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DETERMINATION OF ^{238}U, ^{232}Th AND ^{40}K ACTIVITY IN THE ROCKS USED IN CIVIL ENGINEERING FROM THE MALÉ KARPATY MTS. (SLOVAKIA)

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Abstract: The distribution of natural radionuclides in the main rock-types: granodiorites (granites), biotite-gneisses, black shales and amphibolites from the Malé Karpaty Mts. complex was studied in samples collected from two boreholes. The samples were analyzed by means of gamma-ray spectrometry. The concentrations of ^{238}U, ^{232}Th and ^{40}K were found to be within the range of 0.091 – 37.800 mg/kg (^{238}U), 0.534 – 13.234 mg/kg (^{232}Th), and 0.116 – 5.162 mg/kg (^{40}K). The highest average ^{238}U concentration was in black shale, highest average ^{232}Th concentration in granodiorite-granite and highest average ^{40}K concentration in granodiorite - granite as well. Activities of ^{238}U were determined within the range of 1.092 – 48.960 Bq/kg (with exception of one anomalous value – 453.6 Bq/kg), activities of ^{232}Th within the range of 2.189 – 54.298 Bq/kg and activities of ^{40}K within the range of 30.933 – 1,376.499 Bq/kg. It is considered that the source of ^{238}U and ^{232}Th (and partially also of ^{40}K) is in the granitoide intrusion. Uranium was during the metamorphic process mobilized from granitoides to the black shales. The concentrations and consequently the total activities of ^{238}U, ^{232}Th and ^{40}K in the studied rock samples exceed the permitted limit values for building materials. It is possible to recommend their utilization only for external purposes.

Keywords: uranium, thorium, potassium, building material, radioactivity

1. INTRODUCTION

The components of the natural environment such as soils and rocks contain some naturally occurring radioactive materials. These materials may contain ^{238}U, ^{232}Th, their radioactive daughters and primordial radioactive istotope ^{40}K (Luigi et al., 2000; Ajayi, 2009). The absolute and relative concentrations of naturally occurring radioisotopes ^{238}U, ^{232}Th and ^{40}K in rocks used for civil engineering can vary depending on rock-type and its source (Croft & Hutchinson, 1999). Measurements of natural radioactivity especially in rock raw materials are very important for determination of the natural background activity (Iwaoka et al., 2009; Abel-Ghany, 2010). Recently calculations of the risk caused by activity of the natural radionuclides in rocks utilized for civil engineering started to be intensively studied (Kovler et al., 2002; Petrescu & Bilal, 2006, 2007; Turhan et al., 2008; Rusko et al., 2008 and others). Our study is focused on the Malé Karpaty Mts. Region.

According to the geomorphological classification of Slovakia, the Malé Karpaty Mts. is the part of the Fatra-Tatra Region (Mazúr & Lukniš, 1978; Gajdoš & Škodová, 2009).

The geological structure of the Malé Karpaty Mts. consists of pre-Alpine fundament, Mesozoic mantle and higher Alpine-age nappes. Volcano-sedimentary formation of the crystal-line complex had originated during Silurian (113–416 Ma) and Devonian (416–359 Ma). It consists of pelitic-psammite sequences, carboniferous and black shales (Plašienka et al., 1991).

According to Finger et al. (2003) the overall complex was metamorphosed during the regional Devonian metamorphosis (380 ± 20 Ma; Rb-Sr dating). Subsequently, it was affected by late Variscan periplutonic contact metamorphosis (348 ± 4 Ma or 320 ± 3 Ma; Cambel et al., 1980; Rb-Sr and U-Pb geochronological dating).

The following rocks participate in the structural-tectonic suite: granitic rocks (mainly granodiorite composition), schists, amphibolites, limestones and quaternary sediments. The medium-grained granites – granodiorites are mylonised and sericitised. Schists represented by phylites, mica schists, gneisses and black shales in the west part of the territory are in the form of fragments and breccia consolidated by calcareous cement and sericitic-chloritic phylites. Phylite layers alternate with carbonates (Maheľ, 1961).

There are known various ore (mainly pyrite and Sb) deposits in the Malé Karpaty Mts. such as Pezinok and Pernek (Fig. 1), Krížnica, Kuchyňa, Trojárová and etc. Sb mineralisation occurs locally along with Pb-Zn mineralisation (e.g. at the Pod Babou Locality) and Cu-(Au-Ag) ± Ni-Co mineralisation in Častá (Chovan et al., 1992).

2. MATERIALS AND METHODS

The studied area is situated near Pezinok, about 400 m north from a fishpond near the town (about 200 m from vineyards). The samples used were from boreholes KV-44 and KV-46 (Fig. 1 displays localization of the boreholes).

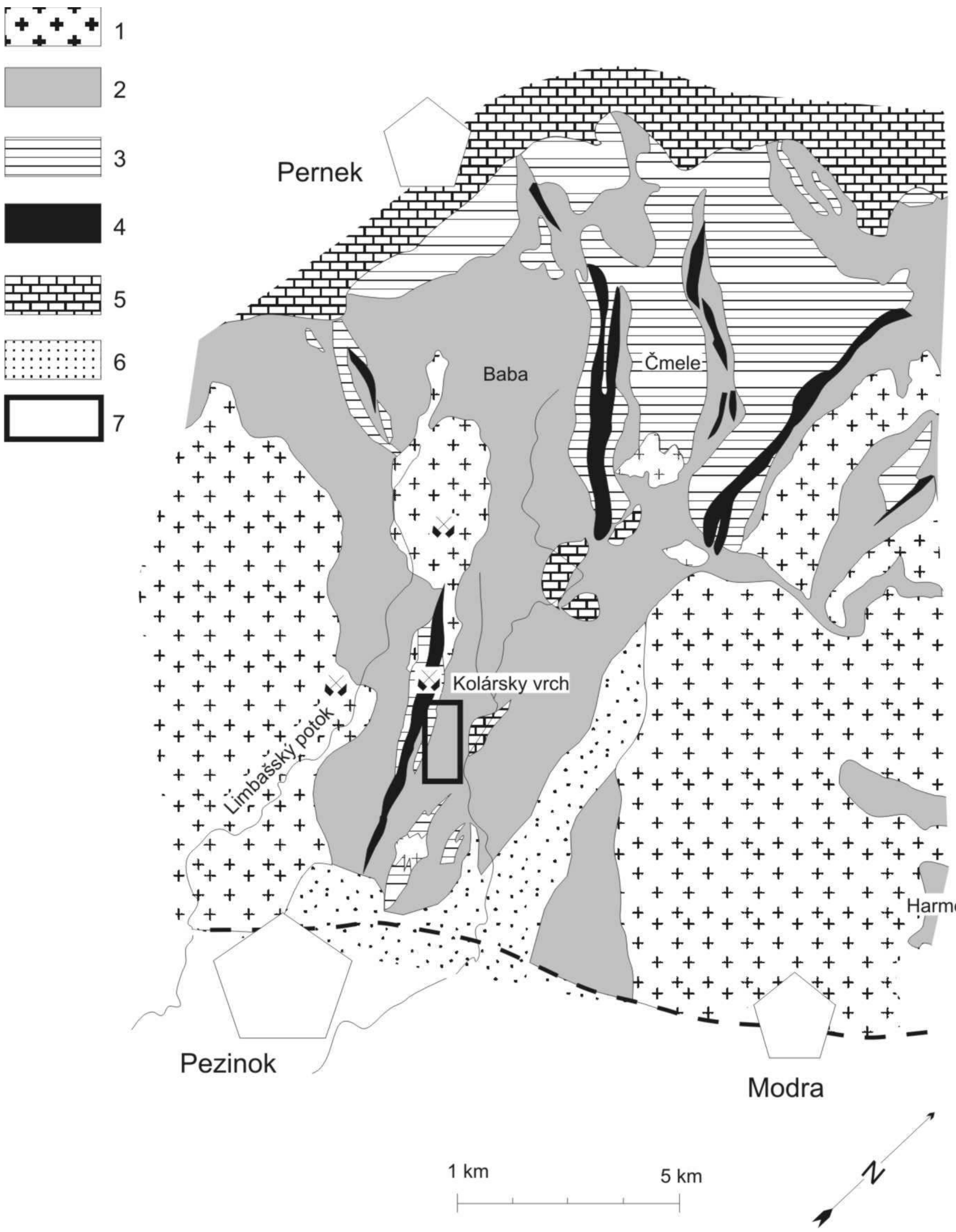

Figure 1. Surroundings of the Kolársky Vrch Deposit and localization of KV-44 and KV-46 boreholes
1 – granitic rocks, 2 – shale strata (phylites – gneiss), 3 – amphibolites, 4 – black shale with mineralization (so-called productive zones), 5 – carbonates, 6 – quaternary sediments, 7 – area of the boreholes KV-44 and KV-46

Collected samples reflect important rock-types of the Malé Karpaty Mts. crystalline complex used for the civil engineering: grano-diorites (granites), biotite-gneisses and amphibolites. The set of the samples was completed with black shales from the so called „*productive zones*" containing ore mineralisation. Chemical analyses of the main rock components were realised by X-ray fluorescence analysis (Philips) in the laboratories of the Geological Institute of the Slovak Academy of Sciences in Bratislava (Boris Toman).

Atomic absorption spectrometry (AAS) of Ba, Pb, Cu, Zr, Co, Ni, V, Ca, Cr, Sr, La, and B was realised from 0.5 g of rock sample pulverised and powdered to analytical fineness by atomic absorption spectrophotometer Philips/Pye Unicam PU – 9000 with deuterium background correction (Geological Institute of the Slovak Academy of Sciences; Emília Paulínyová).

The samples intended for analytical measurements of ^{238}U and ^{232}Th concentrations were crushed to granularity < 50 mm in the laboratories of the Geological Institute of the Slovak Academy of Sciences in Banská Bystrica (Ing. Dana Troppová). Concentrations of U, Th and ^{40}K (and Ra) were determined by gamma spectroscopy (analyzer 1024 NTA-512 B; Vlastimil Kátlovský).

Correlations between individual elements were calculated according to Hudec (2005):

$$r = \frac{\sum x_i y_i - n \cdot \bar{x} \cdot \bar{y}}{\sqrt{\left(\sum x_i^2 - n \cdot \bar{x}^2\right) \cdot \left(\sum y_i^2 - n \cdot \bar{y}^2\right)}}$$

^{238}U, ^{232}Th and ^{40}K concentrations were calculated to Bq/kg according to methodology by Yousef et al. (2007):

^{238}U mg/kg (ppm) = Bq/kg 80.33 x 10^{-3}
^{232}Th mg/kg (ppm) = Bq/kg 247 x 10^{-3}
^{40}K mg/kg (ppm) = Bq/kg 3.862 x 10^{-3}

3. RESULTS

3.1. U and Th concentrations in individual rocks

The U and Th concentrations were determined in all important rock types. Average values of ^{238}U, ^{232}Th and ^{40}K in individual rocks are listed in table 1.

Concentrations of U, Th and other elements and as well as complete rock analyses are listed in tables 2 and 3.

The highest average ^{238}U concentrations were determined in black shale (14.43 mg/kg) and the lowest in amphibolite (1.78 mg/kg; Fig. 2). In case of ^{232}Th it was possible to observe opposite trend: the lowest average concentrations were determined in black shale (3.52 mg/kg) and the highest in granodiorite and granite (7.75 mg/kg, Table 1, Fig. 3).

Table 1. Average values of U, Th and ^{40}K in individual rocks

Rock	No. of samples	x ^{238}U (mg/kg)	x ^{232}Th (mg/kg)	x ^{40}K (%)
Granodiorite	11	2.55	7.75	2.319
Amphibolite	2	1.78	7.70	1.757
Biotic gneiss	10	7.14	6.56	1.708
Black shale	3	14.43	3.52	1.463

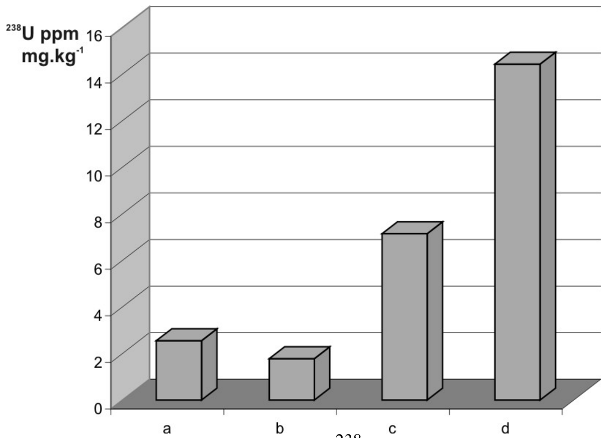

Figure 2. Average content of ^{238}U in various rock-types
Explanatory notes on figures 2 - 4: a) granodiorite and granite, b) amphibolite, c) biotite gneiss, d) black shale

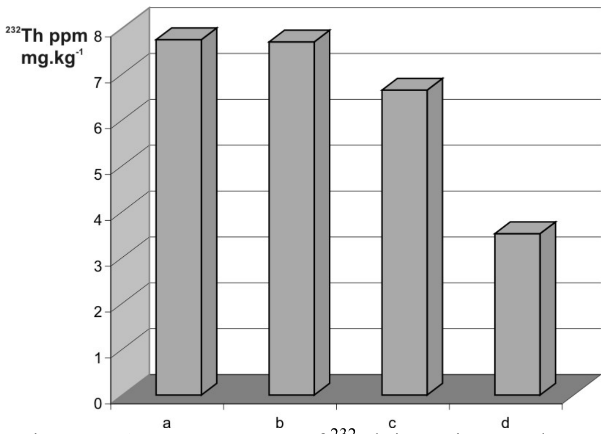

Figure 3. Average content of ^{232}Th in various rock-types

3.2. ^{40}K concentrations in individual rocks

Another radioactive component of the studied rocks is ^{40}K isotope. The highest ^{40}K concentrations were determined in granodiorite (5.123% and 5.162 %) and in biotic gneiss (2.822%). The lowest concentrations were determined in black shale (0.116 % and 2.146 %; Tables 2 and 3).

Average values of ^{40}K (Table 1) were descending in order: granodiorite (2.319%) → amphibolite (1.757%) → biotite gneiss (1.7082%) → black shale (1.463%; Fig. 4). This dependency is caused by mineral composition of individual rocks (main carriers of ^{40}K are K-feldspar and amphibolites; (Tables 2 and 3).

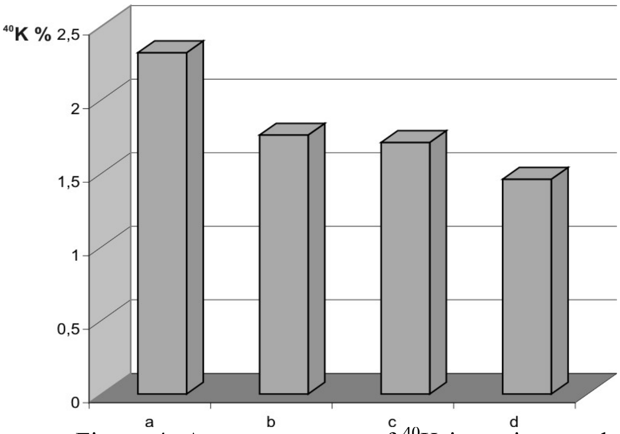

Figure 4. Average content of ^{40}K in various rock-types

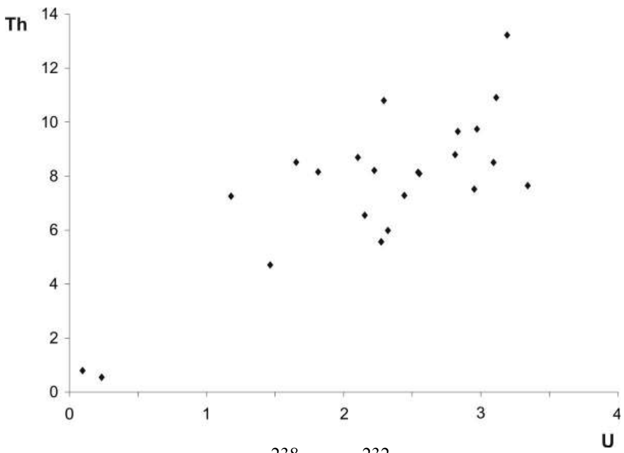

Figure 5. Correlation of ^{238}U vs. ^{232}Th (after exclusion of the couple of extreme values from borehole KV-46)

3.3. Correlation of distribution of ^{238}U and ^{232}Th with selected ore elements

While the positive correlation between concentrations of $^{238}U/^{232}Th$ (if we exclude the only couple of extreme values from borehole KV-46: 37.8 U vs. 1.524 Th) is high (the correlation coefficient r = 0.86; Fig. 5), the ^{238}U/Cu correlation (r = -0.43582) and ^{238}U/Ni correlation (r = - 0.13461; figure 6) are negative. Similarly, the correlation relations of ^{232}Th/Ni (r -0.21663) and ^{232}Th/Cu (r = -0.54757) are negative (Fig. 7).

Interesting is also the correlation between the annealing-loss and U contents (Table 2, 3).

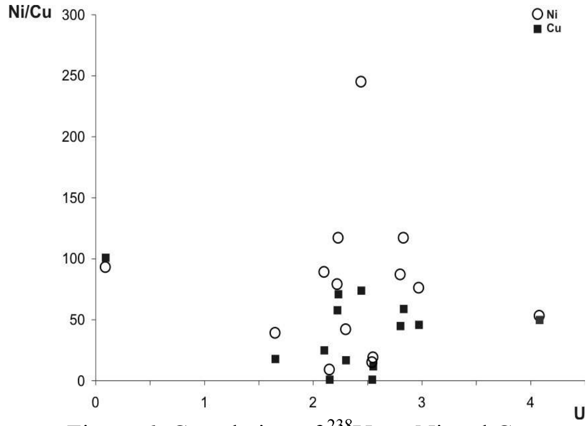

Figure 6. Correlation of ^{238}U vs. Ni and Cu

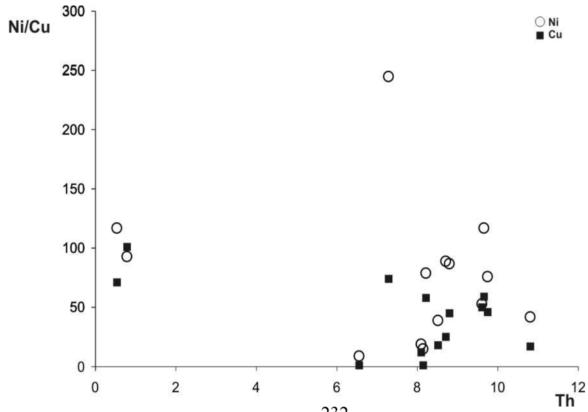

Figure 7. Correlation of ^{232}Th vs. Ni and Cu

These findings indicate that exist high positive correlation relation between ^{238}U and ^{232}Th but no direct correlation between metal elements (Ni, Cu) accompanying hydrothermal Sb mineralization and radioactive elements ^{238}U and ^{232}Th.

The correlation between concentrations of $^{238}U/^{40}K$ is after exclusion of the couple of extreme values from borehole KV-46 positive (r = 0.378; Fig. 8) and also between concentrations of ^{40}K and ^{232}Th was determined correlation dependency (r = 0.4842; Fig. 9).

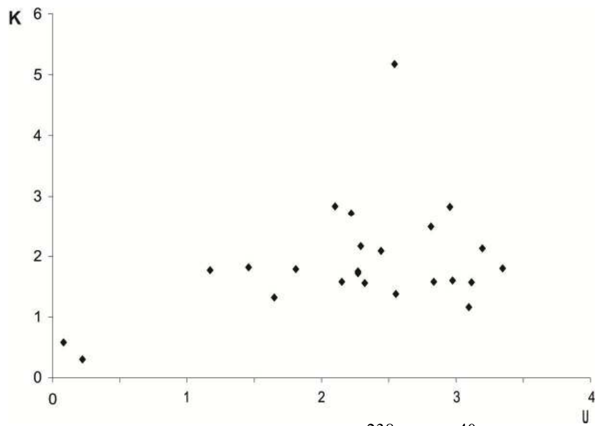

Figure 8. Correlation of ^{238}U vs. ^{40}K

Table 2. Silicate analysis, gamma spectroscopy of ^{238}U, ^{232}Th, ^{40}K and AAS of selected elements in rocks of the Pezinok Crystalline Complex, borehole KV-44

Rock		Biotite gneiss	Biotite gneiss	Granodio-rite	Biotite gneiss	Granite	Granodio-rite	Granodio-rite	Black shale	Granodio-rite	Black shale	Granodio-rite	Granodio-rite	Amphibo-lite	Amphibo-lite
Depth (m)		10-15	20	25	26 - 27	60 - 70	142 - 150	150 - 160	236 - 244	293 - 294	310	329 - 330	333 - 368	398 - 402	408 - 409
$\sum Fe_2O_3$	%	8.01	8.37	7.22	9.05	1.97	924	2.50	6.48	1.45	17.21	9.05	6.14	4.11	6.05
MnO	%	0.20	0.06	0.08	0.05	0.04	0.08	0.03	0.07	0.21	0.12	0.16	0.09	0.08	0.08
TiO_2	%	0.88	0.92	0.85	0.96	0.26	0.86	0.988	0.99	1.46	0.43	1.58	0.76	0.65	0.71
CaO	%	0.41	0.65	0.55	0.44	1.21	1.28	1.11	4.14	7.93	6.83	7.31	2.37	2.19	2.39
K_2O	%	2.80	2.49	2.23	1.90	5.46	2.82	5.83	2.74	1.32	1.38	1.49	2.71	2.08	1.72
SiO_2	%	60.16	58.56	61.62	58.47	73.89	59.76	66.89	57.59	51.33	49.28	53.62	64.42	69.61	66.97
Al_2O_3	%	17.82	17.87	18.65	19.71	12.69	16.91	17.73	19.63	15.58	11.33	15.06	15.30	13.89	15.53
MgO	%	1.22	2.81	2.85	2.86	1.26	3.69	1.40	2.86	5.41	4.17	7.47	2.51	2.20	2.49
Na_2O	%	3.43	2.78	3.67	2.64	0.56	1.32	1.03	4.42	3.06	0.31	2.63	2.71	3.76	2.49
dry. los.	%	1.18	1.08	0.45	0.77	0.22	0.16	0.18	0.30	0.20	0.25	0.19	0.33	0.19	0.08
ann. los.	%	3.91	4.45	2.24	3.77	2.84	3.88	2.54	0.84	2.05	9.04	1.42	2.68	1.14	1.48
U	ppm (mg/kg)	2.440	3.088	2.968	2.831	4.080	2.953	2.539	2.290	3.110	3.188	2.324	1.463	1.806	1.746
Th	ppm (mg/kg)	7.275	8.497	9.738	9.649	9.596	7.505	8.143	10.801	10.913	13.234	5.980	4.702	8.151	7.251
Th/U	ppm (mg/kg)	2.981	2.572	3.281	3.407	2.351	2.541	3.206	4.714	3.508	4.131	2.751	3.212	4.513	4.231
^{40}K	%	2.072	1.144	1.576	1.557	5.123	2.813	5.162	2.146	1.545	2.1125	1.538	1.801	1.765	1.752
Ba		710		1,550	890	1,780		1,480	2,630					220	
Pb		<10		<10	<10	<10		12.6	49					<10	
Cu		74		46	59	50		<10	17.4					70	
Zr		316		500	510	219		251	282					115	
Co		35		15.1	31.6	25.7		<10	15.5					<10	
Ni		245		76	117	52.5		14.8	42					30	
V		95.5		78	95,5	191		22.9	135					65	
Ca		20.9		20	25.1	<3		11	<3					20	
Cr		78		89	81	74		15.9	62					74	
Sr		95.5		245	195	71		151	430					112	
B		71		29.5	42	288		263	14.1					40	

Explanatory notes on tables 2 and 3:
dry. los. - drying losses
ann. los. - annealing losses

Table 3. Silicate analysis, gamma spectroscopy of ^{238}U, ^{232}Th, ^{40}K and AAS of selected elements in rocks of the Pezinok Crystalline Complex, borehole KV-46

Rock		Biotite gneiss	Biotite gneiss	Black shale	Granodio-rite	Granodio-rite	Granodio-rite	Granodio-rite	Biotite gneiss	Biotite gneiss	Biotite gneiss	Biotite gneiss	Biotite gneiss
Depth (m)		20	50 - 60	109 - 111	131	139 - 140	173 - 176	194 - 195	180 - 200	287	292	299	300
$\sum Fe_2O_3$	%	8.97	10.62	high Fe content	5.70	7.30	6.98	5.45	8.45	8.65	8.62	8.08	8.39
MnO	%	0.13	0.18		0.08	0.10	0.13	0.10	0.10	0.13	0.13	0.11	0.12
TiO_2	%	1.03	1.27		0.98	1.45	1.73	0.97	0.98	1.00	1.05	0.80	0.92
CaO	%	1.308	11.81		5.05	7.45	7.25	4.87	1.87	1.72	1.63	1.22	1.37
K_2O	%	0.24	0.34		2.03	1.86	1.70	1.81	2.81	2.98	2.61	2.58	2.48
SiO_2	%	48.76	49.53		60.83	57.54	55.91	61.05	59.05	59.46	58.70	59.71	59.94
Al_2O_3	%	19.38	15.01		17.96	15.84	15.44	17.72	17.82	17.58	18.85	18.00	18.18
MgO	%	5.89	6.85		2.61	3.61	4.91	2.79	3.79	3.37	3.41	3.18	3.38
Na_2O	%	1.87	2.59		3.79	3.49	3.13	3.39	2.39	2.56	2.89	2.76	2.55
dry. los.	%	0.18	0.39	0.11	0.22	0.29	0.35	0.28	0.28	0.49	0.35	0.36	0.46
ann. los.	%	0.88	1.29	8.29	0.91	1.15	2.23	1.49	2.49	2.30	1.88	2.14	2.18
U	ppm (mg/kg)	0.231	0.091	37.800	2.147	2.545	1.646	2.274	2.274	2.097	2.813	3.341	2.219
Th	ppm (mg/kg)	0.534	0.777	1.524	6.543	8.090	8.511	5.563	5.563	8.690	8.788	7.637	8.208
Th/U	ppm (mg/kg)	2.313	8.483	0.040	3.046	3.178	5.168	2.445	2.445	4.143	3.123	2.285	3.698
^{40}K	%	0.283	0.561	0.116	1.562	1.355	1.304	1.734	1.700	2.822	2.466	1.776	2.701
Ba		<300	<300		1,230	1,290	1,290		<300	890	890		830
Pb		<10	<10		12	10.4	<10		<10	<10	13.5		15.9
Cu		71	101		1.2	11.7	17.8		82	24.5	45		57.5
Zr		123	155		174	340	263		132	288	224		195
Co		45	62		<10	13.6	25.7		53	<3.4	22.4		18.6
Ni		117	93		9.1	18.6	39		111	89	87		79
V		288	295		110	138	229		280	170	170		155
Ca		13.2	24.5		22.9	20.9	10.4		19	35	17.4		14.1
Cr		200	96		11.7	17.4	74		125	78	101		79
Sr		330	316		490	600	470		320	204	224		239
B		7.1	7.4		7.4	11.7	9.8		72	5.75	31.6		43

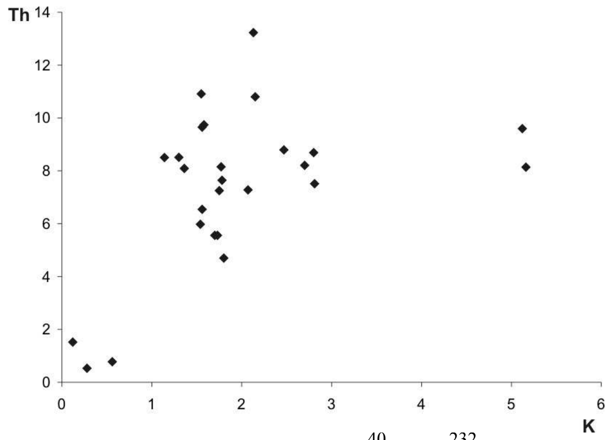

Figure 9. Correlation of ^{40}K vs. ^{232}Th

Preferential binding of ^{232}Th to granitoides indicates that the ^{232}Th addition is in connection with the granitic intrusion into the crystalline shale sequence.

^{238}U occurs in black shale together with Sb mineralisation but its concentrations do not show any positive correlation to metals (Ni, Cu) of hydrothermal mineralisation. This phenomenon is probably connected with ^{238}U mobilisation from granitic rocks. It is highly presumable that the addition of ^{238}U and ^{232}Th is connected with identical geological event (granitoide intrusion). Due to lower mobility of Th (IV) in comparison with U(VI) (Polanski & Smulikowski, 1978; Rollinson, 1998), the subsequent U(VI) mobilisation and its reduction and stabilisation occurred in the geochemical barrier which consisted of black shale with syngenetic pyrite-pyrrhotite mineralisation.

Even though ^{238}U and ores of Sb mineralisation do not show any features of positive correlation of concentrations of individual elements, it is obvious that the addition of U and Th connected with granitic rocks was the mobilisation tool of hydrothermal solutions which brought Sb mineralisation and as well the mobilisation tool of U(VI). Therefore age of intrusion, U/Th mineralisation and Sb mineralisation should be about equal.

4. DISCUSSION

According to classification by Tölgyessy et al. (1998) ^{238}U and ^{232}Th belong among very toxic elements and therefore the study of their distribution in nature is very important. In the presented study the samples from boreholes non-modified by exogenous processes were used to achieve the data on U and Th concentrations in individual rock types not influenced by weathering process. Unfortunately these data are not sufficient to take a stand to radioactive radiation.

U and Th migrate due to the weathering processes into the soil, water and other nature components. Their negative impact in the studied area has not been determined yet. It is mainly due to their very low concentrations in rocks.

The samples with the highest U concentrations, i.e. black shale, are not utilized in the civil engineering. It is satisfactory to handle with U concentrations in other rocks (grano-diorite, amphibolite, biotite gneiss) on, i.e. maximum up to value 4.080 mg/kg determined in granodiorite in the KV-44 borehole in the depth of 60–70 m. The highest Th concentrations (10.913 mg/kg) were determined in granodiorite in the KV-44 borehole as well.

Concentrations of ^{40}K fluctuated within the range of 0.116–5.162 %. The highest values were measured in rocks containing potassium feldspar and amphiboles.

According to Slovak legislative it is not possible to take a definite stand to this issue. The only legislative source on U concentrations is the Resolution of the Government of the Slovak Republic No. 296/2005 Coll. setting requirements on quality and qualitative objectives of surface waters and limit values of pollution parameters of waste waters and particular waters, where the recommended concentration is 50μg/l.

Activity of radionuclide A is the quantity characterizing the radiation source. It indicates the number of disintegrations of radioactive nucleus in material per 1 second. The activity unit is becquerel ($Bq = s^{-1}$).

Half-life of disintegration of ^{238}U is 4.5 billion years. There are 25,381 disintegrations connected with emission of ά particles in 1 gram of uranium per 1 second (Greenwood & Earnshaw, 1990; Yousef et al., 2007). For comparison, activity of gas-silicates used in home building and urban planning before the year 1985 was higher than 400 Bq/kg, whereas nowadays the limit value for building materials is 150 Bq/kg (Philippe, 2007).

If we calculate the radiation effect to the highest measured values at the Pezinok Deposit (37.800 mg/kg in black shale) the radiation intensity will be 453.6 Bq/kg (Table 4) in comparison with the most used valid limit values listed in the EU legislative (150 Bq/kg), in the Regulation of the Ministry of Health Service of the Slovak Republic No. 406/1992 Coll. on requirements on limitation of irradiation from radon and other natural radionuclides and in the Act No. 50/1976 Coll. of the Federal Assembly of Czechoslovakia on land-use planning and construction order (Building Act) and on amendments to certain laws (120 Bq/kg).

Table 4. Calculation of ^{238}U, ^{232}Th and ^{40}K concentrations to Bq/kg activity

Rock	^{238}U mg/kg	Bq/kg	^{232}Th mg/kg	Bq/kg	^{40}K %	Bq/kg	Σ Bq/kg
Granodiorite (+granite)	2.968	35.616	9.738	38.952	1.576	420.256	494.824
	4.080	48.960	9.596	39.343	5.123	1,366.099	1,454.402
	2.953	35.436	7.505	30.771	2.813	750.115	816.349
	2.539	30.468	8.143	33.386	5.162	1,376.499	1,440.353
	3.110	37.320	10.913	44.743	1.545	411.990	494.053
	2.324	27.880	5.980	24.518	1.538	410.123	462.521
	1.463	17.556	4.702	19.278	1.801	480.255	517.089
	2.147	25.764	6.543	26.826	1.562	416.523	469.113
	2.545	30.540	8.090	33.169	1.355	361.324	425.033
	1.646	19.752	8.511	34.895	1.304	347.725	402.372
	2.274	27.288	5.563	22.808	1.734	462.388	512.484
Biotic gneiss	2.440	29.280	7.275	29.828	2.072	552.519	611.627
	3.088	37.056	8.497	34.838	1.144	305.059	376.953
	2.831	33.972	9.649	39.561	1.557	415.190	488.723
	0.231	2.772	0.534	2.189	0.283	75.465	80.426
	0.091	1.092	0.777	3.186	0.561	149.596	153.874
	2.274	27.288	5.563	22.808	1.700	453.322	503.418
	2.097	25.164	8.690	35.629	2.822	752.514	813.307
	2.813	33.756	8.788	36.031	2.466	657.584	727.371
	3.341	40.092	7.637	31.311	1.776	473.588	544.992
	2.219	26.628	8.208	33.653	2.701	720.249	780.53
Amphibolite	1.806	21.672	8.151	33.419	1.765	470.665	525.756
	1.746	20.952	7.251	29.729	1.752	467.199	517.880
Black shale	2.290	27.480	10.801	44.284	2.146	566.853	638.617
	3.188	38.256	13.234	54.259	2.125	566.665	659.180
	37.800	453.600	1.524	6.248	0.116	30.933	490.781

The calculation was realized in case of one anomalous U concentration in rock which is not used in the civil engineering and from the quantitative point of view it presents the insignificant percentage in rock abundance. If we exclude this extreme value, the activity of ^{238}U will fluctuate within the range of 1.092 – 48.960 Bq/kg.

By means of similar calculation (Ramli et al., 2005; Yousef et al., 2007) of ^{232}Th concentrations to Bq/kg activity the interval of values 2.189 – 54.298 Bq/kg for studied rocks of the Pezinok-Pernek Crystalline Complex can be obtained. If we exclude ^{232}Th concentrations in black shale which are presented in low quantity and are not used in the civil engineering ^{232}Th activity will be lower: 2.189 – 44.743 Bq/kg. The activity of ^{40}K is the only one high. The calculation of ^{40}K concentrations to activity was realized according to Yousef et al. (2007). Its values fluctuate within the range of 30.933 – 1,376.499 Bq/kg.

Natural building materials such as building stone, gravel aggregate, gravel, sand, clays, cement, lime and fly ash contain always certain amount of radioactive nuclides (mainly ^{40}K, ^{232}Th and ^{226}Ra) originating by radioactive decomposition of ^{238}U. Mass activities of ^{232}Th a ^{226}Ra in the building materials are usually at tens of Bq/kg and in case of ^{40}K nuclide at hundreds of Bq/kg. Occurrence of such radioactive elements in the building materials in buildings causes man's irradiation in two ways: a) external irradiation (γ radiation) due to radioactive decomposition of natural radionuclides; b) internal irradiation due to inhalation of radioactive nuclides originating in the air from radon which is created in the construction materials from radium. The activity of building materials and raw materials for their production is limited. Criterion of utilization of building materials in terms of content of natural radionuclides is stated in the Regulation of the Ministry of Health Service of the Slovak Republic No. 406/1992 Coll. and in the Building Act No. 50/1976 Coll.

On the basis of above listed ideas it is possible to assume that ^{238}U concentrations (and obviously as well ^{232}Th concentrations) are in the studied rocks very low and they do not present any major environmental or health risk. Total radioactivity is significantly influenced by ^{40}K activities (30.933 –

1,376.499 Bq/kg). These induce that majority of investigated rock samples significantly exceed total limit activity values for building materials (120 Bq/kg) and fluctuate within the range of 80.426 – 1,454.402 Bq/kg. This determination enables us to state the negative opinion on their assumed utilization in the form of building materials. On the other hand their utilization on road-works and similar exterior works does not present any environmental risk.

In the future would be interesting measure also contents of Ra to calculate the radioactivity index (^{226}Ra/300 + ^{232}Th/200 + ^{40}K/3000), one of the accepted standards for building materials established by International Commission on Radiological Protection.

5. CONCLUSIONS

The highest ^{238}U concentrations were determined in black shale and the lowest in amphibolite. The highest ^{232}Th concentrations were determined in granodiorite (and granite) and the lowest in black shale.

There was determined high positive correlation between concentrations of ^{238}U and ^{232}Th. No correlation between ^{238}U and ^{232}Th concentrations versus selected ore elements connected with hydrothermal Sb mineralization was recognized.

^{238}U and ^{232}Th source is in granodiorite intrusion but ^{238}U was mobilized from grano-diorite - granite during metamorphic process and was accumulated together with synsedimentary pyrite-pyrrhotite and hydrothermal Sb mineralization in black shale presenting geochemical barrier where the ore precipitation occurred.

Concentrations of ^{238}U and ^{232}Th were very low (^{238}U 0.091 – 37.800 mg/kg, ^{232}Th 0.534 – 13.234 mg/kg). Their radiation intensity corresponds to maximum values of ^{238}U = 37.800 Bq/kg (generally to <3.000 Bq/kg) and ^{232}Th = 13.234 Bq/kg. It is possible to assume that they do not present any environmental risk to nature and human activities. They do not exceed permitted limit values for building materials (150 Bq/kg; 120 Bq/kg) as well. The risk for civil engineering is the total activity of ^{238}U, ^{232}Th and ^{40}K (80.426 – 1,454.402 Bq/kg).

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