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## TRACE ELEMENTS IN THE SOILS AND ASHES OF THE PLANTS VIOLLA ALSHARICA AND THYMUS ALSHARENSIS OF THE ALSHARSITE-MACEDONIA

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### ИЗВОД

Во трудот се презентирани резултатите од истражувањата на застапеноста на одделни микроелементи во почвата кај наоѓалиштето Алшар и нивното присуство во растенијата *Violla alsharica* и *Thymus alsharensis*, распространети на истиот локалитет. При тоа е утврдена значителна корелација особено во однос на концентрациите на талиум и на цинк.

**Клучни зборови:** микроелементи, геохемиски истражувања

### Introduction

The paper presents detailed geochemical investigations carried out in part of the Alshar polymetallic deposit in terms of the presence of individual microelements in the soils and plants such as *Violla 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 soils and plants. It can be inferred that the plants in the area under investigation contain increased concentrations of thallium, zinc, lead, manganese and copper (fig. 1).

For the results of previous studies of the Alshar deposit, the reader is referred to Ivanov (1965), Percival and Boev (1990), Percival et al. (1992),

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).

### Methods

The aim of the investigation was to determine the correlation between individual micro elements present in the soils and those in the ashes of *Viola alsharica* and *Thymus Alsharænsis*. 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 micro elements such as Sb, Se, W, Zn, Ba, Tl, As, Co, Cu, Mn, Ni and Pb.

Besides samples taken from the soils, samples of plants such as *Viola Alsharica* and *Thymus Alsharænsis* 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 micro elements (those of Sb, Se, W, Zn, Ba, Tl, As, Co, Cu, Mn, Ni and Pb) was performed by the ICP-AES method.

### Results 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 *Viola alsharica* and *Thymus Alsharænsis* (Fig.2).

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.

**Table 1.** Microelements in the 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	388	5	18	181	14	54
20	7	<5	<10	18	1700	3.1	137	2	25	26	5	37
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	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 sample material was also collected from plants

The Zn content in the rocks ranges from 11 to 465 ppm and compared to the Zn content in the ashes of *Viola Alshatica* (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 *Viola* of several hundred times can be noticed compared to its contents in the rocks and soil where the plant grows.



Fig.1. Panoramic view of the old dumps in the Alcharsite

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 *Viola* than *Thymus*. Data obtained indicate that Tl and As are more abundant in *Viola* due to their geochemical connection (fig.3, 4).

In contrast, Zn as a significant biogenic 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 *Viola* (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 biogenic 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

through investigations as well as establish the correlation in the abundance of individual microelements in different plants and organs.



Fig.2. Foto of the Viola Alch arica

**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

## Conclusions

The results presented in the paper lead to the conclusion that there is pronounced correlation between the distribution of individual microelements in the soils 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 the soils.

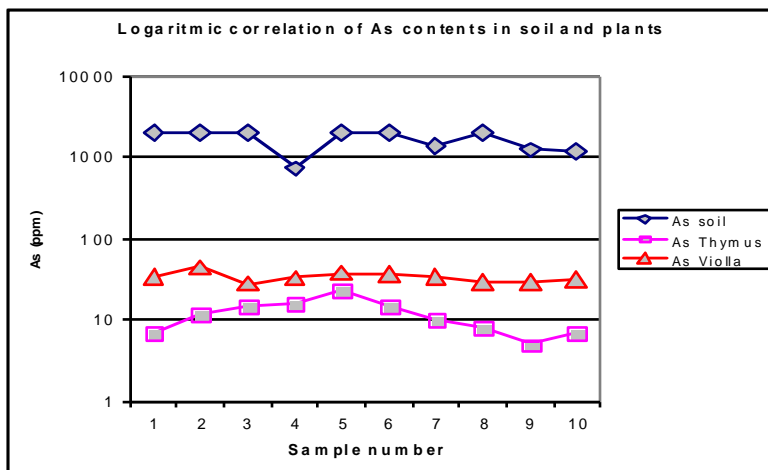


Fig. 3. Logarithmic correlation diagram of As contents in soil and plants from the Alsar

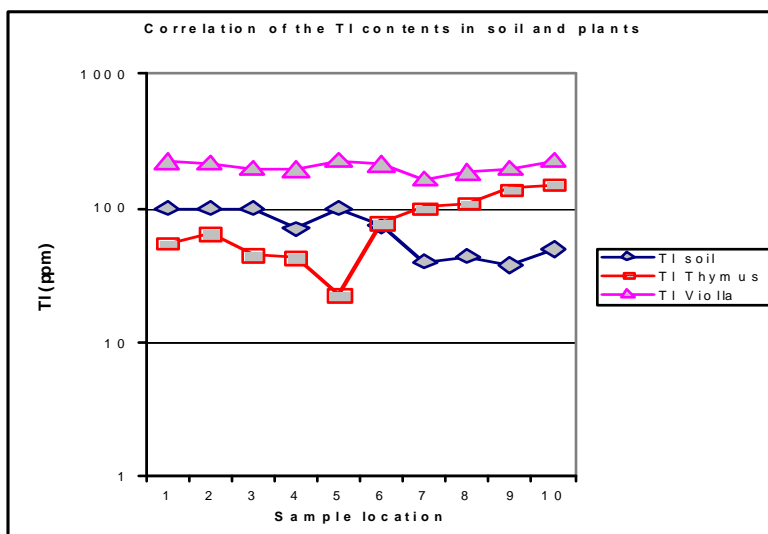


Fig. 4. Logarithmic correlation diagram of Tl contents in soil and plants from the Alsar

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