: Latest laboratory examinations on monomineral probes of galena, sphalerite, pyrite and chalcopyrite of the Toranica Pb-Zn deposit studied the most important elements in the deposit. The correlation between characteristic pair of elements was also studied. Mass spectometric analyses determined the content of some fourty elements in the flotation concentration products. The examinations also determined the presence of rare earth elements, particularly those of lead and zinc concentrates.

Mention should be made that examinations carried out by atomic absorbtion on major monomineral probes gave the expected results. Notably, Ag and Bi occur in increased amounts in galenas and are in good correlation as well (of over 90%); the high Fe, Cu, In and Co are noticeable in sphalerites. Pronounced correlation can be noticed with Co-Fe (of over 80%) and In and Fe (proved by Serafimovski et al., 1992). Increased contents of Pb, Zn and Mn, accompanied by In, Ag and Bi have also been established in chalcopyrites. Besides the high contents of Pb and Zn in pyrites, high contents of copper (of over 0.8% Cu) as well as those of Mn, Co and Bi have also been established.

The distribution of elements in the galenas and sphalerites studied indicated that Fe and Cd in sphalerites are most common.

Key words: Toranica deposit; ore metals; ore minerals; association of elements; distribution of elemenets; correlation of elements.

INTRODUCTION

The lead-zinc deposit is poorly investigated with regard to its geochemical associations of elements. It is one of the rare poorly investigated lead-zinc deposits in the Republic of Macedonia and in the world that is in the process of exploitation. Over the past years only contents and distribution of basic ore metals were investigated, first of all those of lead and zinc. Distribution of elements has not been investigated although a number of semi-quantitative analyses were conducted during the stage of investigation and preparation of the mine for operation.

It should also be mentioned that basic data about the geology of the Toranica deposit can be found in the papers of Bogoevski (1990), Bogoevski and Gasteovski (1990), Serafimovski and Aleksadrov (1995), Stankovski (1997) etc. The first data on the minerals and geochemical associations in the Toranica deposit and its vicinity can be found in the papers of Ivanov et al. (1960), Hristova and Eskenazi (1981), particularly in the papers of Serafimovski et al. (1992, 1994, 1997). It is worth mentioning that in terms of its mineral composition the Toranica deposit is of interest for exploration since it is in the process of operation and prives good samples for up to date laboratory studies.

CONTENT AND DISTRIBUTION OF ELEMENTS IN THE TORANICA DEPOSIT

Latest laboratory examinations carried out by the authors determined a rich geochemical association of minerals of about 40 elements, distributed in basic and accompanying minerals as well as lead-zinc ores. Examinations were carried out by atomic absorption and mass spectrometry methods. The examinations included distribution of microelements in individual minerals and products of flotation concentration.

Distribution of elements in galenas

Distribution of elements in galenas of the Toranica deposit was studied with 19 monomineral probes taken from all ore bodies and blocks as the most representative elements in the deposit. The results obtained from examinations by atomic absorption method are shown in Table 1.

The Table shows that galenas of the Toranica deposit occur as concentrators of a large number of microelements some of them in increased contents. Lead content indicates that pure monomineral galena samples of several generations with average content of about 86% lead are obtained. Major accompanying elements are Zn, Ag, Fe, Sb, Cu, Bi, etc. Zinc content in galenas varies from 76 to 3000 g/t or an average of 645 g/t. These high values are probably due to intergrowths of galena and sphalerite. This also refers to Fe, since with some probes, iron content exceeds 1000 g/t that probably is a result of myrmekite intergrowths of galena-sphalerite-chalcopyrite or from iron sulphide residues. Part of the iron in galenas possibly originates from the mechanical presence of sphalerites.

Table 1

Content of microelements in galenas of the Toranica deposit (in g/t)

Probe No	Elements									
	Pb%	Zn	Fe	Cu	Ag	Bi	Cd	Co	Ni	In	Mn
1	85.43	2000	930	14	244	46	82	2	1	8	118
2	85.91	120	270	18	538	628	76	1	1	12	44
3	86.13	200	250	42	562	656	76	1	2	4	22
4	85.82	540	850	42	2360	582	82	2	2	12	32
5	86.19	76	195	20	364	368	74	1	1	8	24
6	86.19	96	150	42	292	64	68	1	1	4	16
7	86.03	900	410	58	472	388	80	0	1	8	26
8	84.94	140	840	2	242	44	72	1	2	4	144
9	86.24	110	150	0	258	32	72	1	2	10	24
10	86.19	92	100	28	302	46	72	1	2	2	14
11	86.07	200	270	4	242	28	72	1	2	4	40
12	85.96	190	320	8	660	920	76	0	1	6	48
13	86.18	100	70	20	392	88	66	0	2	10	18
14	82.24	3000	190	36	220	80	88	0	4	8	272
15	85.20	600	120	28	592	710	68	1	2	10	24
16	86.13	160	100	30	358	268	72	0	1	4	18
17	86.02	88	90	12	596	714	74	0	1	8	20
18	81.80	1100	1100	2	214	44	80	2	2	6	122
19	86.07	220	170	18	440	60	68	2	1	10	14

Analyses are performed in the laboratories of the Sasa Mines, M. Kamenica
Atomic absorption method
Analyst: D. Ivanovska

Copper content in galenas is fairly low amounting to 30 g/t. This is normal for lead-zinc deposits of pronounced character, although part of Cu possibly originates from sphalerite admixtures.

Silver and bismuth occur in permanent amounts in galenas, with pronounced geochemical relationship to galenas. Silver contents vary from 200 to 600 g/t, only in one probe (Table 1, an. 4) silver content exceeds 2 000 g/t that can be interpreted as an abundant probe or one indicating to mechanically mixed minerals.

The contents of Ag are accompanied by those of Bi, but in the galenas of Toranica, unlike other lead-zinc deposits in the country, Bi contents are lower. The lowest recorded values do not exceed 700 g/t.

The Table also displays that Cd, which is not geochemically related to galenas or that their contents are probably mechanically mixed sphalerites, occur in increased amounts. Unlike these, Co and Ni, although not characteristic of galenas, occur in very low amounts indicating that galenas are a product of later mineralization phases. Manganese also occurs in low contents, its overall presence being a result of mechanical presence of some minerals as their concentrators.

Distribution of elements in sphalerites

Latest laboratory examinations included a small number of sphalerite probes since they are fine-grained and closely intergrown with other minerals that makes monomineral separation difficult. Nevertheless, dozens of monomineral probes from all ore bodies were performed except for Block IV. The results of sphalerite examinations with atomic absorption are shown in Table 2.

The Table shows that increased contents of over 10 elements was determined in sphalerites studied. Some of them belong to the group of characteristic ones (Fe, In, Cd, Ni, Co), whereas others are a result of mechanical admixtures. Most of the sphalerites studied are not mechanically pure that is seen from the low zinc present (about 61%) and particularly the high Pb of over 2.5% present in individual probes.

The high Fe content amounting to almost 7% Fe is characteristic of marmatitic kinds formed in earlier phases of the hydrothermal stage of development. This assumption is supported by the high Ni and Co contents concentrated in high temperature minerals.

Table 2

Content of microelements in sphalerites of the Toranica deposit (in g/t)

Elements	Probe No.								
	1	2	3	4	5	6	7	8	9
Zn %	54.40	58.19	59.05	61.74	61.88	61.88	61.62	58.90	60.40
Fe %	5.88	4.75	6.32	3.72	4.36	4.55	4.90	6.91	5.19
Pb	9700	10000	9800	6400	300	25000	1300	600	800
Cu %	8220	3620	2380	1760	1220	2360	800	2720	3620
Cd	4180	4260	4460	4680	4700	4220	4640	4620	4800
Ag	13	10	12	4	1	14	2	7	3
Bi	22	20	19	15	15	17	12	16	11
In	22	12	21	26	23	41	42	63	30
Co	139	115	418	15	30	137	257	437	6
Ni	24	21	61	11	10	20	24	16	12
Mn	5140	4200	4090	3450	10610	4040	4170	2400	3720

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The most permanent occurrence was observed with Cd which is the most indicative element in sphalerites. This is also true with In, although there is a tendency of decrease of the In content in some probes.

In most parts of the Toranica deposit In and Fe, particularly in marmatitic kinds, occur in high contents exhibiting pronounced correlation dependence that was not found with certain number of probes.

The high contents of Cu amounting to 0.8% Cu in some probes are due to the presence of emulsions and metasomatic chalcopyrite aggregates. Such sphalerite types are most developed in the deposit. Other elements also occurring in high contents are Mn that does not exceed 1% Mn due to mechanical admixtures of Mn carbonates.

Distribution of elements in chalcopyrites

The laboratory examinations included four monomineral analyses on chalcopyrite that yielded the contents of some more characteristic elements (Table 3).

Table 3
Content of microelements in chalcopyrites of the Toranica deposit (in g/t)

Elements	Probe No.			
	1	2	3	4
Zn	6500	3500	10200	6000
Fe %	30.77	30.28	32.83	41.41
Pb	15000	9500	4000	4400
Cu %	30.10	30.30	28.70	31.10
Cd	44	23	70	35
Ag	35	30	28	22
Bi	67	77	123	51
In	29	143	43	28
Co	23	23	27	23
Ni	18	16	31	19
Mn	162	178	271	153

Analyses were performed in the laboratories of the Sasa Mines, M. Kamenica
Atomic absorption method
Analyst: D. Ivanovska

The Table shows that atomic absorption examinations discovered the presence of 10 elements occurring in large amounts.

High contents of Pb and Zn occur in chalcopyrite due to the mechanical presence of galena in sphalerite, particularly in sphalerite, developed locally as stars and series within chalcopyrite as a result of solid solutions.

The increased contents of Ag and Bi are partially related to the mechanical presence of galenas and some of the elements are related to chalcopyrites.

The contents of Co and In are within the normal for chalcopyrites of this type of deposits. The content of manganese is due to the mechanical admixtures, mainly Mn calcites.

Distribution of elements in pyrites

Examinations included 16 analyses of monomineral probes on pyrite taken from different parts of the deposit. The results obtained by atomic absorption analyses are shown in Table 4.

The Table shows that high contents of Pb, Zn, Co and Cd, In, Ag and Bi as well as permanent contents of Mn have been determined in pyrites. The high contents of Pb and Zn due to the mechanical presence of galena in sphalerite, the halo of scatter of these two metals in almost all mineral paragenesis are noticeable. Copper was encountered in high contents, in some places to 0.8% Cu due, in part, to intergrowth with chalcopyrite, and, in part, to replacement of Fe and Cu in pyrites themselves. Part of the Ag and Bi determined are due to the primary concentration of these elements during the crystallization phase of pyrites due, in part, to the mechanically admixed pyrites.

Individual high contents of Co, which is a characteristic of the pyrites, developed at high temperatures are also noticeable. The contents of In are due to the normal distribution during the hydrothermal system, because such contents are also characteristic of sphalerites for which it is geochemically related. The content of manganese is constant, similar to other minerals in the deposit.

Table 4

Content of microelements in pyrites of the Toranica deposit (in g/t)

Probe No.	Elements								
	Fe %	Pb	Zn	Cu	Co	Ag	Bi	Cd	In	Mn
1	39.74	6390	900	27	330	72	220	18	21	251
2	43.71	9600	200	163	49	12	130	11	27	16
3	41.16	6000	940	8193	87	15	171	17	39	211
4	43.51	3600	1200	6544	58	6	95	19	27	39
5	42.43	3700	1300	850	85	5	91	33	24	154
6	43.41	6300	700	386	282	28	155	13	25	48
7	40.00	6900	3400	192	228	24	168	36	24	60
8	42.58	4300	1400	91	132	5	97	16	25	728
9	44.44	1500	1700	3597	58	4	91	19	24	19
10	43.58	900	600	7138	81	13	177	13	29	47
11	44.44	1500	1000	1455	164	3	93	14	21	31
12	42.92	2500	9100	975	58	4	100	70	30	131
13	44.20	1300	1200	1256	162	3	94	14	24	62
14	42.04	5100	1500	7377	61	15	215	17	28	40
15	42.79	4200	3800	99	77	4	95	40	19	189
16	43.85	2100	700	824	53	4	104	11	22	17

Analyses were performed in the laboratories of the Sasa Mines, M. Kamenica
Atomic absorption method
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Mass spectrometric examinations of sulphide minerals and concentrates

Latest laboratory examinations are a step forward in understanding the qualitative-quantitative relationships of basic ore metals and microelements in individual sulphide minerals and Pb-Zn concentrates in the Toranica deposit.

The results of mass spectrometric examinations carried out on monomineral probes of galena, pyrite, chalcopyrite and on lead-zinc concentrates of the Toranica deposit are shown in Table 5.

In galenas studied (probe 1), block 2 and (probe 2) block 3 a series of 38 elements was determined. Some elements are determined only qualitatively (Mg, Sc, Cr, Tl), and occur as traces (V, Ni, Ga, Mo, Zr), whereas typomorphic elements (Ag, Sb, Bi, Se, Te) occur as traces of which silver contents exceed the limit of 1×10^{-1} %, like the content of selenium and tellurium. Selenium occurs in high contents (from 250 to 660 g/t) and tellurium (from 180 to 1100 g/t). As these microelements are of economic importance, they are interpreted as an indication that the ore-bearing solutions were generated at depths and are important to the right interpretation of the genesis of the deposit.

The increased contents of copper and zinc are due to mermekite intergrowths between galena, sphalerite and chalcopyrite and/or micron inclusions of sphalerite in galena.

The contents of other elements determined in monomineral fractions are within the normal occurrence of galena for this type of deposits.

Qualitative-quantitative relationships determined in sphalerites are similar to those in galenas, the only difference being that in galenas typomorphic elements (Cd, In, Ga) and elements such as Fe, Cu, Mn etc. occur in increased amounts. The large amounts of iron of 4.61% point out that the sphalerites are of marmatitic type formed at higher temperatures. These ferruginous sphalerites, according to Ivanov et. al. (1960) and Hristova and Eskenazi (1981) are indicators of increased concentrations of indium. Indium content in these sphalerites amounts to 50 g/t and is more abundant than the average indium content in the sphalerites of the Osogovo Pb-Zn deposits. The increased content of copper in the sphalerites studied is due to the presence of chalcopyrite emulsions in sphalerites.

Table 5

Content of microelements in sulphide minerals in Pb-Zn concentrates of the Toranica deposit (in %)

Elements	Probe No.						
	1	2	3	4	5	6	7
Fe	0.145	0.072	4.61	32	>	2.48	5.64
B	tr.	qual.	0.0046	–		0.0003	0.00009
F	0.0012	tr.	–	0.13	0.016	0.0058	0.001
Na	0.038	0.011	–	0.018	0.067	0.025	0.027
Mg	qual.	qual.	qual.	qual.	qual.	qual.	qual.
Al	0.078	0.018	0.0087	>	>	>	>
Si	>	>	0.048	>	>	>	>
P	0.019	0.0002	0.0007	0.0006	0.002	>	0.026
S	>	>	>	>	>	>	>
Cl	0.014	0.015	0.016	0.003	0.0018	0.002	0.008
K	0.066	0.018	0.0038	0.03	>	>	>
Ca	0.069	0.007	0.0055	0.028	0.015	>	>
Sc	qual.	qual.	qual.	qual.	qual.	qual.	qual.
Ti	0.006	0.005	–	qual.	qual.	0.078	0.038
V	tr.	tr.	–	0.00004	0.0002	0.003	0.001
Cr	qual.	–	–	qual.	0.01	0.0068	0.02
Mn	0.02	0.022	>	0.004	0.008	>	>
Co	0.0004	0.00008	0.003	0.0002	0.001	0.012	0.008
Ni	tr.	tr.	tr.	tr.	0.02	tr.	0.053
Cu	0.038	0.018	0.094	>	0.043	>	>
Zn	>	0.037	>	>	>	>	>
Ga	tr.	tr.	0.0007	0.00017	0.0003	0.0008	0.0008
Ag	0.0006	0.0001	0.0001	0.018	>	0.041	>
Se	0.066	0.025	qual.	qual.	qual.	0.012	qual.
Rb	qual.	tr.	tr.	qual.	0.001	qual.	qual.
Sr	0.0004	0.00048	tr.	qual.	0.007	0.005	0.022
Y	0.00004	tr.	–	qual.	0.0008	0.0005	0.0004
Zr	0.00008	tr.	–	–	0.0002	0.003	0.0033
Nb	–	–	–	–	0.00001	0.0002	0.0002
Mo	tr.	tr.	–	–	tr.	0.002	0.0028
Ag	>	>	0.00018	0.0075	0.0007	0.064	0.012
Cd	0.042	0.041	>	0.017	0.08	0.027	>
In	0.00018	0.0002	0.005	0.003	0.0001	0.001	0.001
Sn	0.00042	0.0003	0.0006	0.002	tr.	0.002	0.002
Sb	0.058	0.075	0.00016	0.0038	0.002	0.032	0.002
Te	0.11	0.018	–	–	–	0.012	0.0008
Cs	–	qual.	tr.	tr.	tr.	0.0001	–
Ba	0.038	qual.	0.003	0.0001	0.0002	0.003	0.003
La	–	–	–	–	qual.	0.0002	0.0003
Ce	–	–	–	–	0.00001	0.0005	0.0005
Pr	–	–	–	–	qual.	0.00008	0.0001
Nd	–	–	–	–	qual.	0.0003	0.0005
Eu	–	–	–	–	–	0.00002	0.00001
Sm	–	–	–	–	–	qual.	0.00008
Gd	–	–	–	–	–	0.00003	qual.
Tb	–	–	–	–	–	qual.	qual.
Dy	–	–	–	–	–	0.00001	qual.
Ho	–	–	–	–	–	qual.	qual.
Er	–	–	–	–	–	qual.	qual.
Tm	–	–	–	–	–	qual.	qual.
Yb	–	–	–	–	–	qual.	qual.
Hf	–	–	–	–	–	qual.	–
W	–	–	–	–	–	0.00005	0.0001
Au	–	–	–	–	–	qual.	–
Tl	qual.	qual.	–	0.0002	0.00008	0.001	0.00007
Pb	>	>	0.028	>	0.1	–	–
Bi	>	0.035	0.000001	0.0008	0.0001	0.04	0.002

1. PbS – monomineral; 2. PbS – monomineral; 3. ZnS – monomineral; 4. $CuFeS_2$ – monomineral; 5. FeS_2 – monomineral;
6. Pb – concentrate; 7. Zn – concentrate

Fluorine and chlorine have also been discovered in chalcopyrites. Their presence is important to the interpretation of the conditions of development. The presence of Ag, As, Sb, In and the absence of Se and Te indicate that they are later generation chalcopyrite developed at lower temperatures.

Besides fluorine and chlorine present in pyrites, a certain disproportion in the geochemical association of elements was also determined. Examinations revealed the presence of V, Cr, Ni, Co, Cu, Cd, etc. (in some places in increased contents), but very high contents of As (of over 1×10^{-1} %) and, in part, antimony were determined as well.

The relationships are probably due to the frequent and pronounced changes in the physico-chemical conditions of hydrothermal ore-bearing fluids. The presence of light rare earth elements (La-Nd series) was also determined.

The concentrates of lead and zinc examined yielded the same relationship of the geochemical association of elements determined for galenas and sphalerites. The presence of the group of rare earth elements associated with other mineral kinds was found, in contrast to galenas and sphalerites, where it was not found. Elements typical of galenas and sphalerites occur as well.

It can be inferred that the examinations carried out determined a complex geochemical association of elements in the Toranica deposit, some of which have economic importance, some have specific geochemical features but most of them help to understand the conditions for the development of the mineralization in the deposit.

CORRELATION OF ELEMENTS

The low level of investigation, from the point of view of its geochemistry, does not allow a complete study of the correlation of elements. The fact that very few spectrochemical examinations have been performed points out that the geochemical features of elements both in the ore and individual minerals are not known. Latest laboratory examinations, however, carried out within the project made it possible to understand some relationships of some elements.

Correlation of elements

There are few data about the relationships of elements in sphalerites and their correlation. Attempts have been made to discover some relationships.

Correlations between elements determined within sphalerites have been studied for several pairs such as Co-Ni, In-Co, Fe-In, Fe-Cu, In-Cu etc. The contents of individual elements by the use of regression analysis – linear method was used in the study of correlation and linear dependence.

The results obtained by regression analysis indicate that in all pairs there is certain correlation, but of varying intensity or degree of correlation. The highest correlation coefficient of $q = 0.811$ was determined with the Co-Fe geochemical pair, which means that the degree of correlation was over 80 % pointing out that there is certain functional dependence within the elements. Cobalt and iron are geochemically close elements, so their geochemical cycle of evolution made their connection possible. However, they probably concentrated in earlier sphalerites that correspond to marmatitic kinds (Fig. 1).

The correlation dependence of normal trend and coefficient $q = 0.651$ was determined with the Co-Ni pair. The degree of correlation is over 65% providing a pronounced correlation relationship between these two geochemically close elements that can always be found in sphalerites. Such correlation relationships are normal for this type of element pair although the trend of distribution does not have a continuity indicating to the change in the regime of concentration of individual elements during the phase of separation of host minerals from hydrothermal systems (Fig. 2).

Dependence was determined with the pair In-Co, the coefficient of this geochemical pair being lower, amounting to $q = 0.500$, or providing correlation of 50% which can be interpreted as normal dependence but of varying trend (Fig. 3).

The lowest correlation dependence was determined with the Fe-Ni geochemical pair, that can be seen from the correlation diagram. The correlation coefficient with this pair is $q = 0.404$ and the degree of correlation over 40% that is very low for such geochemically close elements that accompany sphalerites.

Serafimovski et al. (1993) determined that, locally, this geochemical pair in the Toranica deposit has a pronounced correlation dependence. Poorly expressed correlation discovered within these sphalerites, is probably due to the small number of samples studied and the number of analyses conducted.

It should also be mentioned that pairs of opposite correlation dependence within the sphalerites studied, and a group of elements in which no mutual dependence determined that their copresence is probably accidental.

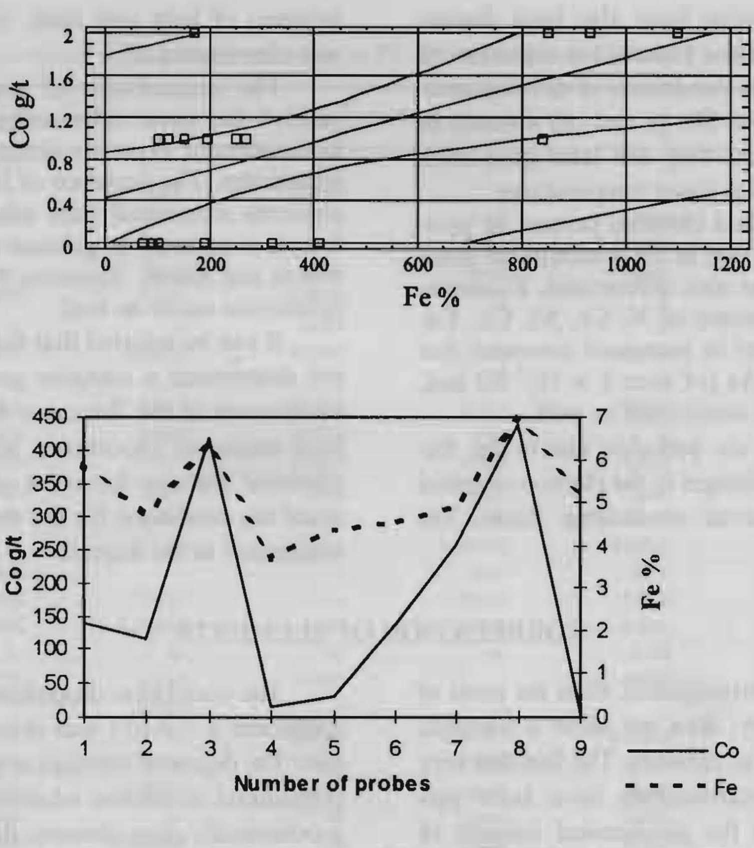


Fig. 1. Correlation diagram between the contents of Co and Fe in sphalerites in the Toranica deposit

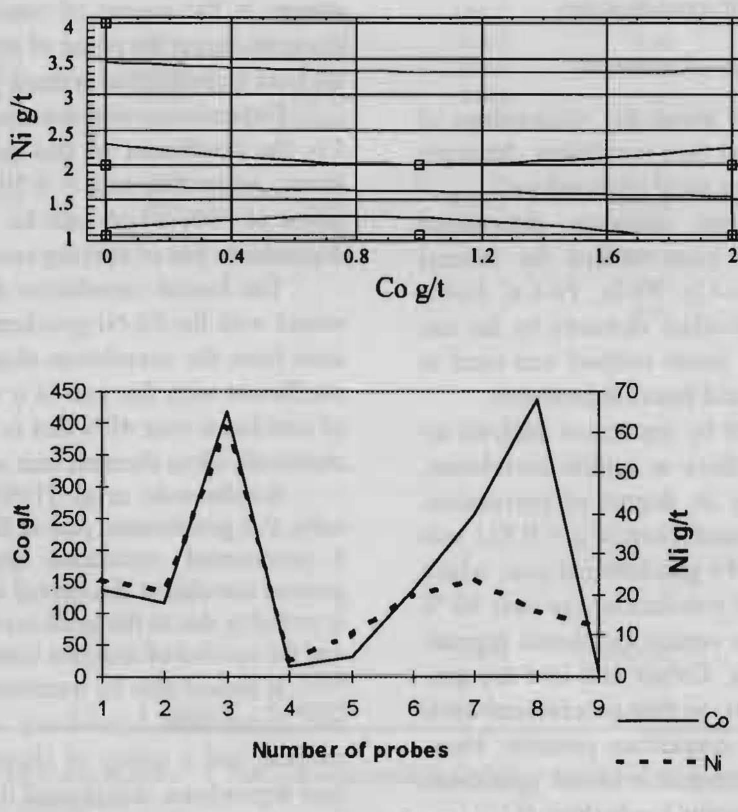


Fig. 2. Correlation diagram between the contents of Co and Ni in sphalerites of the Toranica deposit

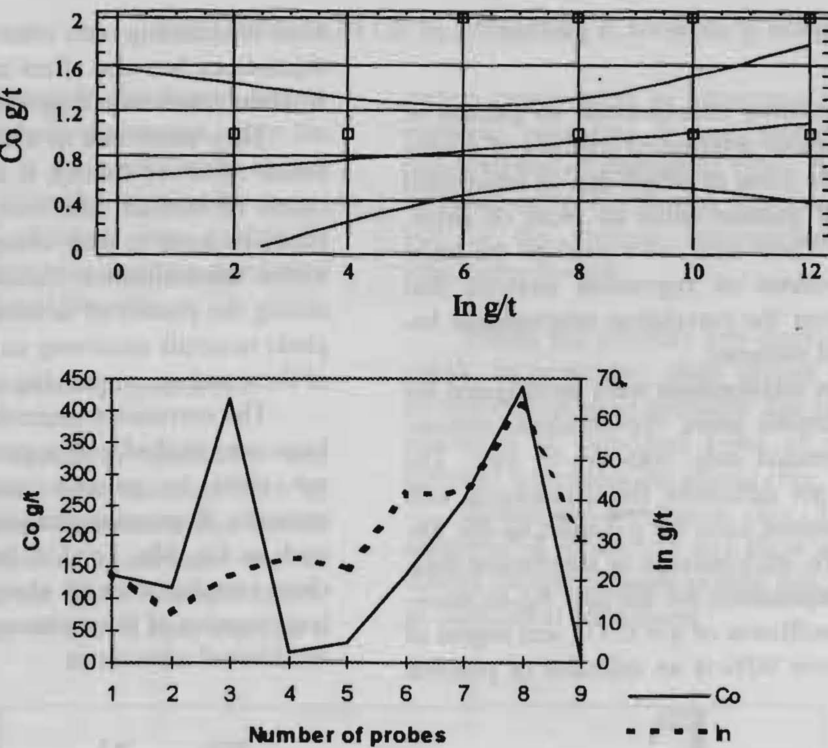


Fig. 3. Correlation diagram between the contents of Co and In sphalerites of the Toranica deposit

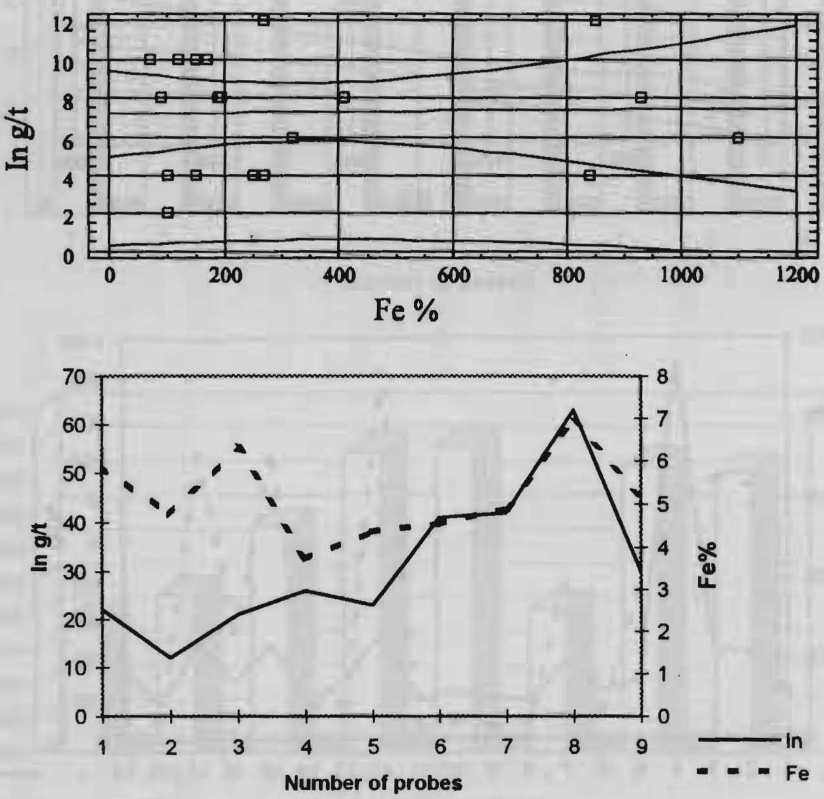


Fig. 4. Correlation diagram between the contents of In and Fe in sphalerites in the Toranica deposit

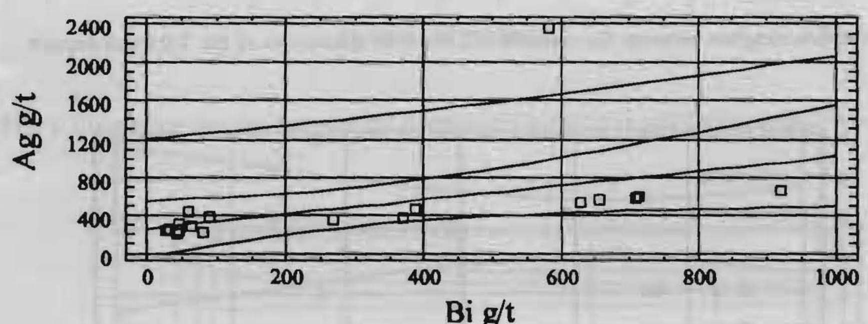
Correlation of elements in galenas

Latest laboratory examinations on galenas of the Toranica deposit determined contents of dozens of microelements some of which can be interpreted as indicators of galenas (such as those of silver, bismuth, etc.). These data were used as the basis for the performance of regression analysis that helped to discover the correlation relationships between individual elements.

Correlation relationships were investigated for several characteristic pairs. Nevertheless, correlation was determined only with Ag-Bi pair. The authors could not determine the dependence with some of the standard pairs for galenas (Ag-Sb, Sb-Bi, Pb-Se, Se-Te, etc.) because of insufficient data. However, the dependence for the pair Ag-Bi showing very high coefficient of $q = 0.931$ and degree of correlation of over 90% is an indicator of possible close relationship with other pairs. The pronounced dependence between silver and bismuth can be seen from the correlation diagrams presented (Fig. 5).

They show that in almost all analyses the increase of silver content is accompanied by the increase of bismuth and vice versa. The close relationships point to their close geochemical evolution within mineralization fluids and their distribution during the phases of development of the main sulphide minerals occurring as principle concentrators of these and accompanying elements.

The correlation dependence of elements in galenas was studied with a group of elements that are not close to galenas and occur in increased amounts. Regression analysis showed that elements such as Cu, Mn, Fe, Cd, In etc. did not yield any close correlation or its absence. This shows that a large number of these elements formed as a result of mechanical admixtures.



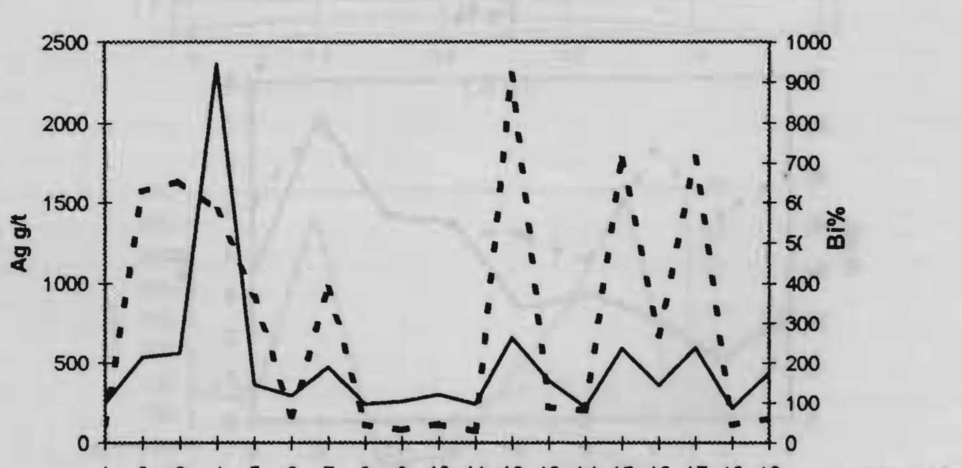


Fig. 5. Correlation diagram between contents of Ag and Bi in galenas of the Toranica deposit

DISTRIBUTION OF ELEMENTS

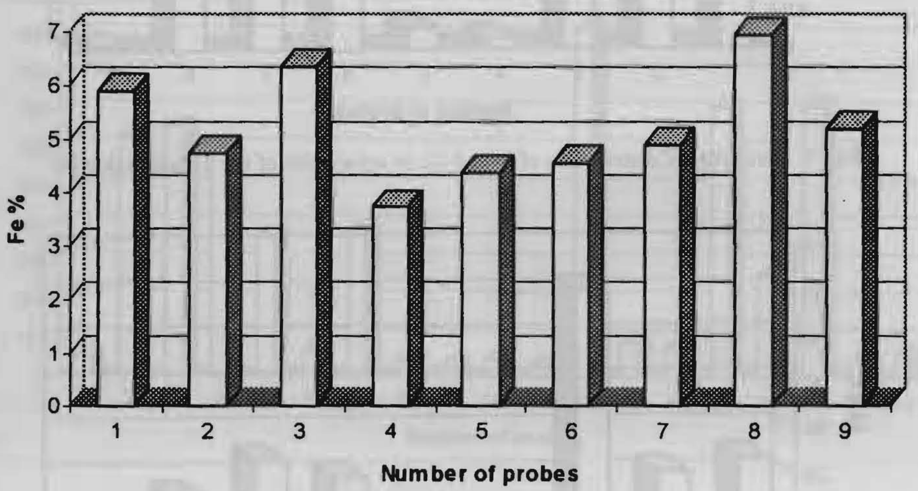
Distribution of elements in the deposit can be followed through the content of elements, since the geochemical distribution is a complex issue related to their sources as well as to their continuing occurrence. Distribution of elements was studied in sphalerites and galenas because a certain number of elements occur in significant amounts.

Distribution of elements in sphalerites

Distribution of elements in sphalerites was studied in several characteristic elements such as Fe, Cd, Co, In, etc. It was determined that certain regularity or continuation of occurrence can be found in some elements, but that it is absent in others. The histogram (Fig. 6) shows that iron has a certain continuation in occurrence (with some deviations), occurring in high amounts which is a characteristic of marmatitic types. A typical normal and continuing distribution was discovered as a result of the uniform concentrations within the sphalerites studied.

Unlike the previous two elements, indium and cobalt, in particular, show certain discontinuation of distribution most probably due to different concentration of individual types of sphalerites and different mineralization phases (Fig. 7.

Nickel and manganese (Fig. 8) are not characteristic of sphalerites and show a regular distribution, except for some probes due, most probably, to mechanical admixtures.



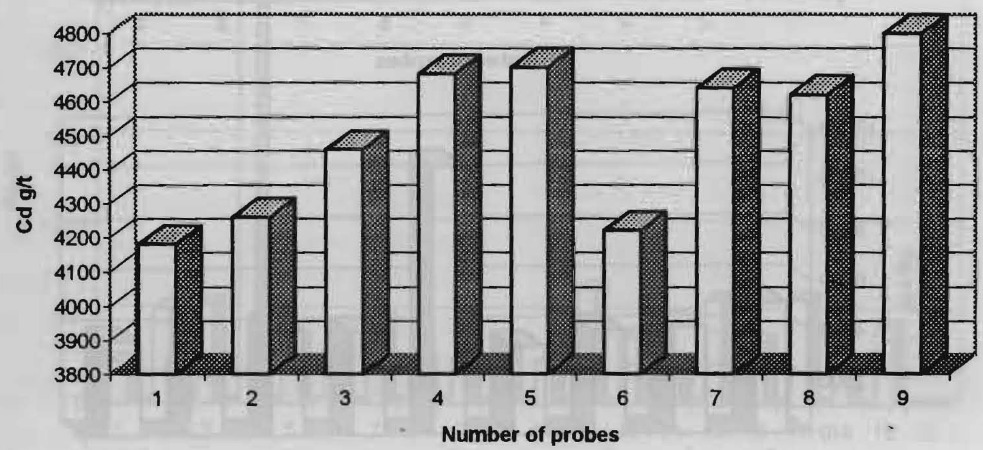


Fig. 6. Histogram of distribution of Fe and Cd in sphalerites of the Toranica deposit

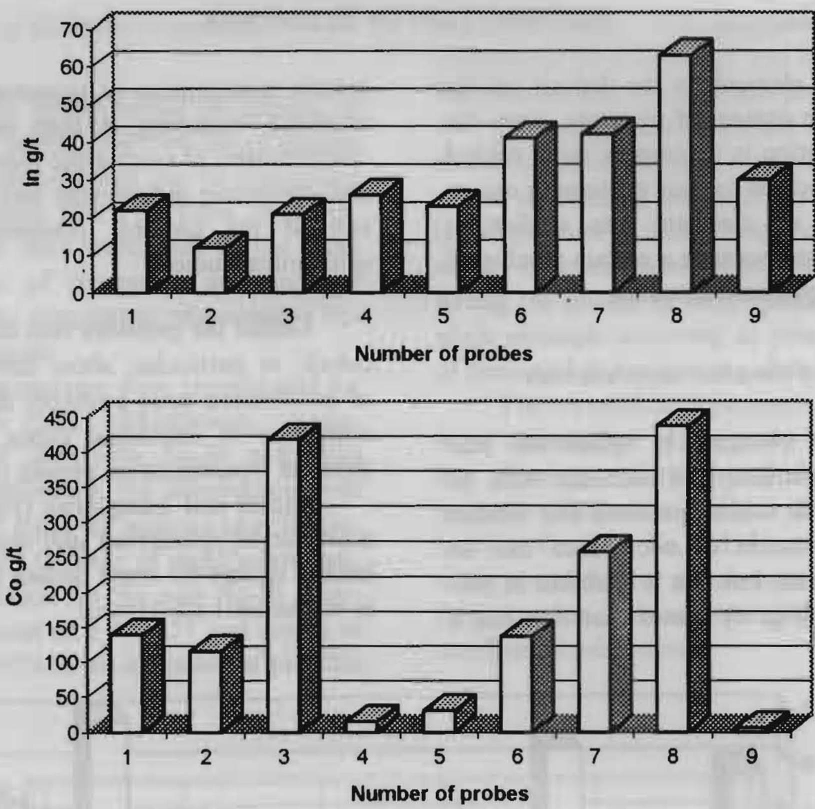


Fig. 7. Histogram of distribution of In and Co in sphalerites of the Toranica deposit

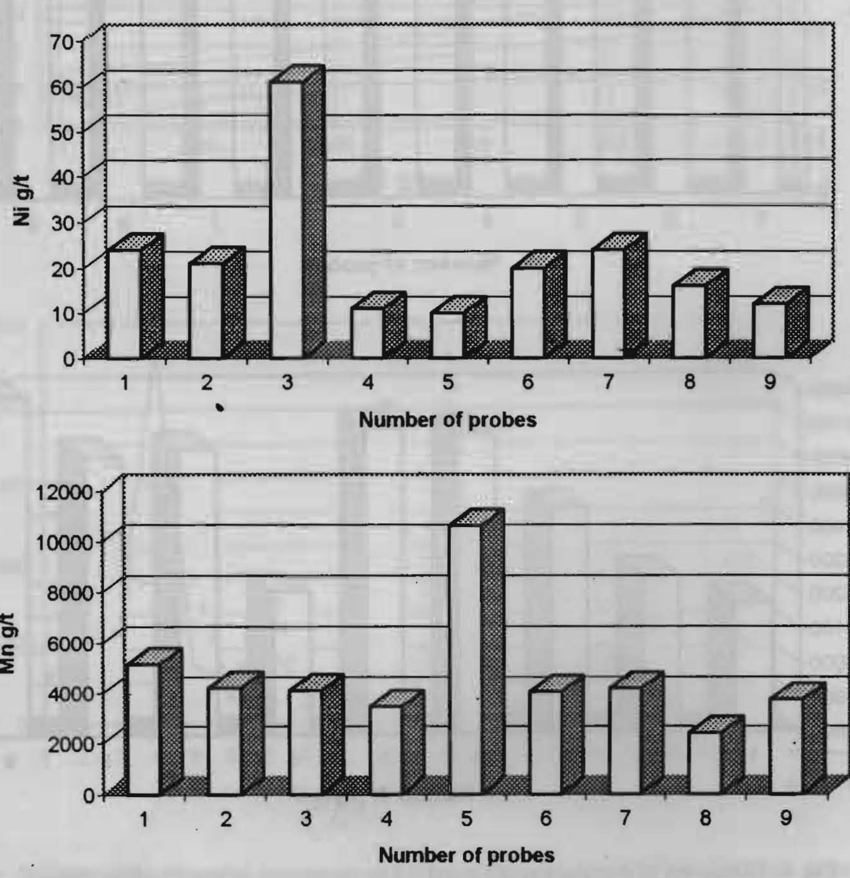


Fig. 8. Histogram of distribution of Ni and Mn in sphalerites of the Toranica deposit

Distribution of elements in galenas

The distribution of elements in galenas was studied in a dozen of probes that display the distribution of their elements. Like with sphalerites, distribution was studied on several most common microelements such as Ag, Bi, Fe, Cu, Mn, etc.

Graphs and histograms of variation obtained (Fig. 9) display that silver is related to normal and continuing distribution originating from its primary distribution during crystallization of galenas. Except for one very high value, all data point to an average continuation of these elements as one of the most indicative of all galenas. Unlike silver, bismuth has certain discontinuity in occurrence due to uneven and variable concentration in galenas of different generations and places. On average bismuth occurs very commonly.

The histogram in Fig. 10 displays the distribution and variation of iron and copper as elements characteristic of galenas that can also concentrate as primary geochemical dispersion. However, high degree of variation is present with iron or a discontinuation and irregular distribution that can be interpreted in various manners. Bearing in mind that iron is mechanically present, then it could be due to variable presence of sphalerite, pyrite, chalcopyrite, locally arsenopyrite, etc. The partial irregularity of occurrence of copper is probably due to its regular distribution in chalcopyrites since most of the copper present is due to mechanical presence of chalcopyrite with which galena is commonly intergrown.

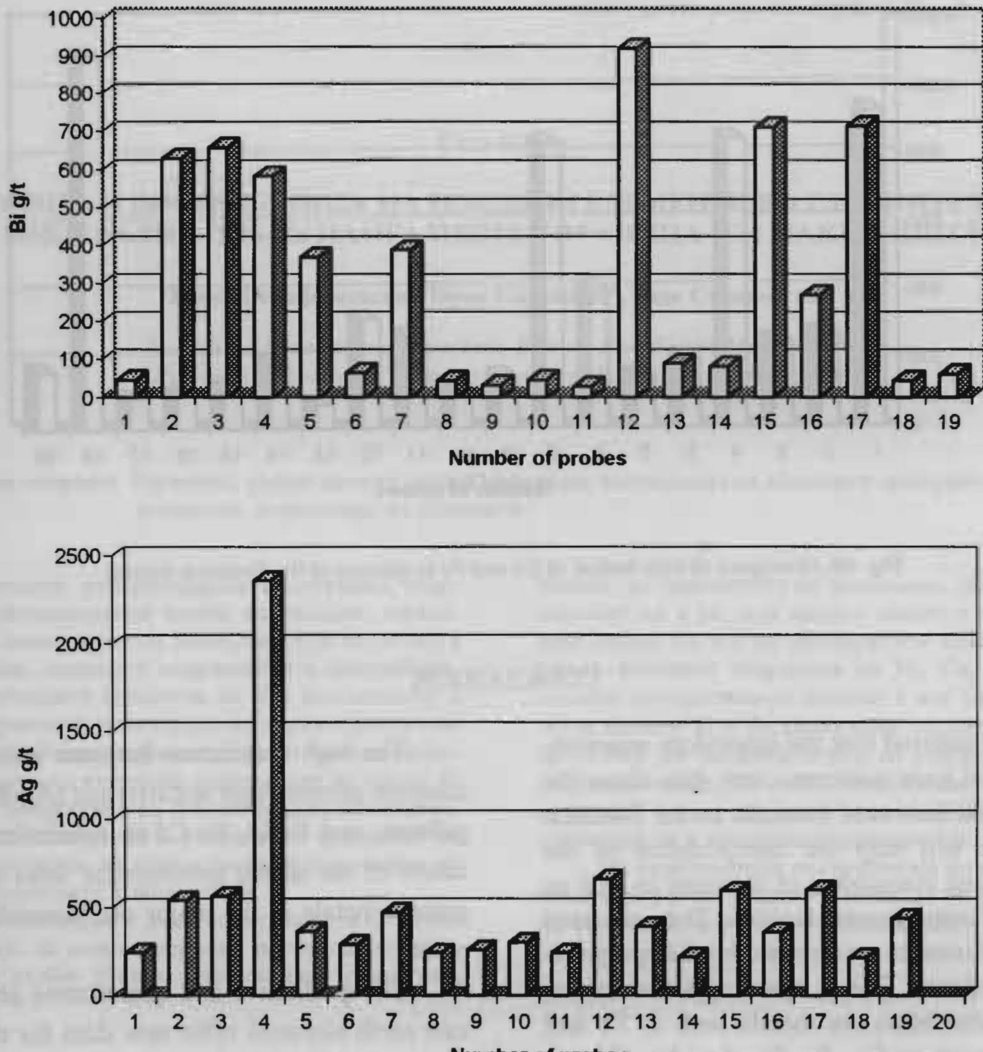
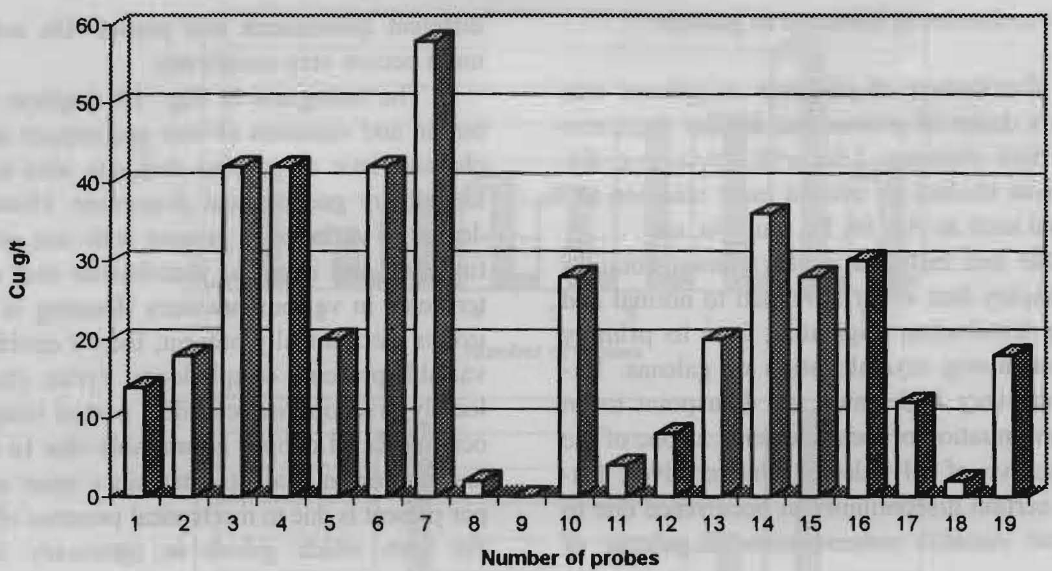


Fig. 9. Histogram of distribution of Bi and Ag in galenas of the Toranica deposit



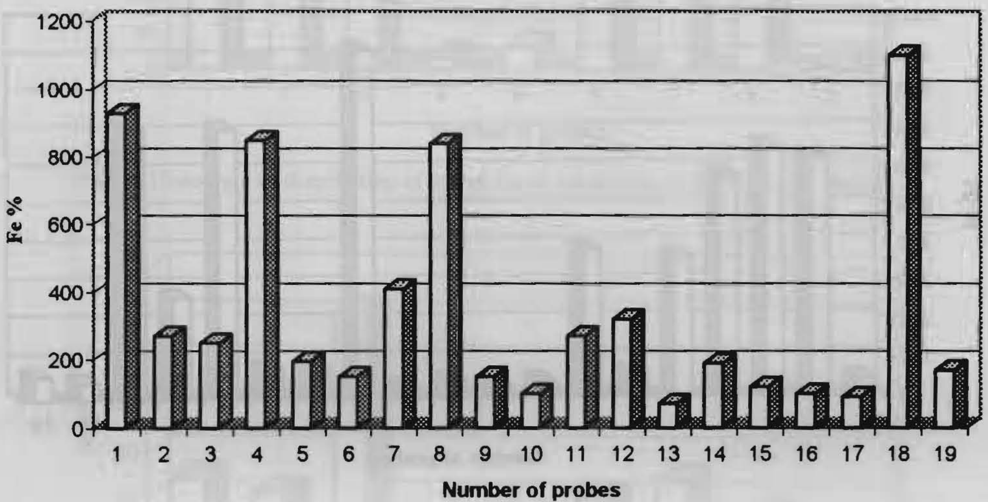


Fig. 10. Histogram of distribution of Cu and Fe in galenas of the Toranica deposit

CONCLUSION

It can be inferred that the laboratory examinations performed gave numerous new data about the contents and ditribution of elements in the Toranica deposit which will help the interpretation of the geochemistrry and association of elements as well as explanation of some genetic features. Data obtained also classify Toranica as a hydrothermal polymetallic Pb-Zn deposit. This is also supported by the fact that, besides basic ore metals such as Pb and Zn, elements such as Cu, Bi, Sb, Ag, Au, Cd etc. always occur in high contents giving the deposit a polymetallic character.

The high correlation between individual most common geochemical occurrences (Ag-Bi, Ag-Sb in galenas; and Fe-In, Fe-Cd in sphalerites) are indicators of the strong geochemical links between cogenetic metals in the major ore minerals in the deposit.

The qualitative and quantitative abundance of rare earth elements offer new data for the interpretation of the genetic processes, particularly because these ore metals generated from great depth.

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Резиме

СОДРЖИНА И ДИСТРИБУЦИЈА НА ПОЕДИНИ ЕЛЕМЕНТИ ВО ГЛАВНИТЕ РУДНИ МИНЕРАЛИ ОД Pb–Zn НАОЃАЛИШТЕ ТОРАНИЦА (СИ МАКЕДОНИЈА)

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Клучни зборови: Тораница; рудни метали; рудни минерали; асоцијација на елементи; дистрибуција на елементи; корелација на елементи

Со најновите лабораториски испитувања извршени врз мономинерални проби на галенит, сфалерит, пирит и халкопирит од наоѓалиштето на олово и цинк Тораница, следена е содржината и дистрибуцијата на позначајните елементи во ова наоѓалиште, а наедно е извршена и корелација на карактеристичните парови на елементи. Освен тоа, со mass-спектрометриски анализи е утврдена содржината на околу 40 елементи во продуктите од флотациската концентрација. Со овие испитувања е утврдено и присуство на елементи од групата на ретки земји, и тоа главно во оловните и цинковите концентрати.

За одбележување е дека испитувањата со атомска апсорпција на мономинерални проби од главните минерали ги дадоа главно очекуваните резултати. Имено, во галенитите со зголемена содржина се појавуваат Ag и Bi, кои наедно имаат и добра корелација (преку 90 %); во сфалеритите посебно се издвојуваат високите содржини на Fe, Cu, In и Co. Нагласена корелативност постои и кај Co-Fe (преку 80 %) и помеѓу In и Fe (докажана од Серафимовски и др., 1992). Во халкопиритите се утврдени зголемени содржини на Pb, Zn и Mn, следени од In, Ag и Bi. Во пиритите, покрај високите содржини на Pb и Zn, констатирани се и високи содржини на Mn, Co и Bi.

Од испитуваната дистрибуција на елементите во галенитите и сфалеритите може да се констатира дека најголема постојаност покажуваат Ag во галенитите и Fe и Cd во сфалеритите.