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GEOCHEMICAL CHARACTERISTICS OF MINERALIZED PERMIAN ROCKS OF THE POVAŽSKÝ INOVEC MTS.

(Figs. 5, Tab. 6)

Abstract: The Permian rocks of Považský Inovec are represented mainly by clastic sediments, accompanied by quartz porphyries and their tuffs. The mineralization appears in the upper horizon, prevailingly in tuffaceous sandstones and in the lower horizon predominantly in conglomerates. Dominant elements of mineralization are: U, Pb and Cu, accompanied by Mo, Ni, Co, Y and V.

Резюме: Пермские породы Поважского Иновца представляют главным образом кластические отложения, которые сопровождают кварцевые порфиры и их туфы. Минерализация выступает во верхнем горизонте, главным образом в туффитических песчаниках и в нижнем горизонте, главным образом в конгломератах. Главными элементами минерализации являются U, Pb и Cu в сопровождении Mo, Ni, Co, Y и V.

The envelope Permian of the crystalline core of the Považský Inovec appears in the northwestern part of the mountains. According to J. Kamenický, 1967 (in: M. Mahel' et al., 1967), the continental sediments of the Permian are approximately 200 m thick and they are represented first of all by violet, green and grey shales, by intercalations of pale arkoses and small-fragmental conglomerates, material, consisting of fragments of vein quartz and of the underlying rocks of the Permian. Recently, in consequence of the determination of uranium mineralization, an intense geological research is carried out by the workers of the Uranium Industry in the area. On the basis of technical works and in cooperation with the workers of the Uranium Industry, the author was enabled to study mineralogically and geochemically the mineralization of the rocks. The author would like to express his thanks to the co-workers from the Uranium Industry, especially to I. Štimmel and to J. Matúš, who enabled the sampling and took care of a part of the analyses.

Horizons with uranium mineralization appear in tuffaceous rocks and in the lower horizon of strongly unassorted conglomerates and sandstones. In horizons with uranium mineralization and with younger carbonate-quartz veinlets there were determined mainly: pitchblende, brannerite, pyrite, galena, chalcopyrite, tetrahedrite and other ore minerals (I. Rojkovič, in press).

Petrographic characteristics of the rocks

The studied rocks are represented mainly by clastic sediments, particularly by sandstones and conglomerates, less by shales of grey, green and violet colours. A part of the sediments is of tuffaceous character. Volcanic rocks are represented by quartz porphyries and by their pyroclastics.

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Fig. 1. Quartz porphyry with a magmatically corroded quartz phenocryst. Sample UIK-12, passing light, 28 x, X nicols, photo I. Rojkovič.

Fig. 2. Volcanoclastic fragments of quartz in psamitic tuff. Sample UIK-38, passing ligth, 28 x, X nicols, photo I. Rojkovič.

Quartz porphyry is less abundant than the pyroclastics. Macroscopically, quartz porphyries are greyish-white and pale green in colour and with observable phenocrysts of quartz and feldspars. The texture of the rock is porphyric. The groundmass is very fine-grained and its texture is felsitic. The grains of the groundmass vary in the range of 1—10 micrometers. Approximately 95 % of the groundmass consists of quartz and of feldspars. Sericite is only secondary and usually does not exceed 5 %. Porphyric phenocrysts are represented by quartz and feldspars. Quartz phenocrysts are 0.5—2 mm big, a pronounced magmatic corrosion is observable (Fig. 1). The extinction is prevailingly straight, undulatory extinction, however, can also be observed. One part of the phenocrysts is recrystallized. Feldspar phenocrysts are 0.5—2 mm big, mostly sericitised from the rim, sometimes, however, their complete replacement by sericite in the form of pseudomorphoses takes place. Accessorically, columellas of zircon and rutile were observed in the groundmass. Chemical analyses of quartz porphyries, as well as those of the remaining studied rocks are given in Table 1.

Pyroclastic rocks. Acid volcanism is in the studied area represented first of all by ash and psamitic tuffs of quartz porphyries. The mineralogic composition is better discernible in coarser grained varieties, i. e. in psamitic tuffs. Volcanoclastic material is represented, similarly as in quartz

Table 1
Chemical composition of rocks (in weight per cent)

No.	1	2	3	4	5	6
FeO	0.15	0.11	0.16	0.18	0.17	0.12
Fe_2O_3	1.08	1.16	1.01	1.29	1.36	1.32
MnO	<0.01	0.02	0.02	<0.01	0.13	0.02
TiO_2	0.14	0.11	0.11	0.34	0.14	0.22
CaO	0.11	0.07	0.43	0.22	0.38	0.26
K_2O	5.41	5.32	5.20	8.08	5.85	4.98
SiO_2	82.27	85.19	84.98	69.54	83.18	78.71
Al_2O_3	8.14	7.03	6.71	17.03	7.59	10.37
MgO	0.21	0.19	0.36	0.30	0.25	0.35
Na_2O	1.79	0.14	<0.01	<0.01	0.05	0.99
H_2O^+	0.41	0.36	0.14	0.30	0.33	0.52
H_2O^-	0.60	0.54	0.75	2.66	1.00	2.36
Sum.	100.31	100.24	99.87	99.96	100.43	100.22

Rocks: 1—4 quartz porphyry, 5 — psamitic tuff, 6—8 tuffitic sandstone, 9 — 11 sandstone, 12 — cement of conglomerate, 13 — quartz-sericite shale

No.	7	8	9	10	11	12	13
FeO	0.22	0.88	0.75	0.71	2.28	0.55	0.35
Fe_2O_3	1.19	0.89	1.02	1.28	0.15	1.49	1.78
MnO	0.01	0.03	0.03	0.02	0.09	0.01	0.01
TiO_2	0.23	0.48	0.84	1.30	0.72	0.56	0.37
CaO	0.13	0.15	0.15	0.36	3.40	0.26	0.14
K_2O	3.51	3.99	3.59	4.22	4.76	2.86	5.95
SiO_2	81.95	74.90	73.95	70.15	61.19	77.60	72.52
Al_2O_3	9.31	13.07	14.52	15.52	14.89	11.47	13.98
MgO	0.74	1.25	0.66	1.59	3.85	0.84	1.45
Na_2O	0.09	1.68	0.80	1.27	0.21	1.73	0.51
H_2O^+	1.07	0.18	0.69	0.52	0.81	0.35	0.38
H_2O^-	1.76	2.32	3.18	3.24	7.41	2.45	2.62
Sum.	100.21	99.82	100.18	100.18	99.76	100.17	100.06

Analysed by M. Vondrovic by X-ray fluorescence. Fe^{+2} and Fe^{+3} determined by I. Pistlová by titration.

porphyries, mainly by quartz and by feldspars (Fig. 2). The fragments are very angular to acicular and in some of them, there are observable also traces of magmatic corrosion.

Clastic sedimentary rocks are represented by shales, sandstones and conglomerates of violet and green colours which depend on the presence of hematite pigment or from an increased ratio of sericite. According to uranium mineralization, the colour of sediments is grey to black. In sedimentary rocks pyroclastic materials was discernible, according to which it was possible to classify one part of the rocks as tuffaceous shales, sandstones and conglomerates. The distinguishing of pyroclastic material, i.e. that of volcanoclastic fragments of quartz, is sometimes problematic and, because the mineralogic composition is otherwise analogous to that of the clastic sedimentary rocks mentioned above, they are described together.

Conglomerates have prevailingly quartz cement. Feldspar and sericite are less abundant. Pebble material, mostly 2—5 cm large, is relatively poorly rounded. Ratio of pebbles is frequently smaller and conglomerates pass into sandstones. In mineralized black conglomerates is common, besides of uranium minerals, causing the dark colour of the rock, also pyrite. Pebles are represented by the following minerals and rocks:

— quartz, straight and undulatory extinguished;
— quartzite with differently sized allotriomorph grains of quartz or oriented metaquartzites;
— graphitic shales with fragments of quartz and muscovite;
— mica schists mostly of elongated form with parallelly oriented muscovite;
— quartzy ash and psamitic tuffs were established in tuffaceous conglomerate.

Accessorically were found turmaline and zircon. Ore minerals, particularly pyrite are dispersed in the cement but they appear also frequently on cracks across the pebbles.

Sandstones are represented by fine grained, medium-grained and coarse grained sandstones and tuffaceous sandstones. They are frequently inequigranular and their assortment, as well as orientation are poor. Poor is also the rounding of the material. Oriented teqtures can be observed more in fine-grained varieties alternating with shales. Quartz feldspars and sericite occur in their cement. Clastic fragments consist of: quartz, felspars, muscovite, quartzite, sericitic shales. Tourmaline and zircon were found accessorically, while the grains of tourmaline are rounded and the growth of younger generation of paler colour can be observed on them, zircons form rounded, but also poorly rounded, prismatic vrystals. Dispersed pyrite grains are overgrown by quartz and mainly by chlorite, at the same time being oriented with preference in the direction of shaly cleavage, forming, thus, pressure shadows.

Shales are represented by sericitic and quartz-sericitic shales. The fundamental part of these rocks constitute sericite and quartz prevalingly of oriented texture. Larger quartz grains folow parallelly the orientation of sericite scales. From other composites were found in the rocks, studied microscopically: feldspars, muscovite and accessorically tourmaline and zircon.

Geochemical characterization of the mineralization

In consequence of the mostly dispersed form in which the ore minerals occur and due to their fine-grained character, for a more complete characteristic of the mineralization, analyses of chosen trace elements in the studied rocks are necessary. By quantitative spectral analysis were established Pb, Cu, Mo, V, Ni, Co, Zr and Y by RNDr. J. Medveď, CSc. in the laboratory of the Geological Institute of the Slovak Academy of Sciences. Analyses of U, Th and of organic carbon were carried out in the laboratories of the Czechoslovak Uranium Industry. Uranium was determined by luminiscence and, in case of higher concentrations, colorimetrically.

Table 2

Correlation coefficients of elements in the studied rocks (109 transformed data)

	Pb	Mo	Cu	Y	V	Zr	Ni	Co	Corg
U	0,72	0,53	0,59	−0,03	0,36	−0,06	0,20	0,11	−0,10
Corg	−0,17	0,02	−0,10	0,08	0,02	−0,06	0,14	0,30	
Co	0,07	0,27	−0,02	0,34	0,14	0,39	0,58		
Ni	0,27	0,27	0,19	0,37	0,13	0,36			
Zr	0,17	0,14	0,16	0,60	0,27				
V	0,54	0,42	0,39	0,25					
Y	0,30	0,23	0,37						
Cu	0,61	0,40							
Mo	0,16								

116 samples

Occurrence of individual elements

Uranium is bound in uranium minerals out of which could be determined in mineralized rocks pitchblende, brannerite and torbenite. In wall—rocks of ore lenses it occurs in separate dispersed uranium minerals and in zircon. Its average content in nonmineralized quartz porphyries of 22 ppm and in sandstones, including the tuffaceous ones of 9 ppm exceeds reference data for analogous rocks. A. V. Vinogradov (1962) and K. K. Turekian and K. H. Wedepohl (1961) give for granitoids 3.5 and 3.0 ppm and for sandstones and sediments 3.2 and 0.42 ppm. Contents of U in rhyolites are given by J. Forgáč (1970) as 2—13.7 ppm, by J. L. Cheminee (1970) as 4.6 ppm and by V. A. Maximovskij and V. N. Zelupugin (1972) as 3.6 pp. For psamitic rocks bring J. J. W. Rogers — K. A. Richardson (1964) 1.5 ppm for arkoses and 2.1 ppm for greywacks, H. D. Holland — I. L. Kulp (1954) 2 ppm and L. S. Jevsejeva — A. I. Pereľman (1962) 4 ppm. From the above mentioned follow the higher contents of U also in wall—rocks of ore lenses in the area of Považský Inovec.

Lead occurs chiefly in galena and in a lesser extent in uranium minerals as radiogenic lead.

Copper occurs in chalcopyrite, tetrahedrite, bornite, diagenite, covellite and torbenite.

Molybdenum is bound in molybdenite which was microscopically determined only rarely.

Nickel and cobalt do not form separate minerals but isomorphously substitute Fe in pyrite.

Vanadium substitutes probably in consequence of close ionic radii isomorphously Fe, Ti and Al in minerals as rutile, sericite and others. Separate minerals of vanadium were not determined so far.

Zirconium occurs in the mineral zircon which is a current accessory mineral of the studied rocks.

Thorium is bound to uranium minerals given above. Its contents very on the detectivity limit of the analysis with small variability which does not allow a sufficient interpretation of its distribution.

Ytrium occurs in uranium minerals as well as in zircon which is con-

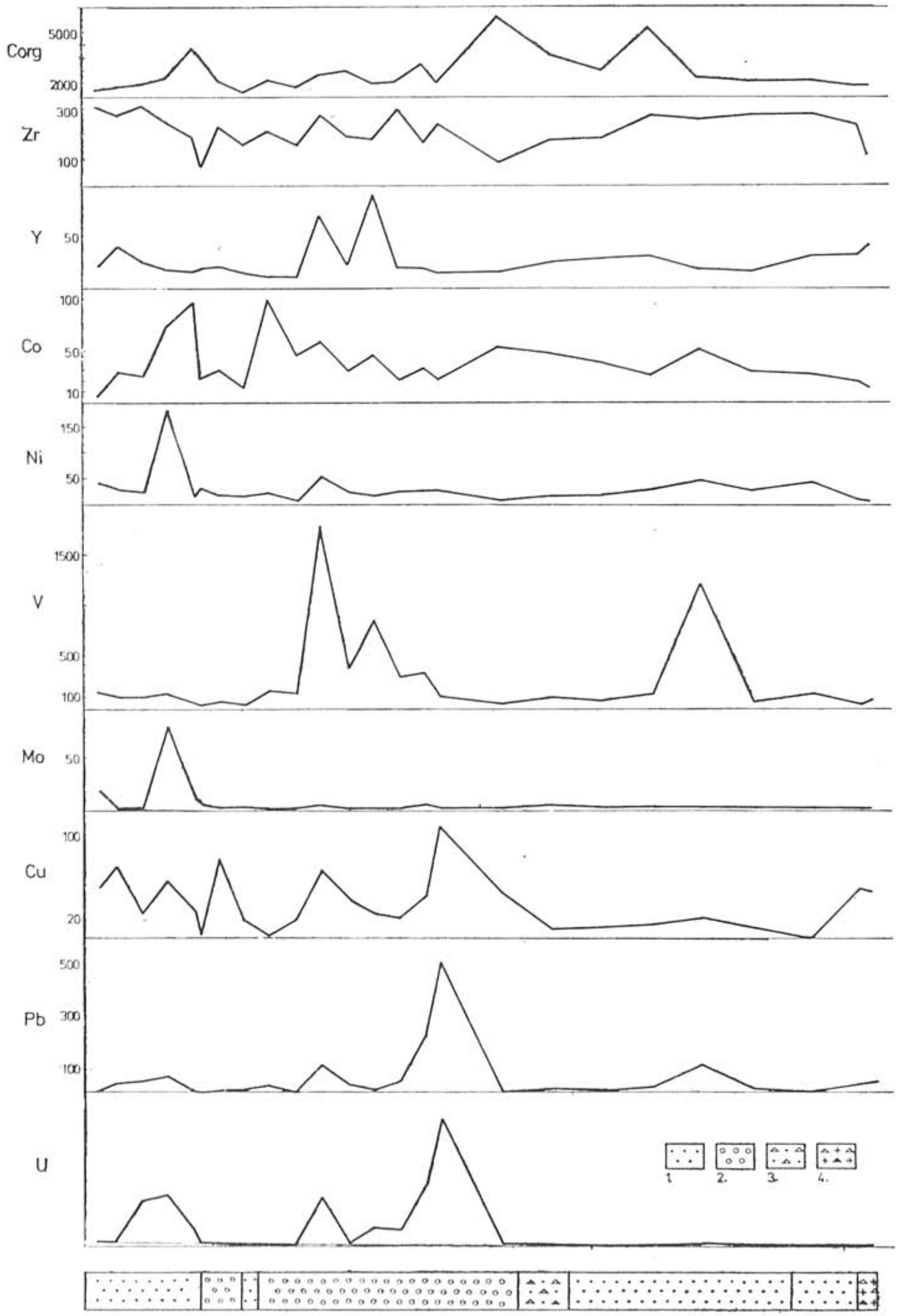

Fig. 3. Geochemical section of the drilling 744. 1 — sandstone, 2 — conglomerate, 3 — tuffaceous sandstone, 4 — psamitic tuff.

firmed by the results achieved by the X-ray microanalyser as well as by an expressive positive correlation Y/Zr (Table 2).

Geochemical sections of drillings and from mines show occurrence of maximum concentrations in essence in two horizons (Fig. 3, 4). The upper horizon of mineralization is represented mostly by psamitic and ash tuffs

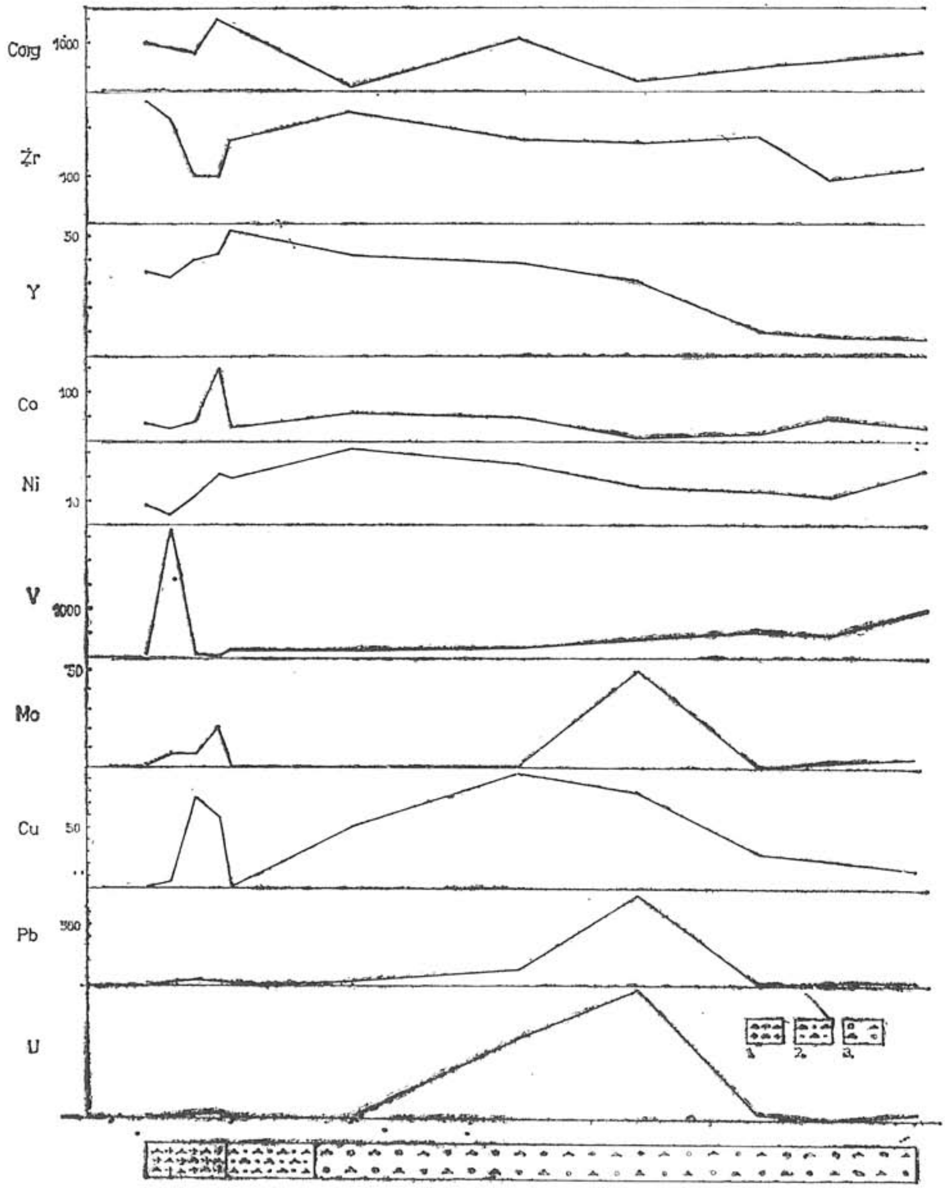

Fig. 4. Geochemical section of the driling 44 A. 1 psamitic tuff, 2 — tuffaceous sandstone, 3 — tuffaceous conglomerate.

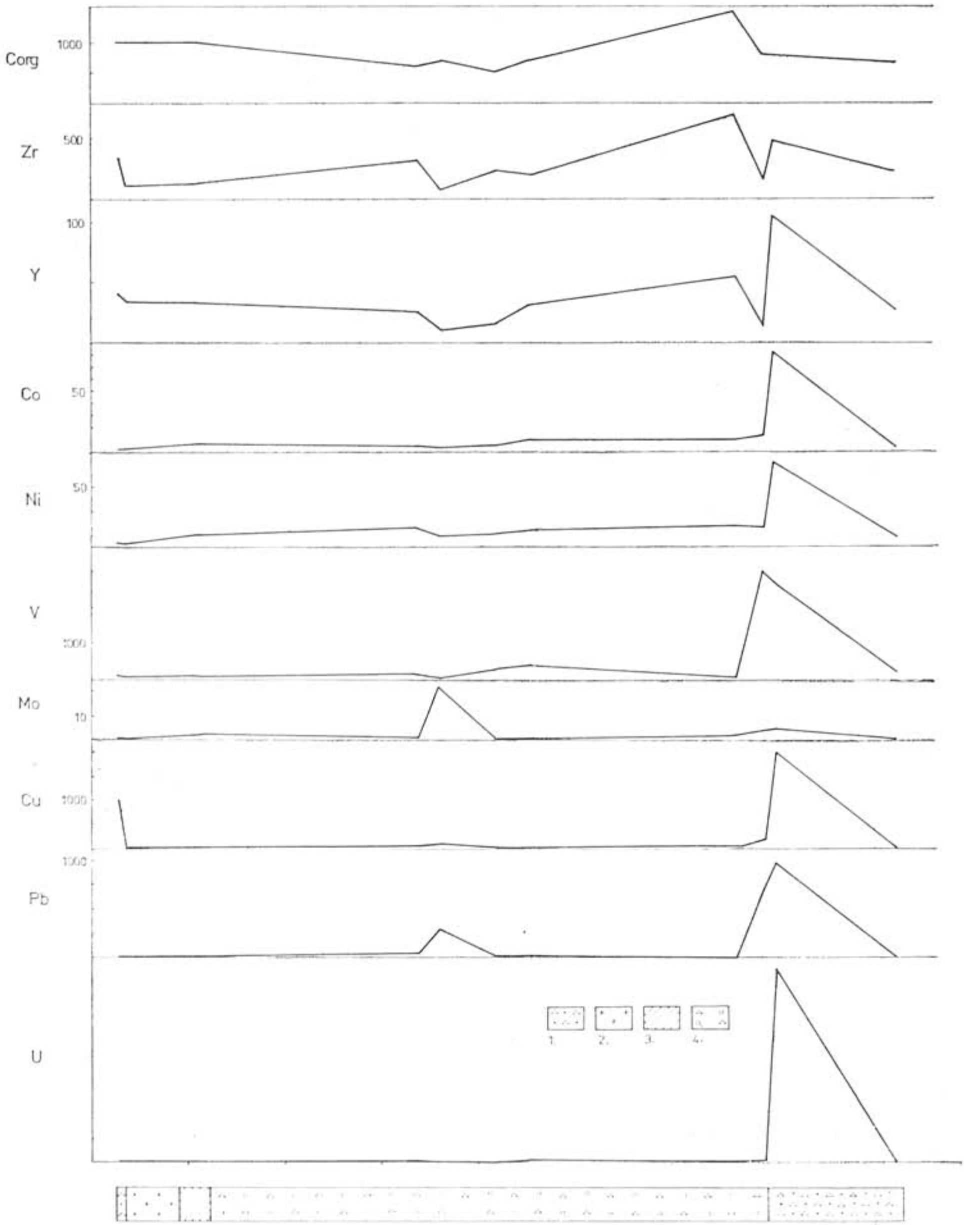

Fig. 5. Geochemical section of the driling GP-44, 1 — tuffaceous sandstone, 2 — quartz porphyry, 3 — sericitic shale, 4 — tuffaceous conglomerate.

and sandstones, often with pyroclastic material (Fig. 4). The lower mineralized horizon occurs mostly in conglomerates (Fig. 3), or tuffaceous conglomerates (Fig. 4) with a subordinate ratio of psamitic rocks. U, Pb, Cu,

Table 3

Arithmetical average contents of elements in nonmineralised rocks in ppm

	Quartz porphyry	Tuff	Conglomerate	Tuff. conglomerate	Tuff. congl.-congl.	Green sand-stone	Tuff. green sandst.	Tuff. green s.+g.s.	Violet sandstone	Shale
U	22	11	17	20	18	14	4	5	2	1
Pb	14	25	119	59	96	46	14	30	1	4
Mo	4	5	2	4	3	7	2	5	1	1
V	42	375	251	348	288	198	82	137	80	37
Cu	13	144	67	39	56	227	120	171	1	5
Ni	5	9	16	17	16	27	6	16	34	18
Co	16	40	30	22	27	32	28	30	33	79
Zr	118	166	156	231	185	227	177	201	229	150
Y	27	34	24	22	23	25	29	27	21	41
Th	—	3	3	2	3	4	4	4	2	—
Corg	—	775	1925	667	1506	1811	1500	1647	867	1000
n	2	8	13	8	21	10	11	21	3	2

n=number of samples

Y and Mo, less Ni and Co are distinctly increased in both horizons. The best coincidence of maximum concentrations with U in vertical sections shows Pb. The highest contents of Cu correspond with U, but they are increased in a wider extent, uparticularly in the direction from the lower to the upper horizons (Fig. 4). The highest concentrations were found in the upper horizon, especially in tuffs, however, in some drillings, there were found higher contents of ore elements rather in the lower horizon. From vertical sections is evident the different distribution of Zr, V and organic C. Sometimes can be observed their moderate increase in the overlying ore horizon (Fig. 5) but also in the underlying of the lower horizon (Fig. 5). Cross sections, as well as longitudinal sections of ore lenses show the zonality of ore concentrations with maximum concentrations in the centres of the lenses.

Asociation of ore elements

Association of ore elements reflects the mineralogical association of ore mineralization represented mainly by pitchblende, galena and chalcopyrite, accompanied in horizons with uranium mineralization and younger quartz-carbonate veins by the following ore minerals: arsenopyrite, bornite, brannerite, covellite, digenite, goethite, hematite, molybdenite, pyrite, sphalerite, tetrahedrite and torbernite.

Association of ore elements show statistical values as for instance the coefficients of liner correlation, arithmetical and geometrical means and standard deviations. The coefficients of linear correlation show high correlation with uranium in lead and a distinct one in copper and molybdenum, i.e. association of galena, chalcopyrite, tetrahedrite and molybdenite with uranium minerals (Table 2). The relation of organic carbon to ore elements is interesting from the point of view of the origin of ore mineralization. From the calculated coefficients it is possible to eČclude their mutual relation. With its low content of organic carbon in sediments, as well as by the

Table 4

Arithmetical and geometrical means (in ppm) and standard deviations of elements in ash and psamitic tuffs.

	—U	+U	±U		
	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}_g$	s
U	11				1,29
Pb	25	332	260	79	0,66
Cu	144	472	395	162	0,63
Mo	5	18	15	3	0,58
Co	40	37	38	24	0,42
Ni	9	46	37	28	0,39
V	375	592	541	257	0,53
Y	34	172	140	48	0,45
Th	3	—	3	—	—
Zr	166	283	255	182	0,28
Corg	775	—	775	674	0,27
n	8	26	34	34	34

Expanations: $\bar{x}$-arithmetical mean; $\bar{x}_g$-geometrical mean; s-standard deviation (in log transformed data); n-number of samples; —U—rocks without uranium mineralization; +U—uranium mineralized rocks.

absence of its relation to uranium, the Permian of the Považský Inovec Mts. is similar to the Permian of the north-gemerides (I. Rojkovič, 1968), in contrast to the sediments of the Permian of the Choč nappe, rich in carbonized remnants of plants, binding uranium mineralization (L. Novotný — J. Badár, 1971; I. Rojkovič, 1974).

The average contents of the analysed elements show (Tab. 3, 4, 5, 6) a distinct increase of uranium content but also of Pb, Cu, Mo, V and partly Y, Ni and in ore-mineralized rocks. Due to a frequently problematic distinction of pyroclastic material in the sediments, the statistical values are given also together for psephitic and psamitic rocks without regard to the presence or absence of pyroclastic material in some of them (Tab. 5, 6). A distinct decrease of organic carbon contents can be observed in relation to the presence of pyroclastic material. The lowest contents of organic carbon are in tuffs, higher ones in tuffaceous rocks and the highest ones in sandstones and in conglomerates (Tab. 4, 5, 6). The highest concentrations of ore elements, especially those of uranium, in a lesser extent of Cu and Pb were found in ash and psamitic tuffs of the upper mineralized horizons. That is the cause why the highest average contents of these elements are in tuffs. On the contrary, the violet sandstone and sericitic shales show distinctly lower contents of ore elements than green and grey psephitic and psamitic rocks (Table 3).

Average contents of elements in quartz porphyries and in non-mineralized psamitic sediments correspond quite well with their average contents in granitoids and sandstones, as described by A. P. Vinogradov (1962) and K. K. Turekian and K. H. Wedepohl (1961). Increased contents in the Považský Inovec Mts. show U in quartz porphyry and U, Pb and Cu in psamitic sediments.

In camporison with quartz porphyries of the Permian of the north-gemerides, the quartz porphyries of the Považský Inovec Mts. show analogous

Table 5

Arithmetical and geometrical meas (ni ppm) and standard deviations of elements in conglomerates and tuffitic conglomerates

	conglomerate			tuffitic conglomerate			conglomerate + tuffitic conglomerate				
	—U	+U	±U	—U	+U	±U	—U	+U	±U		
	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}_g$	s
U	17			20			18				0,94
Pb	119	222	166	59	173	108	96	205	145	45	0,73
Cu	67	328	186	39	89	60	56	243	140	45	0,61
Mo	2	39	19	4	2	3	3	26	13	2	0,51
Co	30	26	28	22	15	19	27	22	25	14	0,49
Ni	16	18	17	17	14	16	16	17	17	14	0,27
V	251	469	351	348	661	482	288	537	399	226	0,45
Y	24	20	23	22	29	23	23	23	23	19	0,28
Th	3	3	3	2	0	2	3	2	3	—	—
Zr	156	192	173	231	127	187	185	169	178	154	0,23
Corg	1925	1120	1559	667	768	738	1506	988	1254	972	0,32
n	13	11	24	8	6	14	21	17	38	28	38

Explanations: $\bar{x}$-arithetical mean; x_g-geometrical mean: s-standard deviation (in log transformed data); n-number of samples; —U—rocks without uranium mineralization; +U—uranium mineralized rocks.

Table 6

Arithmetical and geometrical means (in ppm) and standard deviations of elementes in sandstones and tufftic sandstones

	Sandstone			Tuffitic sandstone			Sandstone + tuffitic sandstone				
	—U	+U	±U	—U	+U	±U	—U	+U	±U		
	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}$	$\bar{x}_g$	s
U	14			4			9				1,19
Pb	46	182	85	14	476	209	30	378	156	29	0,84
Cu	227	526	312	120	456	261	171	479	283	39	0,82
Mo	7	28	13	2	4	3	5	12	7	3	0,53
Co	32	32	32	28	32	37	30	32	31	21	0,43
Ni	27	63	37	6	25	20	16	38	27	20	0,32
V	198	288	224	82	573	289	137	478	61	110	0,49
Y	25	25	25	29	34	31	27	31	28	25	0,20
Th	4	2	3	4	4	4	4	3	4	—	—
Zr	227	270	239	177	214	193	201	233	212	200	0,15
Corg	1811	1350	1669	1500	787	1183	1647	975	1387	1111	0,28
n	10	4	14	11	8	19	21	12	33	33	33

Explanations: x-arithmetical mean; x_g-geometrical mean; s-standard deviation (in log transformed data); n-number of samples: —U—rocks without uranium mineralization; +U—uranium mineralized rocks.

contents, except of a lower content of Cu (I. Rojkovič, 1969). Ore bearing psamitic and psephitic rocks of the Považský Inovec Mts. show lower contents of nearly all analysed elements when compared with similar rocks from the Permian of the north-gemerides (I. Rojkovič, 1968) and from the Choč nappe in the Vikartovský chrbát area (I. Rojkovič, 1975). Similar content shows only V and in comparison with the Permian of the north--gemerides, also Pb and organic carbon. The association of elements of ore-mineralization is pointed out by the dispersion of contents. The average contents are high not only in elements of ore mineralization with high concentrations in the ore lenses, but also in elements with high concentrations in ore lenses as well as in non-mineralized rocks which do not have any relation to ore mineralization. In contrast, the standard deviation (in log) compared to their means shows a relative enrichment of elements in the ore lenses. Some elements with high contents vithout relation to ore mineralization, as organic carbon and zirconium, have a relatively low standard deviation, because they are relatively uniformly dispersed in the rocks (Tab. 5, 6). On the contrary, some elements with lower contents as molybdenum, less yttrium, nickel and cobalt are concentrated in the ore lenses and therefore their standard deviation is also relatively high. The value of the standard deviation of the elements, concentrated in ore lenses, i.e. of U, Pb, Mo and Cu is approximately above 0,5. Typical elements of mineralized rocks among them are U, Pb and Cu, showing maximum values of means.

From the above mentioned it follows that for the uranium mineralization in the Permian of the Považský Inovec Mts. is typical the following association of elements:

1. Dominant elements of ore mineralization: U, Pb, Cu
2. Adolitional element: Mo
3. Accompanying elements of ore mineralization: Ni, Co and partially Y and V.

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