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MICROELEMENTS IN THE ROCKS AND ASHES OF THE PLANTS *VIOLLA ALSHARICA* AND *THYMUS ALSHARENSIS* OF THE ALSHAR SITE

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A b s t r a c t: The paper presents detailed geochemical investigations carried out in part of the Alshar polymetallic deposit in terms of the presence of individual microelments in the rocks and plants such as Viollа alsharica and Thymus alsharensis. The investigated area covers the northern portion of the deposit. Elements analyzed included Sb, Se, W, Zn, Ba, Tl, As, Co, Cu, Mn, Ni, Pb, Cd and Be. Investigations carried out demonstrated large geochemical correlation between the distribution of individual elements in the rocks and plants. It can be inferred that the plants in the area under investigation contain increased concentrations of thallium, zinc, lead, manganese and copper.

Key words: Thymus; Viollа; geochemistry; microelements

INTRODUCTION

The Alshar complex Sb-As-Tl-Au deposit is one of the unique deposits in the world not because of its size, but mineral composition. It contains significant thallium concentrations that classify it as a unique deposit containing that metal. Besides economically significant antimony and arsenic concentrations, the Alshar deposit is the first Carlin-type deposit in the Balkan Peninsula and further afield. The deposit was discovered during the mid 1980s.

The latest mining activities started in 1881 and, with some interruptions, lasted till 1913. During that period mainly arsenic ore was excavated and exported to Thessalonika, Greece, and Germany. The mineral potential of arsenic in the deposit is estimated at some 15 000 tons. According today's criteria arsenic is a harmful component that results from antimony processing. During the final years of the last century the first thallium minerals were discovered (lorandite, vrbaite) as constituents of arsenic-antimony ore.

Exploration for antimony carried out from 1953 to 1957 and from 1962 to 1965 resulted in the discovery of significant reserves of low grade ore. The latest exploration for antimony was carried out in 1970–1973. Mineral potential of the Alshar deposit, both mined and available ore exceeds 20 000 tons of antimony with 0.5% Sb as cut of grade.

Special interest for thallium as possible solar neutrino detector gave new impulse for systematic investigations of thallium mineralization in the north part of the Alshar deposit. The mineral potential of thallium in the Alshar deposit has been estimated at 500 tons.

For the results of previous studies of the Alshar deposit, the reader is referred by Ivanov (1965), Percival and Boev (1990), Boev and Serafimovski (1996), and for investigation of minerals to Caye et al. (1967), Balic-Zunic et al. (1986), El Goresy and Pavicevic (1988), Frantz (1994), etc.

Some results related to the methods applied in the determination of individual microelements in plants of the Alshar deposit can also be found in the papers of T. Kadifkova-Panovska et al. (1995, 1996, 1997).

METHODS APPLIED

The aim of the investigation was to determine the correlation between individual microelements present in the rocks and those in the ashes of Violla alsharica and Thymus alsharensis. In this regard a number of samples were collected from the rocks in the site. Samples were collected in oblong grids in which the distances between profiles amounted to 100 meters, whereas the distance between the samples collected amounted to 50 meters. Samples were analyzed by the method of instrumental neutron activation in order to determine the contents of individual microelements such as Sb, Se, W, Zn, Ba, Tl, As, Co, Cu, Mn, Ni and Pb.

Besides samples taken from the rocks, samples of plants such as Violla alsharica and Thymus alsharensis were also collected for analysis. It is worthwhile to point out that samples taken from the plants were representative of the whole plant. The samples were dried at temperature of 105° C until there was no loss in weight. Samples dried in this manner were heated at temperature of 700° C for two hours and then determination of individual microelements (those of Sb, Se, W, Zn, Ba, Tl, As, Co, Cu, Mn, Ni and Pb) was performed by the ICP-AES method.

RESULTS OBTAINED AND DISCUSSION

Bearing in mind that the biochemical method is one of the most important and common methods in geochemical examinations, the major goal in the examinations was to determine the correlation between the presence of individual microelements in the rocks and soil in the area under consideration and microelements in the ashes of Violla alsharica and Thymus alsharensis.

The two plants served as local indicators, since they are characterized by their abundance in the site and the specific size of certain organs in the plant compared to the same kinds found in other areas.

It can be inferred from the data obtained and shown in Table 1 that, in terms of the average abundance, there is multiple increase in the As, Zn and Tl contents in some microelements in the rocks and soil relative to their average concentration in the rocks.

It should also be mentioned that the abundance of certain microelements is also influenced by the Fe and Zn contents present in the soil since their hydroxides and oxides consume some microelements such as As, Cu, Ni, Se, Mo, Pb, Co, Zn, Tl, etc.

The Zn content in the rocks ranges from 11 to 465 ppm and compared to the Zn content in the ashes of Violla alsharica (Table 2) it can be inferred that the abundance of microelements is uniform in almost all samples studied and several times higher than that of Zn in the rocks.

Increased contents of Tl in Violla of several hundred times can be noticed compared to its contents in the rocks and soil where the plant grows.

Arsenic, which is common microelement in the rocks in the area, is less present in the plants than Tl and Zn, but more abundant in the ashes of Violla than Thymus. Data obtained indicate that Tl and As are more abundant in Violla due to their geochemical connection.

In contrast, Zn as a significant biogene element, is very common in the two plants in amounts that are several times higher than those in the rocks – the amount of Thymus being higher than that of Violla (Table 3).

Other microelements were not found in significant amounts and their presence will not be the subject matter of this paper.

Bearing in mind that the elements under consideration are heavy metals, known for their toxic properties, the increased amounts of certain microelements, first of all those of As and Tl, which are not known as biogene microelements, point out that these plants potential toxic materials for the living world in the area. Efforts should be made to analyze a large number of plants along with the analysis of the presence of certain microelements in individual plant organs. It will make possible to carry out thorough investigations as well as establish the correlation in the abundance of individual microelements in different plants and organs.

The results obtained by scanning electronic microanalysis carried out on blossoms of plants investigated are shown in Fig. 1.

Table 1

Microelements in rocks and soils in part of the Alshar site (INAA method, in ppm)

	Sb	Se	W	Zn	Ba	Tl	As	Co	Cu	Mn	Ni	Pb
1	5	<5	<10	40	1900	1.4	20	7	9	443	21	21
2	9	<5	<10	74	770	2.1	49	20	34	1250	65	28
3	15	<5	<10	74	270	0.5	5	24	54	1260	71	12
4	5	<5	<10	79	770	2.0	35	23	40	1520	72	36
5	18	<5	<10	81	400	1.5	27	25	45	1440	82	23
6	8	<5	<10	78	410	1.3	36	27	50	1690	83	23
7	5	<5	<10	55	240	0.5	15	20	26	1720	62	13
8	14	<5	<10	97	500	0.9	31	22	32	767	78	23
9	5	<5	<10	79	330	0.5	5	25	46	1150	75	23
10	7	<5	<10	55	760	0.9	5	18	26	588	59	23
11	5	<5	<10	102	350	0.5	36	24	46	1240	62	23
12	18	<5	<10	19	20	1.6	39	5	6	374	17	9
13	11	<5	<10	26	520	0.6	42	34	15	522	580	13
14	28	<5	<10	34	730	5.1	132	34	23	678	519	16
15*	129	<5	<10	72	1100	100	2000	19	19	973	56	22
16	12	<5	<10	20	100	44	2000	6	20	183	38	21
17	7	<5	<10	36	20	38	1243	5	13	154	20	10
18	5	<5	<10	28	2000	50	1172	14	39	713	18	50
19	8	<5	<10	21	1900	9.0	388	5	18	181	14	54
20	7	<5	<10	18	1700	3.1	137	2	25	26	5	27
21	5	<5	<10	32	1800	14	856	9	23	250	18	54
22	11	<5	14	64	170	9.8	395	15	11	537	25	5
23*	5	<5	<10	100	420	8.7	443	20	12	232	23	15
24*	12	<5	<10	227	20	4.7	583	14	6	84	17	10
25*	8	<5	<10	119	1100	38	1249	8	10	22	24	42
26	5	<5	<10	71	1700	4.0	151	14	33	399	26	45
27	16	<5	<10	100	1700	4.7	209	32	22	1040	30	40
28*	16	<5	<10	331	720	2.6	1232	63	22	435	70	30
29*	5	<5	15	401	700	69	2000	217	59	6410	146	32
30	5	<5	<10	11	20	0.5	103	6	3	140	8	11
31*	11	<5	25	465	340	10.5	1830	97	68	5370	190	28
32*	10	<5	14	130	960	9.2	761	25	27	5050	43	33
33	5	<5	25	93	480	3.4	866	27	17	8970	42	13
34	5	<5	<10	69	220	4.1	558	17	17	1100	34	26
35*	5	<5	<10	199	450	100	2000	45	15	2700	87	48
36*	5	<5	<10	70	210	100	2000	17	43	557	42	35
37*	5	<5	<10	79	1600	71	733	16	22	511	32	47
38*	5	<5	<10	149	1200	100	2000	33	26	1690	55	59
39*	11	<5	<10	172	1100	74	2000	42	32	4930	72	52
40*	17	<5	<10	72	1500	40	1392	21	37	1530	34	57

* Sites where besides geochemical samples material was also collected from plants.

Table 2

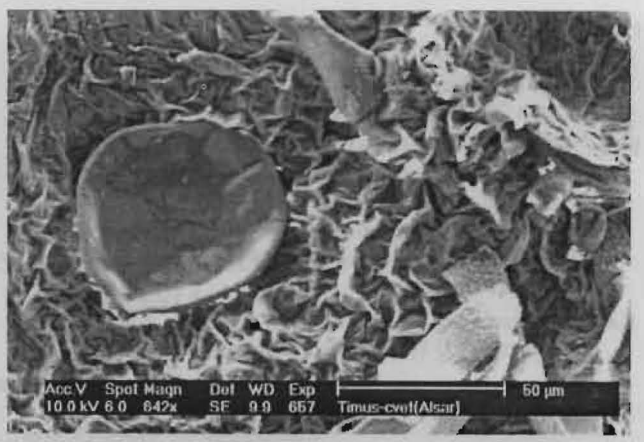
Microelements in the ashes of Violla alsharica (ICP-AES method, in ppm)

	Be	Cd	Mo	Zn	Ba	Tl	As	Co	Cu	Mn	Ni	Pb
1	1	1.9	6.1	320	320	224	34	2.5	41	1800	43	76
2	1	1.5	7.8	280	450	218	45	1.8	40	1700	43	67
3	1	0.9	9.2	230	340	200	28	1.7	43	1560	42	75
4	1	2.0	8.5	250	230	195	33	1.5	42	1600	45	72
5	1	2.5	3.5	350	280	230	38	2.9	39	1800	38	81
6	1	1.0	4.3	340	320	215	37	2.7	45	1700	37	69
7	1	1.2	10.1	180	340	167	34	2.5	35	1400	33	70
8	1	1.9	6.7	170	360	187	29	2.0	28	1900	33	81
9	1	1.5	6.5	310	380	200	30	2.2	32	1800	45	45
10	1	0.8	6.9	320	310	229	31	1.8	41	1800	45	67

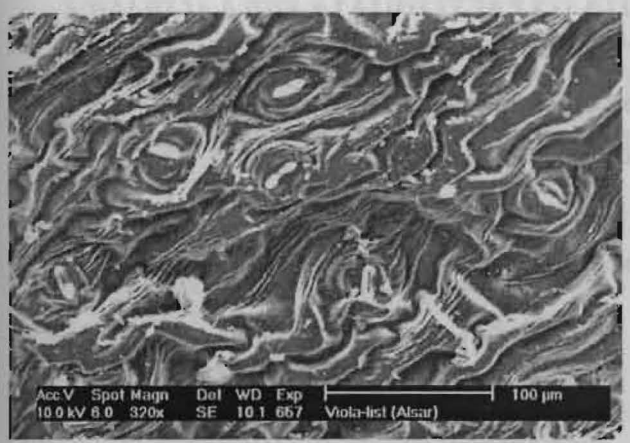
Table 3

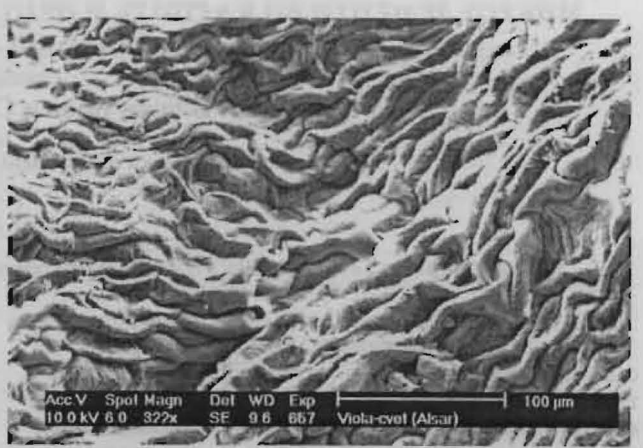
Microelements in the ashes of Thymus alsharensis (ICP-AES method, in ppm)

	Be	Cd	Mo	Zn	Ba	Tl	As	Co	Cu	Mn	Ni	Pb
1	1	–	7	424	866	55	7	12	120	1400	110	65
2	1	1	6	450	890	65	12	23	110	1500	120	45
3	1	0.9	5	430	895	45	15	15	98	1300	130	47
4	1	1.1	7	440	950	43	16	18	78	1600	80	53
5	1	–	6	410	940	23	23	20	65	1200	75	55
6	1	1.2	8	390	980	78	15	21	110	1400	78	52
7	1	1.6	4	380	870	102	10	22	70	1600	95	61
8	1	–	6	360	880	110	8	10	85	1300	92	60
9	1	–	5	420	954	140	5	11	90	1800	81	56
10	1	1.3	7	380	820	150	7	16	95	1600	76	57



a) Thymus alsharensis





b) Violla alsharica

Fig. 1. Scanning electronic microfotography of Thymus alsharensis and Viola alsharica

CONCLUSION

The results presented in the paper lead to the conclusion that there is pronounced correlation between the distribution of individual microelements in the rocks of the Alshar deposit and those found in Violla alsharica and Thymus alsharensis. The correlation is particularly pronounced in elements such as Tl which is very common in the plants mentioned. This concentration distinguishes them as separate kinds known as Violla alsharica and Thymus alsharensis. Zinc also occurs in large contents in the plants discussed and is an indicator of the possible presence of significant individual concentrations of some microelements in host rocks.

REFERENCES

Balic-Zunic, T., Scavnicar, S., Engel, P., 1986: *The crystal structure of rebulite.* Zt. f. Krist., 160, ½, 199.

Boev, B., Serafimovski, T., 1996: *General genetic model of the Alshar deposit, Plate Tectonics Aspects of the Alpine Metallogeny in the Carphato-Balcan Region.* Proceedings of the Annual Meeting of IGC Project 356, Vol. **1**, pp 75–85, Sofia.

Caye, R., Picot, P., Pierrot, R., Permingeat, F., 1967: *Nouveles sur la Vrbaite, sa Teneur en Marcure.* Bull. Soc. Franc. Min. Crist, **90**, 185.

El Goresy, A., Pavicevic, M., 1988: *A new thallium mineral in the Alshar deposit in Yugoslavia.* Naturwiss., 75, 37–39, Springer-Verlag.

Frantz, E., 1994: *Mineralogische, geochemische und isotopengeochemische Untersuchungen der As-Tl Sulfide in der Lagerstatten Allshar*, Doct. Disert. Johannes Gutenberg Universität, Mainz, 160 p.

Ivanov, T., 1965: *Zonal Distribution of Elements and Minerals in the Deposit Alshar*, Symp. "Problems of Postmagmatic Ore Deposition", II, 186–191, Prague.

Percival, T., Boev, B., 1990: *As-Tl-Sb-Hg-Au-Ba Mineralization Alshar District Yugoslavia: A Unique Type of Yugoslavian Ore Deposit*, Int. Sym. On Solar Neutrino Detection with 205 Tl, Dubrovnik.

Кадифкова Пановска, Тања, 1996: *Модификација на аналитички постапки за определување на минералниот состав во претставници од родот Thymus L. со примена на атомска апсорпциона спектрометрија.* Магистерски труд, Фармацевтски факултет, Скопје.

Kadifkova Panovska, T., Stafilov, T., Bauer S., Kulevanova S., Dorevski, K., 1995: *Determination of some macroelements in representatives of genus Thymus L. by atomic absorption spectrometry.* Pharmacia (Sofia), **43**, 18–21.

Kadifkova Panovska, T., Stafilov, T., Bauer, S., Kulevanova S., Dorevski, K., 1996: *Determination of some trace elements in representatives of genus Thymus L. (Lamiaceae) by electrothermal atomic absorption spectrometry.* Acta Pharm., **46**, 295–302.

Kadifkova Panovska, T., Stafilov, T., Kulevanova, S., 1997: *Determination of cadmium in representatives of genus Thymus (Lamiaceae) by electrothermal atomic absorption spectrometry.* Anal. Lab., **6** (3), 158–162.

Резиме

МИКРОЕЛЕМЕНТИ ВО КАРПИТЕ И ПЕПЕЛТА ОД РАСТЕНИЈАТА *VIOLA ALSHARICA* И *THYMUS ALSHARENSIS* ОД ЛОКАЛИТЕТОТ НА АЛШАР

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Клучни зборови: *Thymus; Viollа;* геохемија; микроелементи

Во овој труд се прикажани детаљните геохемиски истражувања на еден дел од просторот на полиметалното наоѓалиште на Sb-As-Tl-Au-Ba Алшар од аспект на застапеноста на одделните микроелементи во карпите и во растенијата од групата на Viola alsharica и Thymus alsharensis. Истражуваниот простор пред сѐ го опфаќа северниот дел од ова наоѓалиште, а елементите кои се истражувани се: Sb, Se, W, Zn, Ba, Tl, As, Co, Cu, Mn, Ni, Pb, Cd, Be. Од спроведените истражувања може да се констатира многу голема геохемиска поврзаност меѓу дистрибуцијата на поедините елементи во карпите и во испитуваните растенија. Генерално може да се констатира зголемена концентрација на талиум, цинк, олово, манган, бакар во испитуваните растенија.