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GEOCHEMICAL ASSOCIATIONS IN RADKA ORE DISTRICT

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ABSTRACT
Results from statistical processing of primary geochemical halo samples from Tsar Asen, Radka and Chervena Mogila deposits are discussed. The concentrations of chemical elements are determined by emissiom-spectra analysis. The data are processed by factor analysis for determination of spatial groups of elements in the tree deposits. The following geochemical associations are recognized: a) in Tsar Asen deposit: ([Ag, Cu] As) Au, [Co, Ni] and [Pb, Zn], where Ba and Mo show independent behavior, b) in Radka deposit: [Ni, Co], (Ba, As, Ag), ([Pb, Zn] Ag) and [Mo, Au] where Cu is independent, c) in Chervena Mogila deposit: ([As, Ag] Pb, Au, Ba), ([Ni, Co] Mo) and [Cu, Zn]. The spatial distribution of the elements and the derived geochemical associations mark the difference in depth and temperature conditions of the ore-forming processes.

BRIEF GEOLOGICAL OVERVIEW

Panagyurishte Ore Region is located about 55-95 km ESE of Sofia (B. Bogdanov, 1981). A complex of Upper Cretaceous sedimentary, volcanic and intrusive rocks is exposed in this region. Three rock units are divided: a) Turonian Terrigenous Group, b) Lower Senonian Volcano-sedimentary Group and c) Upper Senonian Sedimentary Group. The Upper Cretaceous rocks transgressively overlie Pre-Cambrian, Paleozoic and Triassic rocks, and are locally covered by Paleogene, Neogene and Quaternary sediments. The Lower Senonian Volcano-sedimentary group is further subdivided into Krasen-Petelovo, Svoboda-Ovchihulm, Elshitsa and Pesovets volcano-intrusive complexes (K. Popov, 2001a). They include the homonymous effusive formations and related comagmatic subvolcanic and hypabyssal intrusives. The volcano-intrusive complexes are products of different magma chambers and differ in the time of their formation, composition of the rocks and structural evolution.

Radka Ore District is situated in the SE part of the Panagyurishte Ore Region. It is related to the evolution of the Upper Cretaceous Elshitsa volcano-intrusive complex (N. Obretenov *and* P. Popov, 1973; P. Popov *et al.*, 1994). This complex comprises the rocks of Elshitsa stratovolcano, the Elshitsa pluton as well as numerous subvolcanic and

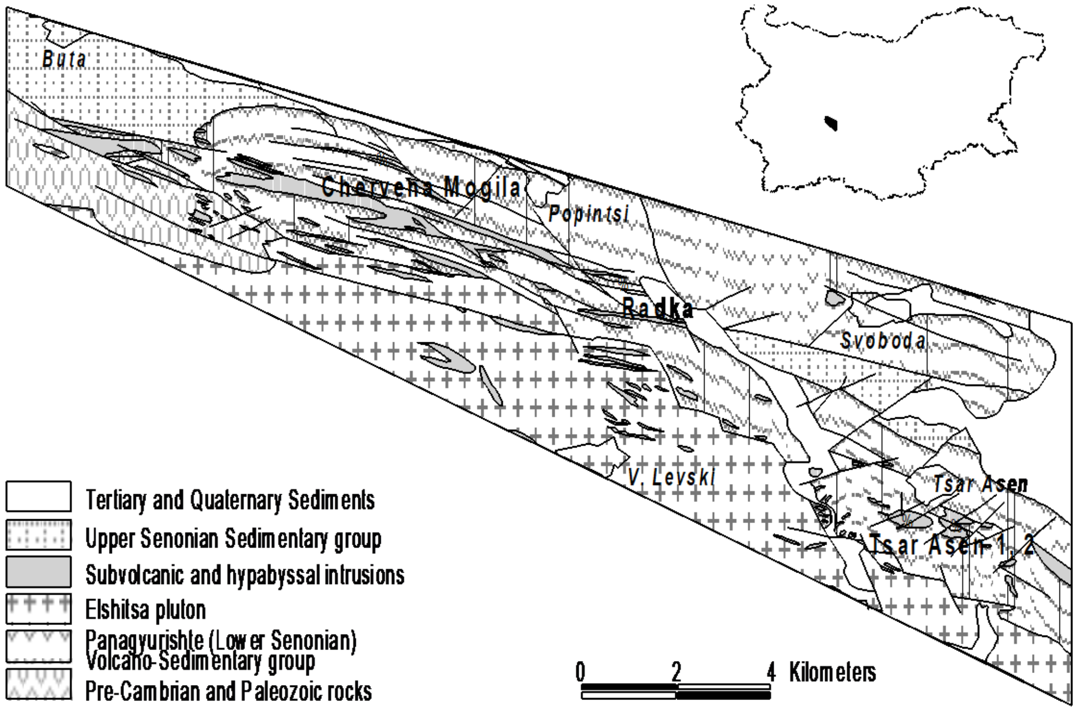

Figure 1. Geological scheme of Radka Ore District.

subvolcanic-hypabyssal minor intrusives and dikes. The ore district is a stripe-like area of E-SE direction, about 20 km long and 4 km wide in the northern slope of the Elshitsa stratovolcano. The Elshitsa pluton is exposed along the southern border as a result of fault uplift of the central block of the volcano. ESE (120-130^o) faults are typical. Two fault groups dominate: a) subvertical to northern dipping (80- 65^o) faults; b) southern dipping (45-60^o) faults. Their relations probably mark a conjugated faulting, which accompanies the uplift of the central part of Elshitsa volcano. Faults of 60-80^o, 150-170^o and 20-40^o direction are also common. They contribute to the higher permeability in some parts of the region.

A porphyry copper – massive sulphide ore system of linear type is developed in the ore district (K. Popov, 2001b). It was formed after the volcano-tectonic faulting and block segmentation of the Elshitsa stratovolcano. The fault swarm of ESE (120-130^o) direction as well as the accompanying stock and dike-like minor intrusions control its spatial position. The ore-forming process is characterized by asymmetrical development along the ore-controlling fault swarm. The Tsar Asen porphyry copper deposit is located in the SE flank of the ore district (Fig. 1). The massive sulphide deposits Radka and Chervena Mogila as well as numerous ore occurrences successively follow to the NW. The amount of sulphosalts, lead-zinc and gold mineralization increases in this direction while the temperature of ore emplacement decreases. K-silicate and propylitic hydrothermal alterations as well as sericitic and argillic alterations in the littocap associate with the Tsar Asen porphyry copper deposit. Predominantly propylitic, sericitic to advanced argillic alterations form successive zones around the massive sulphide deposits.

METHODS OF STUDY

The main aim of this study is to define the geochemical associations in the haloes of Radka, Tsar Asen and Chervena Mogila deposits in Radka Ore District. Groups of elements with similar spatial distribution are interpreted as geochemical associations but they are not identical to the existing mineral parageneses and associations. Modern statistical routines, organized in certain sequence, were used for their differentiation as shown in the following scheme:

Preliminary data preparation
↓
Univariate statistical analysis
↓
Cluster analysis
↓
Factor analysis

The individual stages of the applied method are described below. Factor analysis is mainly used for extraction of geochemical associations, while the objective of prior stages is a preliminary preparation and "familiarization" with data. Each of the applied analyses possesses a character of self-dependent investigation, which serves different geological tasks. Preliminary preparation aim collection, organization and archiving of data in computer form, which is accessible for subsequent analyses. The univariate statistical analysis examines the properties of distribution for element's concentrations, as the anomalies and maps for individual elements could be prepared as the result. Cluster and factor analyses are used for grouping of elements based on the similarity of their spatial distribution. The main objective to combine these statistical procedures in a common sequence is to develop a uniform methodology for study of geochemical haloes and associations.

USED DATA AND PRELIMINARY PREPARATION

The primary geochemical halo data are used for investigation of geochemical haloes in Tsar Asen, Radka and Chervena Mogila deposits. The element contents are determined mainly by semi-quantitative emission-spectra analysis for a standard assemblage of 22 elements. The typical for the studied area assemblage of 10-15 elements is used during later sampling stages, since some of the elements were not detected or were detected only in a few samples in the beginning of the sampling period. The results of statistical processing only for the elements Ba, As, Ag, Pb, Zn, Cu, Ni, Co, Mo and Au, which are commonly studied in the three deposits, are presented in this paper with the aim to make a comparison between the derived geochemical associations. The Au concentrations are determined by emission-spectra analysis after chemical enrichment. Some quantitative determinations for Au and Ag contents by AAS and AES-ICP are used in Chervena Mogila deposit as well. The analytical results are verified by standard inner and outer laboratory accuracy control, whereupon significant deviations where not detected. All concentrations are presented in ppm units.

The Radka deposit halo was studied generally with 417 samples, where 214 are patch rock samples from the surface and 203 drill samples from several boreholes situated along profile line No 15. Tsar Asen deposit was studied with 1838 samples, where 257 were collected from the surface. The rest 1581 are drill samples from boreholes positioned along profiles A and VII from Tsar Asen 1 area and profiles E and XII from Tsar Asen 2. Chervena Mogila deposit was investigated with 783 samples, where 493 are surface samples and 290 are drill samples from five boreholes. Its surface is studied mainly by several trenches and patch samples around them. Generally, the sampling was not done on a regular survey grid and the data from the cross-sections are based on downward survey boreholes. Therefore the obtained results did not represent the entire distribution of chemical elements.

The presence of some elements is not determined in some samples, because of lower concentrations and insufficient sensitivity of emission-spectra analysis. Such data are replaced by a value equal to half of the lower limit of analysis sensibility. These data should not be excluded, because of the possibility to skew statistical distribution of the element and to increase its average content. In cases, when a sample was not analyzed for a particular element, then this sample was not used for calculation of the statistics for this element, as well as for determination of its correlation relationships with the other elements.

Table 1. Statistics calculated on the data from three deposits.

	Mean value	Median	Minimum	Maximum	Variance	Standatd deviation	Skewness	Kurtosis
Tsar Asen deposit								
Ba	758.4875	700	50	7000	188447.2	434.1051	3.381271	27.98798
As	62.84004	50	50	200	575.381	23.9871	1.81213	3.589405
Ag	0.347334	0.2	0.1	3	0.124987	0.353536	2.797355	12.722
Pb	13.8599	7	1	700	1436.767	37.90471	11.57918	164.277
Zn	63.00054	50	15	1000	3964.114	62.96121	6.811959	75.62133
Cu	1070.743	500	0.5	10100	3111321	1763.894	3.339556	12.51682
Ni	7.194233	5	0.5	70	37.25703	6.103853	2.94289	17.87328
Co	10.02584	7	0.5	300	136.8547	11.69849	11.5741	245.4383
Mo	6.86235	5	0.5	150	98.17837	9.9085	6.725931	69.56122
Au	0.024013	0.0015	0.0015	1	0.003875	0.062252	7.396453	86.13288
Radka deposit								
Ba	1341.127	1000	50	10000	906291.3	951.9933	3.897478	23.59711
As	101.9185	100	50	300	1414.58	37.6109	1.196747	3.723692
Ag	0.431175	0.5	0.1	3	0.097235	0.311825	2.874435	16.15526
Pb	33.70983	15	2.5	3000	27515.63	165.8784	14.70323	250.6651
Zn	124.0767	70	15	10000	258556.9	508.4849	17.87245	344.5467
Cu	419	100	3	10050	1060510	1029.811	5.786596	42.71888
Ni	7.94964	7	0.5	30	26.3989	5.137986	1.104547	0.619962
Co	8.31295	7	0.5	30	63.54305	7.97139	1.126899	0.517454
Mo	9.491607	5	0.5	700	1326.589	36.42238	16.85363	313.9194
Au	0.01838	0.0015	0.0015	0.5	0.002913	0.053974	5.728896	39.10217
Chervena Mogila deposit								
Ba	1269.83	1000	100	7250	1047866	1023.653	2.328667	7.489797
As	114.2016	100	50	1250	19604.74	140.0169	6.466718	44.90588
Ag	0.876539	0.5	0.15	49.47	5.977162	2.444823	12.0744	207.8978
Pb	104.1137	20	0.5	7000	191306.7	437.3862	10.15461	125.9087
Zn	117.2542	30	15	5000	112335.9	335.1654	9.739956	124.2805
Cu	129.8212	70	5	7000	117349.9	342.5637	12.70421	221.6551
Ni	5.500639	5	0.5	30	25.17935	5.017903	2.293026	6.609995
Co	4.333333	3	0.5	150	49.539	7.038395	12.24836	237.2022
Mo	3.509817	3	0.5	30	16.7309	4.090342	3.049325	12.41778
Au	0.130043	0.03	0.0015	5.9	0.163005	0.403739	7.786549	79.52349

UNIVARIATE STATISTICS

Descriptive statistics is used as the first stage of statistical data processing. The main aim is initial analysis of the distribution of particular chemical elements by statistics, such as average value, variance, standard deviation, skewness, kurtosis, etc. The majority of elements possess clearly positively skewned distributions as shown in table 1, i.e. the major part of the data have lower concentrations and higher element contents are measured in a small number of samples. Such shape of distribution is most commonly observed in geological studies of chemical element's behavior. Symmetrical distributions are usually typical for equilibrium systems, while the asymmetry prompts for import or export of a particular element. Positive skewness in distribution's shape could be interpreted as a matter influx caused by a superimposed ore forming process.

CLUSTER ANALYSIS

Cluster analysis (Tryon, 1939) combines different algorithms for classification. The main objective is data organization for obtaining reasonable structures. Furthermore, the objects are jointed in such a manner so that every group should consist of similar objects. The cluster analysis is very useful during the exploratory phase of large databases, especially when a prior hypothesis is lacking, nevertheless that this is not a typical statistical procedure and a test for significance of invoked groups is not available (StatSoft, 1999).

Hierarchical grouping method is used in the present paper, since the elements with most similar spatial distribution generate the kernels of groups in the beginning. Each of the other elements is attached to that group, objects of which are mostly similar to it during subsequent steps. The grouping procedure continues until jointing of all elements into a single group. The resulting arrangement of elements represents the structure of their relationships. The Pearson's correlation coefficient *r* is used as a criterion for spatial similarity between elements. Weighted pair-group averaging is used as an assessment for the similarity between an already formed group and other element, which leads to least loss of information during later grouping steps. The number of objects in each group is used as weights in averaging when jointing two groups. The cluster analysis results are shown on figs. 2-4. The elements with highest correlation relationships are enclosed in square brackets while lower correlations are marked by ordinary brackets. The elements which possess a slight tendency for jointing to a particular group are added with "±" symbol. The rest of elements, which are not included in any group, possess independent spatial behavior.

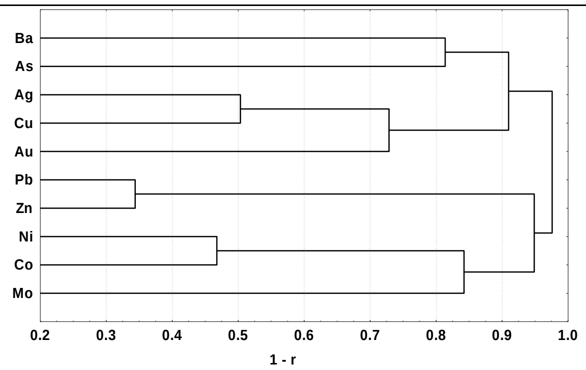

Figure 2. Cluster analysis on Tsar Asen deposit data. Extracted groups are [Pb, Zn], [Ni, Co], (Ag, Cu) +Au.

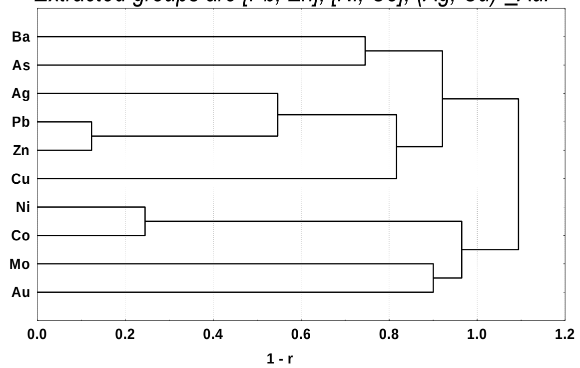

Figure 3. Cluster analysis on Radka deposit data. Extracted groups are [Pb, Zn] +Ag, [Ni, Co].

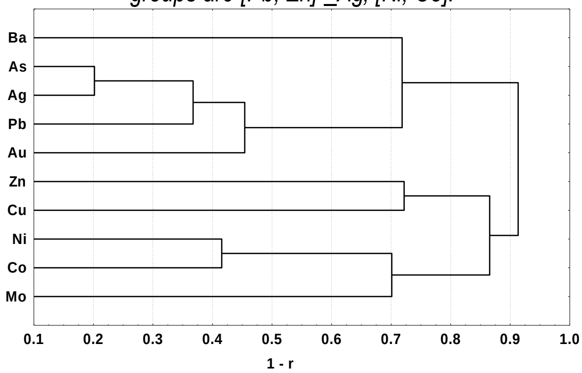

Figure 4. Cluster analysis on Chervena Mogila deposit data. Extracted groups are ([Ag, As] Pb, Au), [Ni, Co] +Mo.

FACTOR ANALYSIS

Factor analysis (Thurstone, 1931) is used to present the structure of studied data by means of their grouping and classification as well as for space dimension reduction of the analyzed variables. It is the main procedure in this methodology for invoking groups of elements with similar spatial behavior, which are interpreted as geochemical associations. The main approach in factor analysis application is based on the idea to represent the data structure by factor communities extraction, based on the similarity between the elements.

The principal component analysis is the most popular variety of factor analysis in which new axes are defined with same number as input variables. The new axes, named principal components, are orthogonal, i.e. the condition for factor independence is accepted. This analysis is based on representation of the covariance matrix as a vector community describing data scattering ellipsoid. The ellipsoid's main axes are requested principal components and they are defined by eigenvectors and eigenvalues of covariance matrix. New axes obtained in this way differ from originally measured sample values, but they are linear combinations of particular variables. Their orientation is parallel to maximum data variance directions, which aims representation of existing "hidden" data structure. Thus, each of the resulting factor axes will account for the joint behavior of a group of dependent variables (if exist) or individual variation of a particular independent variable. The number of factor axes could be reduced as a result, so that only those factors remain which describe existing groups of elements.

R-method of factor analysis is used to represent data investigation for space dimension reduction and for elimination of useless factor axes, which describe single variables (J. Davis, 1973). This procedure analyzes the correlation data matrix, and relations between variables (chemical elements) are considered as correlations between each variable with new mutually independent (orthogonal) factors. Usually, the resulting factors are not well oriented with respect to the direction of regression dependency of a particular group,

Table 2. Factor analysis on data from three deposits.

	Tsar Asen deposit			**Radka deposit**			**Chervena Mogila deposit**		
	Factor 1	***Factor 2***	***Factor 3***	***Factor 1***	***Factor 2***	***Factor 3***	***Factor 1***	***Factor 2***	***Factor 3***
Ba	*0.356424*	-0.270438	-0.005634	**0.584817**	0.080681	-0.074527	**0.517654**	0.113013	-0.203637
As	**0.564405**	-0.150037	-0.097746	**0.548261**	0.040454	0.196027	**0.890475**	0.036145	-0.040895
Ag	**0.831592**	-0.019339	0.141586	**0.553641**	**0.615842**	0.217583	**0.826013**	-0.063165	0.073649
Pb	-0.012358	-0.111107	**0.913869**	-0.038171	**0.951301**	0.077332	**0.752217**	0.098799	0.147461
Zn	0.034869	0.226112	**0.893223**	-0.094317	**0.931630**	-0.083727	-0.033161	*0.318083*	**0.699382**
Cu	**0.710073**	0.149842	0.055786	0.142407	0.200609	0.010657	0.130129	-0.055779	**0.834445**
Ni	0.011791	**0.818641**	0.092808	**-0.812829**	-0.043390	0.124165	0.029211	**0.893558**	0.077196
Co	0.004689	**0.845982**	0.044145	**-0.851658**	0.025131	0.052812	-0.113072	**0.782778**	0.096433
Mo	*0.363490*	*0.344324*	-0.089243	0.019297	-0.039264	**0.708351**	***0.466447***	**0.557625**	0.020087
Au	***0.434278***	0.106800	-0.005758	-0.053381	0.096680	**0.733685**	**0.729855**	-0.115009	0.188704
Expl. Var.	1.963593	1.697769	1.684308	2.368985	2.213962	1.162687	3.090974	1.867477	1.307014
Prop. Total	0.196359	0.169777	0.168431	0.236898	0.221396	0.116269	0.309097	0.186748	0.130701

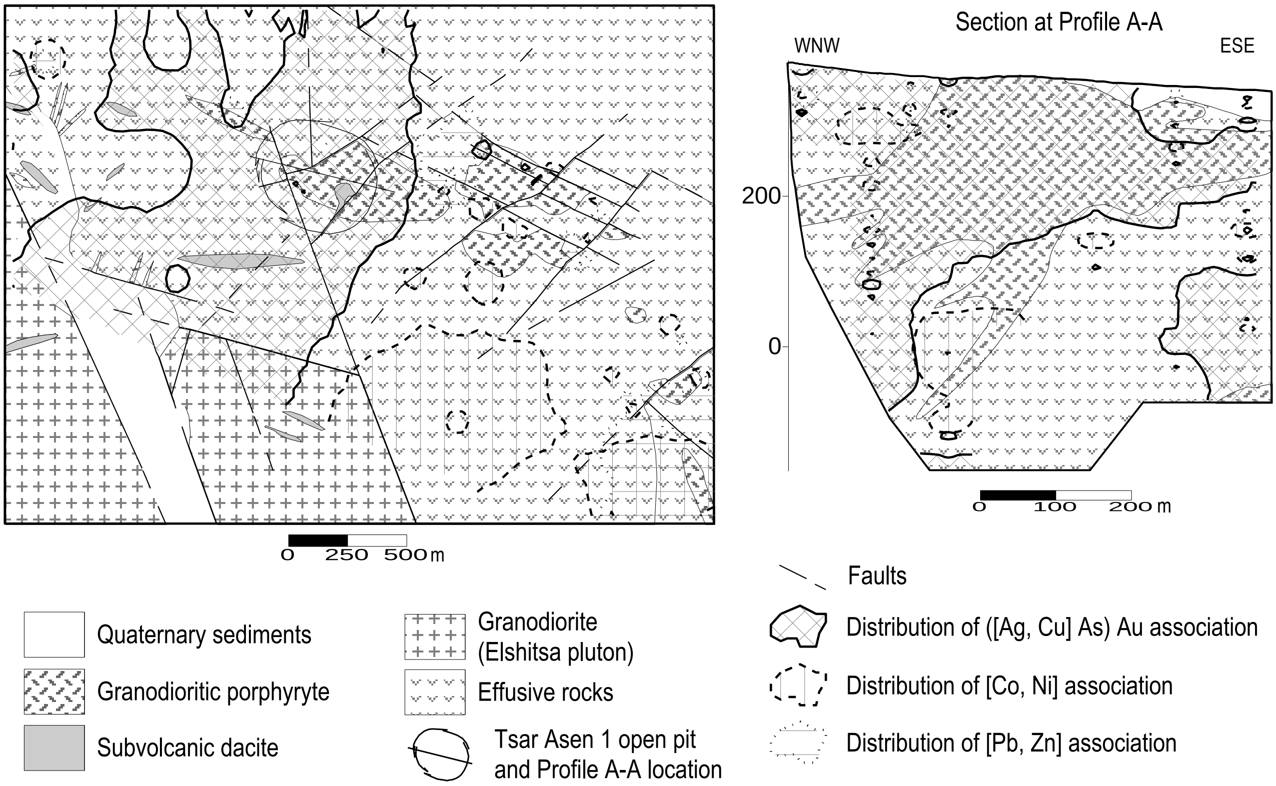

Figure 5. Spatial distribution of geochemical associations in Tsar Asen deposit.

because of the influence of independent variables and the observation of the factor orthogonality condition. Normalized “varimax” rotation is used for additional factor axes fitting to maximum group variances, which produce an additional increase of higher weights and a decrease of lower weights in every factor as well.

The lack of prior information about the necessary number of factors is a certain disadvantage of factor analysis. For this reason, cluster analysis is applied in the used methodology as a previous stage in order to obtain a concept for existing data correlation hierarchy and expected number of groups. Several extractions with different number of factors are commonly used in practice and the most convenient for interpretation variant is selected. Obtaining smaller number of groups with more elements in each group is the effect of using a small number of factors. An increasing number of factors leads to dividing groups into subgroups and appearance of factors representing individual elements. The possibility for calculating factor scores of each sample is a big advantage, which allows drawing of maps for the spatial distribution of each factor (Figs. 5-7).

The results from factor analysis of the used ten elements are shown in table 2. Different extractions at two to five factor axes are applied for derivation of the geochemical associations. The extractions of three factor axes, which was chosen as most representative, are presented below. The weights of elements which build the kernel of each group are bolded (weights higher than 0.5), the weights of elements possessing high tendency for integrating with a particular group are shown in bolded italic font (weights between 0.5-0.4) and the weights of independent elements which possess a slight tendency for joining with some group are shown in italic (weights between 0.4-0.3). The rates of variance explained from each factor in every deposit and their proportions from whole data variance are shown in the last two rows of the tables.

Table 3. Geochemical associations determined by individual factor axes at Tsar Asen, Radka and Chervena Mogila deposits.

Tsar Asen deposit
Factor 1: ([Ag, Cu] As) ± Au, Mo, Ba Factor 2: [Co, Ni] ± Mo Factor 3: [Pb, Zn]
Radka deposit
Factor 1: - [Ni, Co]; + (Ba, As, Ag) Factor 2: ([Pb, Zn] Ag) Factor 3: [Mo, Au]
Chervena Mogila deposit
Factor 1: ([As, Ag] Pb, Au, Ba) ± Mo Factor 2: ([Ni, Co] Mo) ± Zn Factor 3: [Cu, Zn] (-Ba)

The geochemical associations interpreted from the results of the factor analysis (Table 2) are shown in Table 3. The elements with highest weights (factor’s kernel) are enclosed in square brackets, similarly to the grouping by cluster analysis. The elements with lower weights are enclosed in ordinary brackets while independent elements, which possess some slight tendency for joining to a particular group, are added with “±” sign.

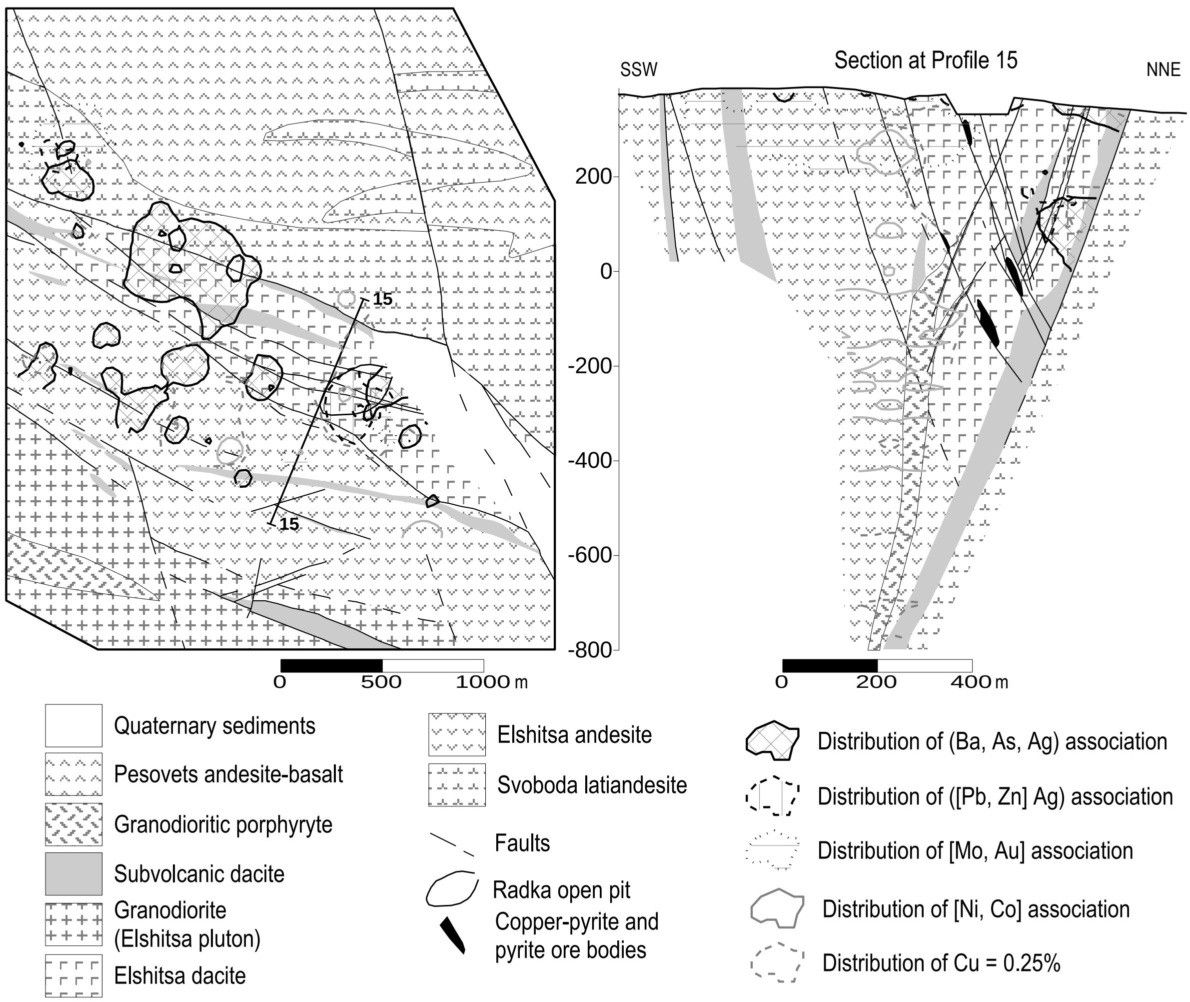

Figure 6. Spatial distribution of geochemical associations in Radka deposit

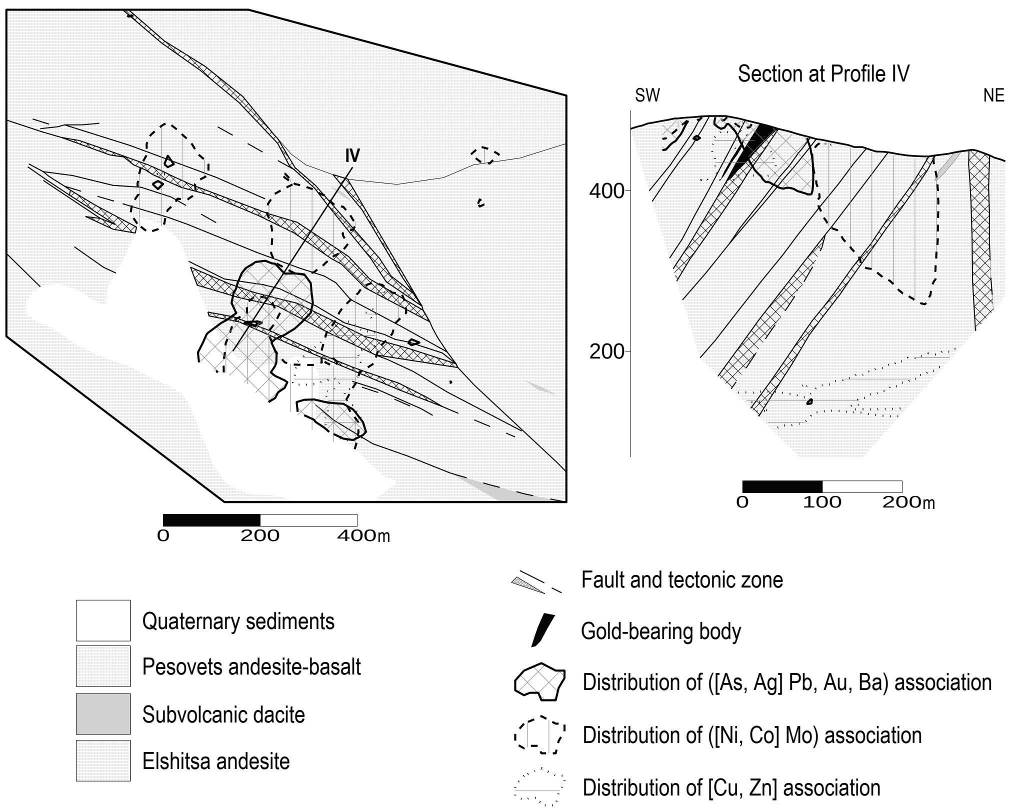

Figure 7. Spatial distribution of geochemical associations in Chervena Mogila deposit

CONCLUSIONS

The paper presents results from statistical processing of a large number of data form Tsar Asen, Radka and Chervena Mogila deposits. The information on the content and distribution of the studied elements is shown in Table 1. Generally, the elements demonstrate a typical for unequilibrium systems asymmetrical distributions, due to hydrothermal and ore forming processes superimposed on the host rocks. The geochemical associations derived from factor analysis are as follows:

in Tsar Asen deposit:
([Ag, Cu] As) Au, [Co, Ni] and [Pb, Zn], where Ba and Mo are independent elements,

in Radka deposit:
[Ni, Co], (Ba, As, Ag), ([Pb, Zn] Ag) and [Mo, Au], where copper is independent,

in Chervena Mogila deposit:
([As, Ag] Pb, Au, Ba), ([Ni, Co] Mo) and [Cu, Zn].

The spatial grouping of the studied chemical elements shows a tendency for differentiating such communities, that group elements related to low-, medium- or high temperature minerals. Thus, the extracted groups reflect the existing zonality in the deposits. A comparison of the results from the factor associations in the three deposits leads to the following conclusions:

1. The extracted associations reflect the existing zonality in the deposits. In Tsar Asen deposit, the distribution of the ([Ag, Cu] As) Au association is very close to the spatial position of the ore body as indicated by the high contribution of Cu in this group (Fig. 5). The second [Co, Ni] association develops around the first one and in depth. The third [Pb, Zn] association is located in the periphery of the first group and mainly on the surface, above of the deposit. The geochemical associations in Radka deposit are related to the periphery of those ore zones, which are located mainly within dacite effusives (Fig. 6). The [Ni, Co] association is located mainly in depth, while (Ba, As, Ag) and ([Pb, Zn] Ag) occur at higher levels and near the surface, surrounding the periphery of the copper ore. The [Mo, Au] association develops on the surface within andesitic rocks. In Chervena Mogila deposit, the first ([As, Ag] Pb, Au, Ba) association is related to areas of gold-bearing ore bodies and around them (Fig. 7). The second ([Ni, Co] Mo) is located along the periphery and near the first group, while the third [Cu, Zn] association tends to develop mainly in the SE areas and at lower levels. The spatial position of the associations in the three deposits reflect their genetic relation to the main ore-controlling tectonic structures.
2. Ag and As are grouped in all three deposits. Cu and Au associate with this group in Tsar Asen, while Pb and Au are joined in Chervena Mogila deposit. The Ag, As and Ba association is not so well developed in Radka deposit, where these elements show a distinct negative correlation with the Ni and Co group. "Inter-associative" behaviour of Ag is observed in Radka deposit as well, since Ag has significant weights in both the first and second factor axes.
3. The Pb and Zn association occurs in Tsar Asen and Radka deposits. Ag joins this group in Radka deposit. Pb and Zn belong to different associations in Chervena Mogila, where Pb associates with As, Ag, Au and Ba, while Zn is grouped with Cu.
4. Ni and Co are grouped in all three deposits. Mo joins these two elements in Tsar Asen and Chervena Mogila Deposit. This group has the highest proportion in the whole data variance in Radka Deposit.
5. The spatial behavior of Cu is specific in all three deposits. This element associates with Ag, As and Au, while it is grouped with Zn in Chervena Mogila and it possess an independent behavior in Radka (very slight tendency for joining to group of Pb, Zn and Ag).
6. Au and Mo show a somewhat specific behavior in each deposit. Au belongs to the group with As-Ag kernel in Chervena Mogila and Tsar Asen, while Mo exhibits a certain inter-associative behavior, because it is grouped with Ni and Co, but shows a tendency for joining the As-Ag association as well. Au and Mo form a self-contained association in Radka deposit, to which Ag shows a slight tendency for joining. The grouping of Au with Cu and Ag in the first factor in Tsar Asen deposit becomes more distinct when decomposition on a larger number of factors is used.

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