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GEOCHEMICAL CHARACTERIZATION OF U-Cu-Pb MINERALIZATION IN THE PERMIAN OF THE CHOČ NAPPE IN THE VIKARTOVSKÝ CHRBÁT AREA (THE WEST CARPATHIANS)

(Figs. 1—6)

Abstract: The stratiform mineralization occurs in the Upper Permian of the Choč nappe in the Vikartovský chrbát area. Distribution of U, Cu, Pb, Zn, Ni, Co, Sb, As, Mo, C org., V, Sr, Zr, Y, Th, Mn and Ti is explained in the paper. Dominant elements of ore association are U, Cu and Pb. Cu is more abundant than Pb in the western part of the Vikartovský chrbát area, and opposite relation was observed in the eastern part. The ore concentrations were formed mainly during the process of diagenesis owing to presence of organic carbon.

Резюме: В верхней перми хочского покрова в области Викартовского хребта обнаружена стратиформная минерализация. В статье описывается нахождение U, Cu, Pb, Zn, Ni, Co, Sb, As, Mo, C орг., V, Sr, Zr, Ý, Th, Mn и Ti, а также их распространение. Главными элементами рудней ассоциации являются U, Cu, Pb. В то время как в западной части Викартовского хребта преобладает Cu над Pb, в восточной части их соотношение обратное. Формирование рудных концентраций произошло главным образом в процессе диагенезиса, под влиянием органического углерода.

U-Cu-Pb mineralization occurs in the Upper Permian of the Choč nappe in the north-eastern part of Nízke Tatry Mts. The upper part of pelitic-psamitic beds of the Upper Permian is mineralized and it is represented mainly by arcosic sandstones, arcosis and aleurolites (L. Novotný — J. Badár 1971). Lenticular bodies of psamites of gray to dark gray colour with the fragments of carbonized plants are mineralized.

The following main ore minerals characterize the ore mineralization: pitchblende, chalcopyrite, galena, pyrite, tennantite, sphalerite and arsenopyrite (I. Rojkovič 1974). The relationship between the ore mineralization and fragments of the carbonized plants is obvious. The highest concentrations of ore minerals were found out in the central parts of lenses with the carbonized plants and especially in the thin 1—3 cm thick interlayers of coal. Sulfides occur also in quartz-carbonate veinlets cutting the ore lenses.

The ore concentrations were formed during diagenesis (L. Novotný — J. Badár 1971, I. Rojkovič 1974). The positive role during their formation played sorbtion properties of the carbonized plants, cross-bedding and litho-facial development of beds (L. Novotný — J. Badár 1971). Sterility of lenses with the carbonized plants with surrounding pelitic rocks demonstrates also diagenetic origin of the mineralization. The absolute age of the ore mineralization was determined by method Pb_{206}/U_{238} 263 m. y. and by $Pb_{207}U/_{235}$ method 274 m. y. (L. Novotný — oral report).

Occurrence of elements

The finegrained ore minerals and mostly their disseminated form of occurrence needs analyses of trace and especially ore elements due to full characterization of mineraliza-

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tion. For that reason were made analyses of arcosic sandstones with different, in some cases even prevailing ratio of carbonized plants. By the chemical, X-ray flourescence and spectral analyses were analysed the following elements: U, Cu, Pb, Zn, Ni, Co, Sb, As, Mo, C org., V, Sr, Zr, Y, Th, Mn and Ti. Majority of analyses were made in the laboratories of the Uranium industry. The quantitative spectral analyses were made in the laboratory of Geological Institute of the Slovak Academy of Sciences by p. g. J. Medveď and S. Klaučová.

Uranium occurs in the ore lenses in uranium minerals, mostly in pitchblende. Lower contents of uranium in sandstones without the carbonized plants detritus occur either in accessoric uranium minerals or in zircon. The average contents of the psamitic rocks in references are in the range 0.4—4 ppm (2 ppm — H. D. Holland — I. L. Kulp 1954, 4 ppm — L. S. Jevsejeva — A. I. Pereľman 1962, 0.45 ppm — K. K. Turekian — K. H. Wedepohl 1961, 1.5 ppm for arcoses by J. J. W. Rogers — K. A. Richardson 1964). Relatively high average content of uranium in the arcosic sandstones except ore lenses (24 ppm) indicates uranium enrichment in ore-bearing beds. The highest contents of uranium in the mineralized lenses were found out in their central parts, especially in the interlayers of the black shiny coal.

Copper occurs in copper minerals, mainly in chalcopyrite and tennantite.

Lead is bound in the rocks studied mostly to galena and partly occurs in uranium minerals as radiogenic lead.

Zinc is bound to sphalerite, which is common accompanying mineral of the ore mineralization. Lower contents of Zn were proved also in tennantite (I. Rojkovič 1974).

Nickel does not form own minerals in the rocks studied, but substitutes Fe in pyrite, as was proved by electron microprobe.

Cobalt occurs similarly as nickel in pyrite. The consistent occurence of Co and Ni is confirmed also by their high positive coefficient of correlation (tab. 1).

Antimony is in small amount bound to tennantite, as was confirmed by its significant correlation with Cu and by the electron microprobe analyses of tennantite.

Arsenic occurs in arsennopyrite and tennantite. The joint occurence of arsenic and copper is confirmed also by their high coefficient of positive correlation (tab. 1).

Molybdenum is enriched in the carbonized plants. There was found only one Pb-Mo-S mineral in the sample with the highest content of Mo, and it is subject of further study.

Organic carbon occurs in the carbonised remnants of plants, occuring mostly in the form of detritus, also in the form of 1—3 cm thick interlayers of coal, or relatively well preserved carbonized wood. The ore minerals occur in them very often, as was confirmed by belonging correlation coefficients of organic carbon to the ore elements (tab. 1, fig. 1—2). In the sandstones describe J. M. Hunt (1961) and A. B. Ronov (1958) 2.200 ppm C org. The average contents of C org. in the rocks studied are 1.565 ppm in the nonmineralized arcosic sandstone and 2.8 % in the mineralized lenses with carbonized plants.

Vanadium is enriched in the places of the highest concentration of the carbonized plants. Vanadium minerals have not been indentified by optic microscope, only by electron microprobe have been observed very finely disseminated vanadium oxides in the carbonized plants. This relationship is also confirmed by significant positive correlation of vanadium to organic carbon (tab. 1, fig. 2).

Strontium occurs either in the carbonized plants or carbonates present in the analysed arcosic sandstones mostly in the form of thin veinlets. It is suggested also

Table 1. Correlation coefficients of analysed elements in the Vikartovský chrbát area

	C. org.	Cu	Zn	Pb	Ti	V	Ni	Co	Zr	Th	As	Mo	Sb	Y	Sr	Mn
U	0,6605	0,6579	0,4648	0,1727	0,0200	0,7197	0,3509	0,3723	0,8400	−0,1347	0,6250	0,4695	0,1045	0,5764	0,7177	0,0435
C		0,6759	0,4215	0,1966	−0,0565	0,6400	0,2030	0,1836	0,6179	−0,0318	0,7331	0,6881	0,1265	0,4595	0,7757	0,1939
Cu			0,4816	0,1894	0,0379	0,8496	0,1744	0,1999	0,5492	0,1025	0,8354	0,6626	0,0663	0,4997	0,8040	0,1943
Zn				0,4117	−0,0435	0,3924	0,2377	0,1658	0,4296	0,1714	0,5208	0,3846	0,0953	0,2199	0,3513	−0,0163
Pb					0,0293	0,0719	0,1425	0,1036	0,2624	0,5672	0,3299	0,1691	0,5927	0,1075	0,0911	−0,0537
V						0,0656	0,0216	0,0770	0,0410	0,0024	−0,0110	0,0416	0,1718	0,0918	0,0333	−0,2498
Ni							0,2125	0,2591	0,5391	−0,1460	0,6920	0,5853	0,1248	0,510	0,8022	0,1553
Co								0,8844	0,3815	−0,0418	0,2652	0,2113	0,2134	0,7638	0,3321	−0,1995
Zr									0,4173	−0,0418	0,3485	0,2976	0,3328	0,7460	0,3530	−0,0918
Ti										0,0827	0,6405	0,4839	0,3571	0,5663	0,5575	−0,1478
Th											0,1793	0,0668	0,1794	−0,1130	−0,1945	0,0753
As												0,7356	0,2611	0,5284	0,7979	0,2057
Sb													0,1118	0,3131	0,5579	0,1467
Mo														0,0787	0,0779	−0,0716
Y															0,7070	−0,0200
Sr																0,3210

Correlation coefficients were calculated from 124 analyses.

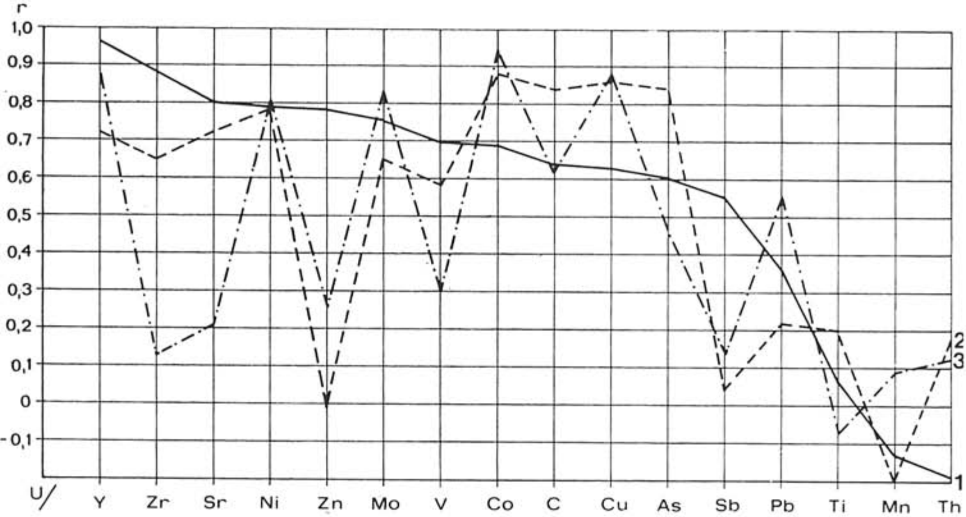

Fig. 1. Values of correlation coefficient of U to other elements (1 — western part of Vikartovský chrbát, 2—3 eastern, 3 — locality with weak mineralization).

by significant coefficient of correlation of Sr with C org. F. Čech (1969) describes for coal in the region Handlová and Nováky average contents from 150 to 1.500 ppm. D. J. Swaine (1972) found out in the ashes of the Australian coals Sr-contents from 100 to 10.000 ppm. Similarly in the Hungarian coal in the Pécs-Szabolcs area were by J. Csalgovits — M. F. Vighné (1969) found out the maximal content of Sr up to 10.000 ppm.

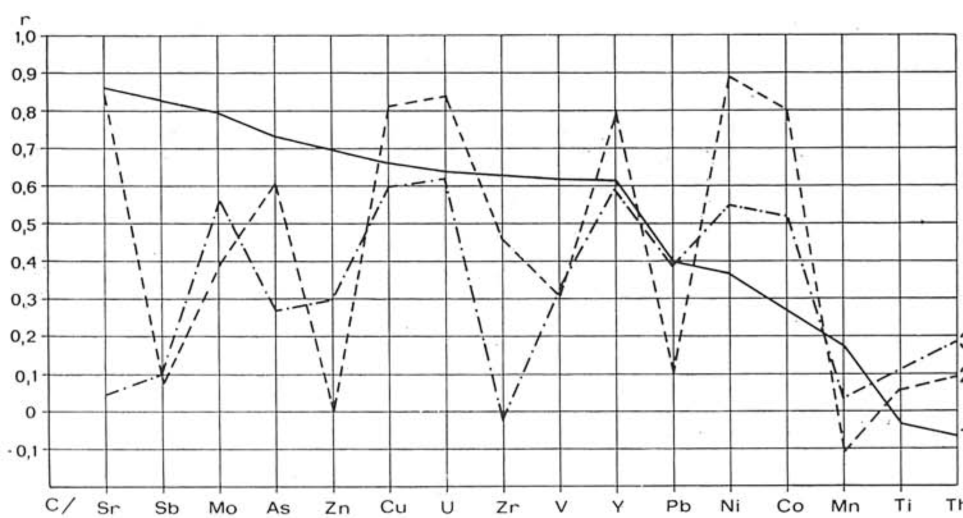

Fig. 2. Values of correlation coefficient of C org. to other elements (1 — western part of Vikartovský chrbát, 2—3 eastern, 3 — locality with weak mineralization).

Z i r c o n i u m is represented by mineral zircon, which is common accessory of the rocks studied. Zr-contents in references are shown 200 ppm (H. D e g e n h a r d t 1957) and 220 ppm (K. K. T u r e k i a n — K. H. W e d e p o h l 1961). In the rocks studied Zr shows moderate increase in the ore lenses (539 ppm) in the comparison with the adjacent nonmineralized sandstone (328 ppm).

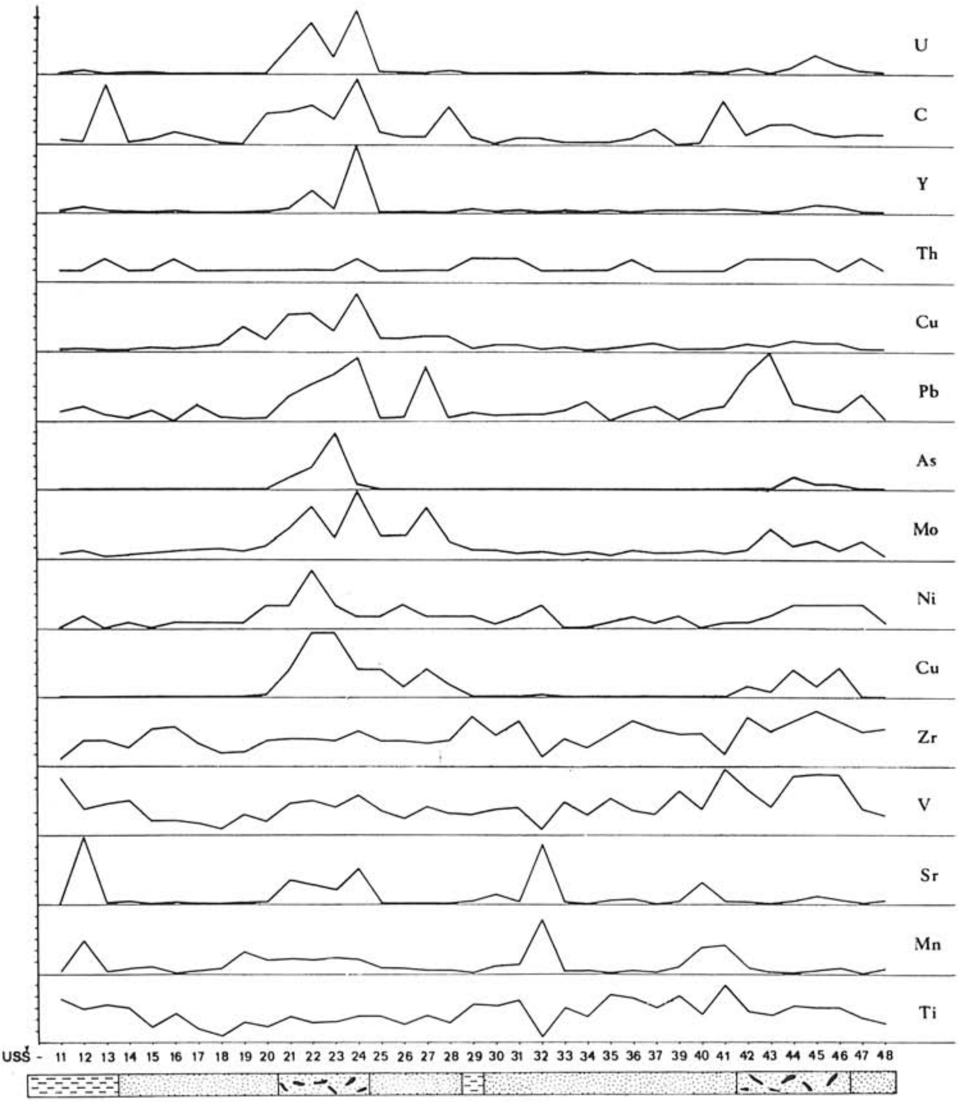

Fig. 3. Geochemical cross-section of the ore-bearing complex in the eastern part of Vikartovský chrbát (1 — aleurolites, 2 — arcosic sandstones, 3 — arcosic sandstones with abundant detritus of carbonised plants).

Y t t r i u m occurs in zircon and uranium minerals. It is confirmed also by significant positive coefficient of correlation of Y with Zr and U. Due to its occurence in the uranium minerals the average content of Y in the mineralized lenses shows significant enrichment (216 ppm) in the comparison with the nonmineralised sandstone (19 ppm).

T h o r i u m is probably bound to either uranium minerals or zircon. Small variability of Th-contents due to low sensitivity of analysis, does not show this relationship.

M a n g a n e s e occurs in the manganese oxides. In the rocks studied does not show any relation to the ore mineralization. There is none significant difference between its contents in the mineralized (695 ppm) and the nonmineralized (544 ppm) arcosic sandstones.

T i t a n i u m occurs in the accessoric minerals, mostly in rutile. There has not been found any relation to the ore mineralization, and its distribution is different as in the case of the elements connected with the ore mineralization. The average contents of Ti in mineralized as well as in nonmineralized rocks are practically the same (3.763 ppm in mineralized and 3.872 ppm in nonmineralized rocks).

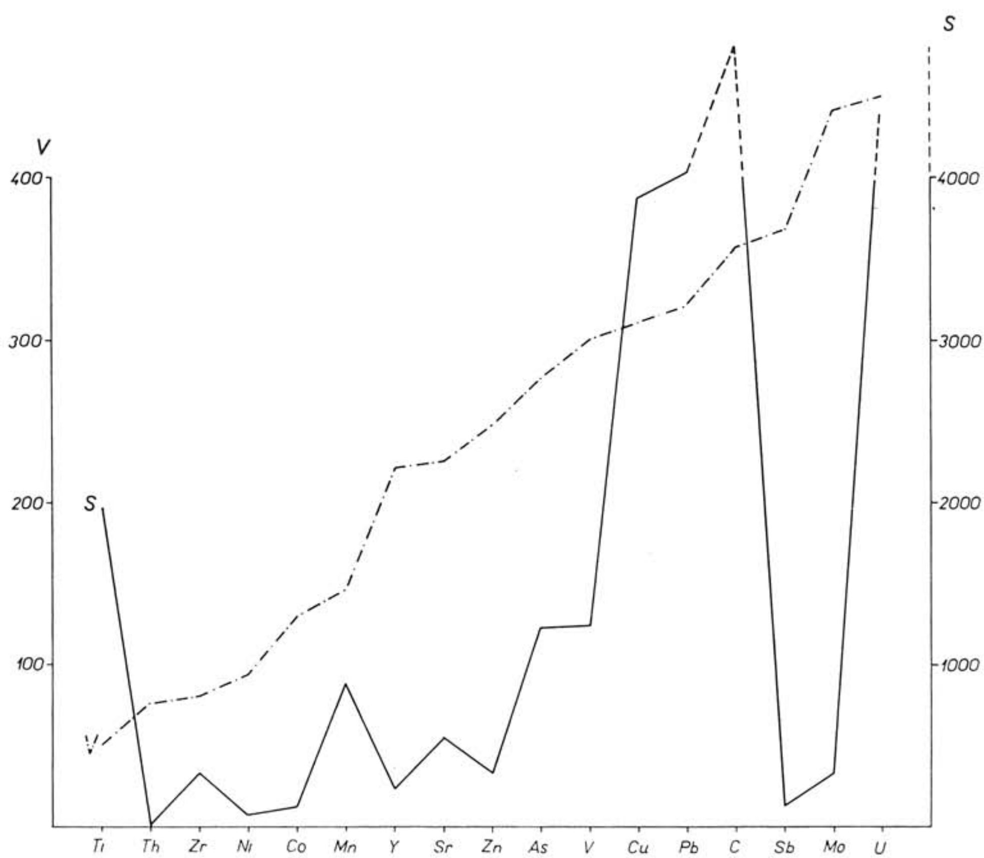

Fig. 4. Values of variation coefficient (V) and standard deviation (s) of the analysed elements in the Vikartovský chrbát area.

Table 2. Statistical evaluation of analysed elements

	1			2			3			4		
	$\bar{x}$	s	V	$\bar{x}$	s	V	$\bar{x}$	s	V	$\bar{x}$	s	V
U			310			198			209			450
C org.	23,908	69,539	291	7,977	11,414	143	2,465	2,836	115	13,013	46,445	357
Cu	2,842	5,590	197	130	191	240	53	62	116	1,244	3,868	311
Zn	185	357	193	241	579	213	46	81	178	159	395	248
Pb	875	2,980	341	2,967	6,317	44	163	188		1,253	4,030	322
Ti	3,513	2,254	64	3,680	1,633	147	4,400	1,666	38	3,825	1,964	51
V	786	1,827	233	190	264	139	90	45		410	1,234	301
Ni	43	51	118	100	82	82	79	49	63	70	66	94
Co	60	97	163	114		124	99	92	93	87	113	130
Zr	496	475	96	412	190	46	322	121	38	420	338	80
Th	17	16	96	17	9	55	13		35	16	12	76
As	855	1,743	204	161	382	238	118	5	301	439	1,216	277
Sb	60	154	255	30	136	452	1	355	59	34	126	368
Mo	40	66	164	163	527	323	13	1	110	76	333	441
Y	145	276	190	137	272	199	49	15	226	101	224	221
Sr	561	986	176	184	307	167	151	112	227	243	548	225
Mn	1,293	1,261	98	202	158	78	652	843	129	607	282	145

$\bar{x}$ – arithmetical average, s — standard deviation, V — variation coefficient; 1 — the western part of the Vikartovský chrbát area, 2 — 3 the eastern part of the Vikartovský chrbát area, 3 — locality with the weak mineralization, 4 — all localities in the Vikartovský chrbát area.

Distribution of elements

Due to nearly horizontal position of the beds only close underlaying and overlaying rocks of the mineralized lenses can be observed in the mines. More complete cross-section is shown in the eastern part of the Vikartovský chrbát ares in the locality with weaker mineralization (fig. 3). From the geochemical cross—section it is possible to see corresponding peaks in the central parts of the ore lenses for U, C org., Cu, Pb, As, Mo and less for Ni, Co, Zr, V, Th and Sr. The increased contents have not been observed in the central parts for Mn and Ti.

Element association of the ore mineralization, typical for the mineralization studied, expressively shows values of standard deviation and variation coefficient. While standard deviation is expression of absolute dispersion, variation coefficient is relative value of dispersion. The high standard deviation is so typical for all elements with the high contents, till higher values of variation coefficient are typical for the elements of the ore mineralization, showing in this way their relative enrichment in the mineralized lenses. This is obvious in the case of Ti. Titanium with the relative high contents has

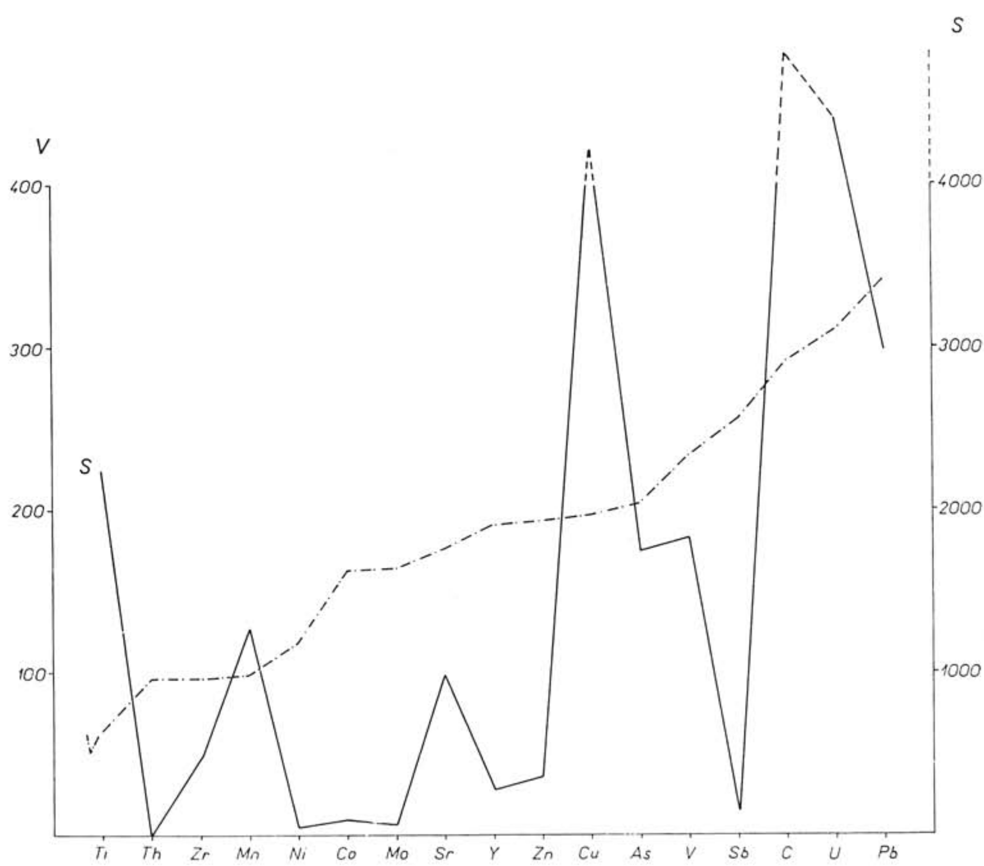

Fig. 5. Values of variation coefficient (V) and standard deviation (s) of analysed elements in the western part of Vikartovský chrbát.

the corresponding value of standard deviation high, but its variation coefficient is the lowest among the analysed elements (tab. 2, fig. 4—6). The elements concentrating in the mineralized lenses have their corresponding values of variation coefficient approximately above 100 (fig. 4—6). Among them show maximal increase of standard deviation in the comparison with variation coefficient the elements of maximal concentration and they are the characteristic elements of individual localities. They are C org., U, Pb and Cu for whole Vikartovský chrbát area (fig. 4). For the western part of area is except C org. and U typical Cu (fig. 5), while in the eastern part prevails Pb instead of Cu (fig. 6). This corresponds very well to the association of the ore minerals. While for mineralized lenses in the western part is except uranium minerals typical chalcopyrite and tennantite, in the eastern part it is galena.

Further comparison of the element association of the ore mineralization show coefficients of linear correlation (tab. 1, fig. 1—2). Most of the elements of the ore mineralization show the significant positive correlation with uranium (above +0.5). It was

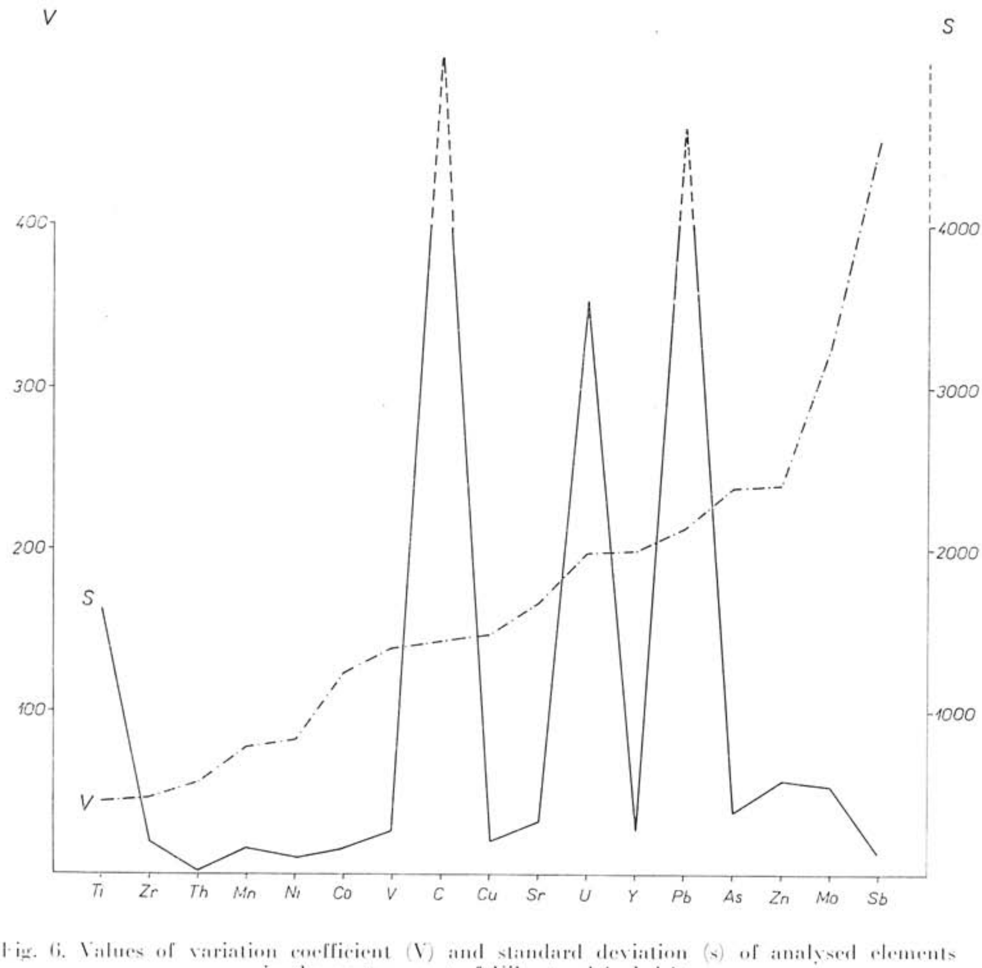

Fig. 6. Values of variation coefficient (V) and standard deviation (s) of analysed elements in the eastern part of Vikartovský chrbát.

not observed in the case of Ti, Mn and Th (Th-probably due to low sensitivity of analysis). Low correlation with Pb and Zn in the eastern part of the Vikartovský chrbát area is caused obviously by their local remobilization in the quartz-carbonate veinlets within mineralized lenses. Low correlation with Sb in the eastern part reflects absence or rare occurence of tennantite.

The described data show, that for the western part of Vikartovský chrbát area are more typical Cu, As and Sb, while for eastern part Pb, Zn and Mo. Regarding these differences the association of the elements typical for U-Cu-Pb mineralization in the Vikartovský chrbát can be characterized as follows:

1. Dominant elements of the ore mineralization: U, Cu, Pb.
2. Additional elements of the ore mineralization: Zn, As, Ni, Co, Mo, Sb, (Y), (Th).
3. Accompanying elements: C org., Zr, Sr, V, (Y), (Th).

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