

NATURAL RADIONUCLIDES IN THE BUILDING MATERIALS FROM THE REGION OF THE SMALL CARPATHIANS

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Abstract

Distribution of radionuclides in the main rock types: granodiorites, biotite-gneisses, black shale and amphibolites at the locality Pezinok - Kolársky vrch was studied in samples from two boreholes. Concentrations of ^{238}U , ^{232}Th and ^{40}K in the samples were analysed by gamma spectroscopy (concentrations of ^{238}U were 0.091 – 37.800 mg/kg, ^{232}Th 0.534 – 13.234 mg/kg, ^{40}K 0.116 – 5.162 mg/kg). The highest average ^{238}U concentration was in black shale, highest average ^{232}Th concentration in granodiorite and highest average ^{40}K concentration in granodiorite. 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. The source of ^{238}U and ^{232}Th (and partially also of ^{40}K) is in the granodiorite intrusion. During the metamorphic process, Uranium was mobilised 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 utilisation only for external purposes.

Key words

^{238}U , ^{232}Th , ^{40}K , building material, radioactivity

Introduction

The geological structure of the Malé Karpaty (Small Carpathians) Mountains consists of pre-Alpine fundament, Mesozoic mantle and higher Alpine-age nappes. Volcanic-sedimentary formation of the crystalline complex had originated within Silurian (113 – 416 Ma) and

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Devonian (416 – 359 Ma). It consists of pelitic-psammite sequences, carboniferous and black shales (Plašienka et al., 1991).

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

The following rocks participate in the structural-tectonic structure: granitic rocks (mainly granodiorite composition), crystalline shale, amphibolites, limestones and quaternary sediments. The Bratislava Massif is represented by medium-grained granites – granodiorites which are mylonised and sericitised at the Borinská Unit interface. Crystalline shales 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 are alternating with carbonates (Mahel', 1961).

There are known various ore (mainly pyrite and Sb) deposits in the Malé Karpaty Mountains, such as Pezinok and Pernek (Fig. 1), Krížnica, Kuchyňa, Trojárová etc. Sb mineralisation occurs locally along with Pb-Zn mineralisation (e.g. at the Pod Babou Locality) and Cu-(Au-Ag) \pm Ni-Co mineralisation in Častá (Cambel, 1959; Chovan et al., 1992).

Geological and tectonic structure of the Sb-deposits

The most important Sb-deposit in Malé Karpaty Mts. is Pezinok. It is connected with SE-NW tectonic zone known as productive (pyrite zone) about 2 km in length. The deposit covers only 430 m in length of it; tectonic zone width near the surface is barely of 25 – 50 m, but deeper, its extension can be seen. According to Cambel (1959), the deposit is situated between two amphibole complexes of 50 – 250 m where the ore-bearing volcanic-sedimentary sequence is presented. It is presented mainly by muscovite-clay and black-carboniferous shale, which are generally folded in detail and petrologically very variable. Various metamorphosed pyroclastic rocks, apophyses of granitic rocks and tiny loading bodies of amphibolites are less presented.

The deposit consists of two bigger ore bodies of stratiform character of unspecified genesis: central and base. The central deposit is bound to wide dislocation zone inclining about 75° to SW, NW-SE and its width on the surface is within the range of 25 – 60 m. Some younger research papers (Andráš, 1983) refer to epigenetic character of the mineralisation.

Antimony mineralisation in the central deposit is tectonically transformed and is uprising in crushed and mylonised rocks where the shale with the organic material addition is of major importance. Exploration works determined the occurrence of smaller accumulations of Sb ores under the antimony adit horizon as well. They consist of small and irregular ore bodies (Cambel, 1959).

The Pernek and Kuchyňa deposits are time-spatially very close to the Pezinok deposit and have the same/similar characteristics of mineralisation genesis as the Pezinok deposit and therefore we do not pay attention to them in more detail.

Cambel and Viliňovič (1987) found out that the contents of U and Th ($X - X_0$ ppm i.e. $0.000X - 0.00X_0$ wt %) are in the Modra Massif lower in comparison with analogous granitic

rocks in the Bratislava Massif. Other rock types and relation of U and Th concentrations to ore mineralisation were not studied in more detail.

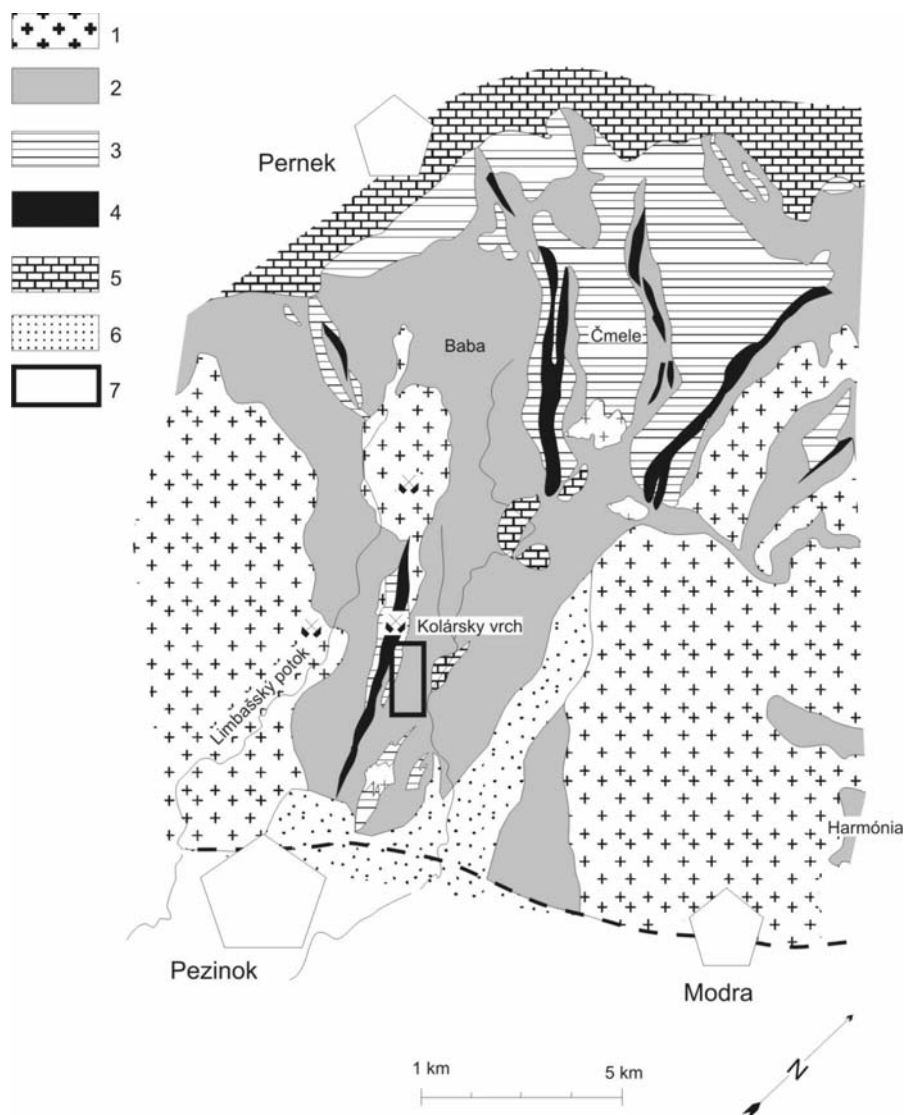


Fig. 1 Surroundings of the Kolársky Vrch deposit and localisation of KV-44 and KV-46 boreholes

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

Materials and methods

The studied area (Fig. 1) is situated near Pezinok, about 400 m north from a fishpond near the town (about 200 m from vineyards).

The samples from surface boreholes KV-44 and KV-46 were used. They were obtained during the research carried out in Pezinok near Kolársky Vrch in 1981 by the Geological

Survey Bratislava, stored in the depository of the Geological Institute of the Slovak Academy of Sciences in Banská Bystrica (Fig. 1 displays localisation of the surface boreholes).

The collected samples reflect all important rock types of the Malé Karpaty Mts. crystalline complex (granodiorites, biotite-gneisses, black shale and amphibolites).

The samples of weight 1 – 5 kg were crushed to size under 0.05 mm, sulphide minerals were separated by flotation and optically repurified under the binocular loupe.

Chemical analysis of the main rock components (silicate analysis) was carried out from the samples powdered to analytical fineness by X-ray fluorescence analysis (Philips) in the laboratories of the Geological Institute of the Slovak Academy of Sciences in Bratislava (Ing. Boris Toman).

Atomic absorption spectrometry (AAS) of Ba, Pb, Cu, Zr, Co, Ni, V, Ca, Cr, Sr, La, and B was carried out from 0.5 g of rock sample gently pulverised and powdered to analytical fineness by single-beam atomic absorption spectrophotometer Philips/Pye Unicam, model PU – 9 000 with deuterium background correction from HCl.

Rock decompositions and their preparation for Au determination according to methodology by Rubeška et al. (1977) were carried out from 5 g of sulphide minerals and 10 g of rock samples respectively.

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; RNDr. Vlastimil Kátlovský, PhD.).

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

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

^{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 80.33×10^{-3} ; ^{232}Th mg/kg (ppm) = Bq/kg 247×10^{-3} ; ^{40}K mg/kg (ppm) = Bq/kg 3.862×10^{-3} .

Results

^{238}U and ^{232}Th concentrations in individual rocks

^{238}U and ^{232}Th concentrations were determined in all important rock types of the Malé Karpaty Mts. Crystalline Complex (granodiorite, biotite gneiss, black shale and amphibolite). The samples of rocks from the surface boreholes KV-44 and KV-46 from Pezinok (near Kolársky Vrch) were used (Fig. 2).

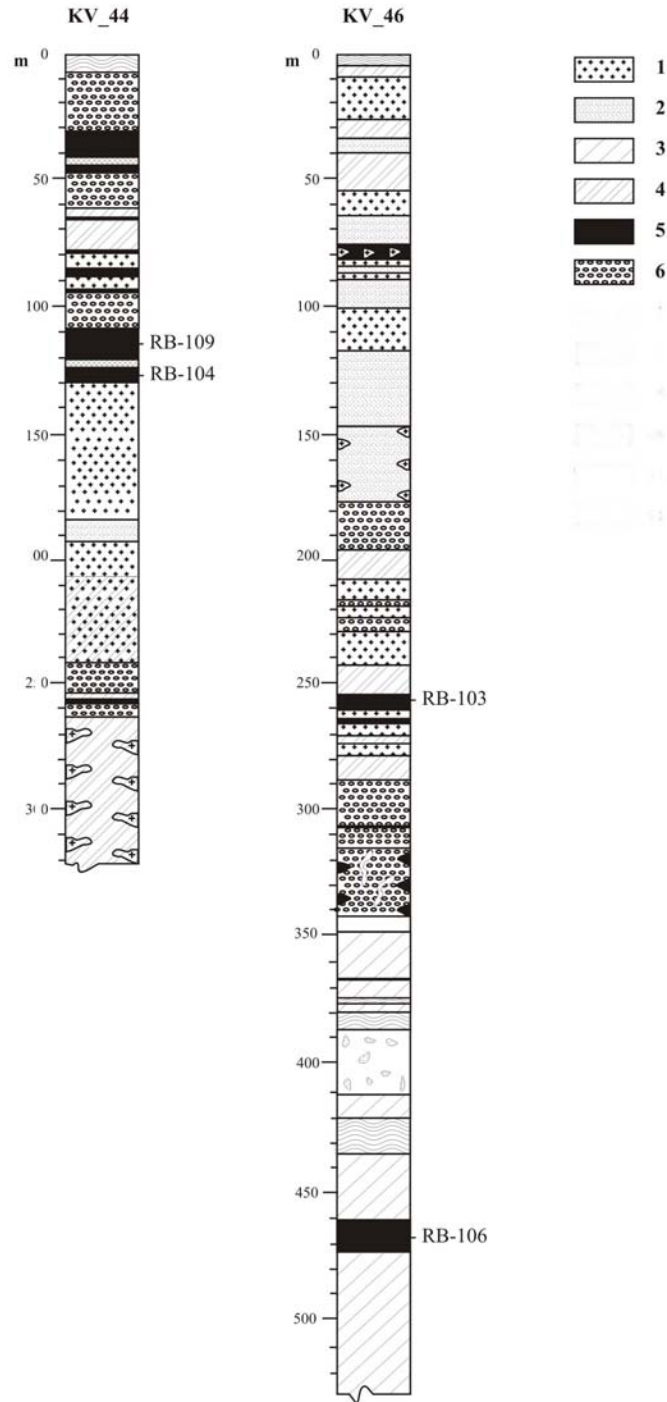


Fig. 2 Boreholes KV-44 and KV-46; Expanations: 1 – granodiorite, 2 – biotite gneiss, 3- amphibolite, 4- actinolite schist, 5 – black schist, 6 – hydrothermally altered rocks

Average values of ^{238}U , ^{232}Th and ^{40}K in individual rocks are listed in Tab. 1. Concentrations of U, Th and other elements and as well as complete rock analyses are listed in Tables 2 and 3.

AVERAGE VALUES OF U, Th AND ^{40}K IN INDIVIDUAL ROCKS

Table 1

| Rock | No. of samples | $\times \text{}^{238}\text{U}$ (mg/kg) | $\times \text{}^{232}\text{Th}$ (mg/kg) | $\times \text{}^{40}\text{K}$ (%) |
|----------------|----------------|--|---|-----------------------------------|
| Amphibolite | 2 | 1.78 | 7.70 | 1.757 |
| Biotite gneiss | 10 | 7.14 | 6.56 | 1.7082 |
| Black shale | 3 | 14.43 | 3.52 | 1.463 |
| Granodiorite | 11 | 2.55 | 7.75 | 2.319 |

^{238}U concentrations in granodiorite fluctuated from 1.463 to 4.080 mg/kg and ^{232}Th concentrations fluctuated from 4.702 to 10.913 mg/kg. In biotite gneiss ^{238}U concentrations ranged from 0.091 to 3.341 mg/kg and ^{232}Th concentrations ranged from 0.534 to 9.649 mg/kg. In amphibolites ^{238}U concentrations were determined from 1.746 to 1.806 mg/kg and ^{232}Th concentrations from 7.251 to 8.151 mg/kg. In black shale ^{238}U concentrations ranged from 2.290 to 37.800 mg/kg and ^{232}Th concentrations from 1.524 to 13.234 mg/kg (Tables 2, 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). In case of ^{232}Th , it was possible to observe opposite trend: the lowest average values were determined in black shale (3.52 mg/kg) and the highest in granodiorite (7.75 mg/kg, Tab. 1).

In the KV-44 borehole, ^{238}U concentrations in granodiorite ranged from 1.463 to 4.080 mg/kg and ^{232}Th concentrations from 4.702 to 10.913 mg/kg. In the KV-46 borehole, ^{238}U concentrations in granodiorite fluctuated from 1.645 to 2.274 mg/kg and ^{232}Th concentrations from 5.563 to 8.511 mg/kg. The highest ^{238}U concentrations (4.080 mg/kg) were in the depth of 60 – 70 m and the highest ^{232}Th concentrations (10.913 mg/kg) in the depth of 293 – 294 m. ^{232}Th concentrations in granodiorite were 2 - 3 times higher than ^{238}U concentrations (Tables 2 and 3).

In the KV-44 borehole, ^{238}U concentrations in biotite gneiss were measured within the range of 2.440 – 3.088 mg/kg and Th concentrations ranged from 7.275 to 9.649 mg/kg. In the KV-46 borehole ^{238}U concentrations in biotite gneiss were determined within the range of 0.091 – 3.341 mg/kg and ^{232}Th concentrations ranged from 0.534 to 8.788 mg/kg. The highest ^{238}U concentrations (3.341 mg/kg) were in the depth of 299 m and ^{232}Th concentrations (9.649 mg/kg) in the depth of 26 – 27 m. On the basis of comparison of ^{238}U and ^{232}Th concentrations in biotite gneiss it was possible to state that ^{232}Th concentrations were 2 – 3 times higher than ^{238}U concentrations (Tables 2 and 3).

In the KV-44 borehole, in the depth of 236 – 244 m, Th concentrations in black shale were almost 5 times higher (10.801 mg/kg) than ^{238}U concentrations (2.290 mg/kg). In the depth of 310 m, ^{232}Th concentrations in black shale were 4 times higher (13.234 mg/kg) than ^{238}U concentrations (3.188 mg/kg). In the KV-46 borehole, in the depth of 109 – 111 m, ^{238}U concentrations in black shale were 37.800 mg/kg and ^{232}Th concentrations 1.524 mg/kg. The highest ^{238}U concentrations (37.800 mg/kg) were determined in the depth of 109 – 111 m and ^{232}Th concentrations (13.234 mg/kg) in the depth of 310 m (Tables 2 and 3).

^{232}Th concentrations in amphibolite, in the KV-44 borehole ranged from 7.251 to 8.151 mg/kg and were 4 times higher than ^{238}U concentrations (1.746 – 1.806 mg/kg). The highest ^{232}Th and ^{238}U concentrations in amphibolite were determined in the depth of 398 – 402 m (Tables 2 and 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-44

Table 2

| Rock | | Biote gneiss | Biote gneiss | Granodio- rite | Biote gneiss | Granodio- rite | 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 |
| $\Sigma\text{Fe}_2\text{O}_3$ | | 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 | 9.88 | 0.99 | 1.46 | 0.43 | 1.58 | 0.76 | 0.65 | 0.71 |
| CoO | | 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 ₂ O | | 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 ₂ O 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 ₂ O | | 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 | 2.440 | 3.088 | 2968 | 2.831 | 4.080 | 2.953 | 2.539 | 2.290 | 3.110 | 3.188 | 2.324 | 1.463 | 1.806 | 1.746 |
| Th | (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 | | 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 | 2813 | 5.162 | 2.146 | 1.545 | 21.125 | 1.538 | 1.801 | 1.765 | 1.752 |
| Au | | 0.41 | 0.115 | 0 | 0 | 0 | 0.050 | 0.123 | 0.126 | 0.023 | 0 | 0 | 0 | 0.029 | 0 |
| Ba | | 710 | | 1,550 | 890 | 1,780 | | 1,480 | 2,630 | | | | | | |
| Pb | | < 10 | | < 10 | < 10 | < 10 | | 12.6 | 49 | | | | | | |
| Cu | | 74 | | 46 | 59 | 50 | | < 10 | 17.4 | | | | | | |
| Zr | | 316 | | 500 | 510 | 219 | | 251 | 282 | | | | | | |
| Co | | 35 | | 15.1 | 31.6 | 25.7 | | < 10 | 15.5 | | | | | | |
| Ni | | 245 | | 76 | 117 | 52.5 | | 14.8 | 42 | | | | | | |
| V | | 95.5 | | 78 | 95.5 | 191 | | 22.9 | 135 | | | | | | |
| Ca | | 20.9 | | 20 | 25.1 | <3 | | 11 | <3 | | | | | | |
| Cr | | 78 | | 89 | 81 | 74 | | 15.9 | 62 | | | | | | |
| Sr | | 95.5 | | 245 | 195 | 71 | | 151 | 430 | | | | | | |
| B | | 71 | | 29.5 | 42 | 288 | | 263 | 14.1 | | | | | | |

Explanatory notes for tab. 2 and 3
dry. los. - drying losses
ann. los. - annealing losses

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

Table 3

| Rock | | Biotite gneiss | Biotite gneiss | Black shale | Granodiorite | Granodiorite | Granodiorite | Granodiorite | 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 |
| $\Sigma\text{Fe}_2\text{O}_3$ | % | 8.97 | 1062 | 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 |
| CoO | | 13.08 | 11.81 | | 5.05 | 7.45 | 7.25 | 4.87 | 1.87 | 1.72 | 1.63 | 1.22 | 1.37 |
| K ₂ O | | 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 ₂ O 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 ₂ O | | 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 | | 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 | | 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 |
| Au | ppm (mg/kg) | 0.461 | 0.038 | 0.219 | 0.138 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ba | | < 300 | < 300 | | 1,230 | 1,290 | 1,290 | | | 890 | 890 | | 830 |
| Pb | | < 10 | < 10 | | 12 | 10.4 | < 10 | | | < 10 | 13.5 | | 15.9 |
| Cu | | 71 | 101 | | 1.2 | 11.7 | 17.8 | | | 24.5 | 45 | | 57.5 |
| Zr | | 123 | 155 | | 174 | 340 | 263 | | | 288 | 224 | | 195 |
| Co | | 45 | 62 | | < 10 | 13.6 | 25.7 | | | < 3.4 | 22.4 | | 18.6 |
| Ni | | 117 | 93 | | 9.1 | 18.6 | 39 | | | 89 | 87 | | 79 |
| V | | 288 | 295 | | 110 | 138 | 229 | | | 170 | 170 | | 155 |
| Ca | | 13.2 | 24.5 | | 22.9 | 20.9 | 10.4 | | | 35 | 17.4 | | 14.1 |
| Cr | | 200 | 96 | | 11.7 | 17.4 | 74 | | | 78 | 101 | | 79 |
| Sr | | 330 | 316 | | 490 | 600 | 470 | | | 204 | 224 | | 239 |
| B | | 7.1 | 7.4 | | 7.4 | 11.7 | 9.8 | | | 5.75 | 31.6 | | 43 |

⁴⁰K concentrations in individual rocks

Another radioactive component of the studied rocks is ⁴⁰K isotope. The highest ⁴⁰K concentrations were determined in granodiorite (5.123 % and 5.162 %) and in biotite gneiss (2.822 %). The lowest concentrations were determined in black shales (0.116 % and 2.146 %, Tables 2 and 3).

Average values of ⁴⁰K (tab. 1) were descending in order granodiorite (2.319 %) → amphibolite (1.757 %) → biotite gneiss (1.7082 %) → black shales (1.463 %). This dependency is caused by mineral composition of individual rocks (main carriers of ⁴⁰K are potassium feldspar and amphibolites).

⁴⁰K concentrations were determined in the KV-44 borehole within the range of 1.144 % - 5.162 %. In the KV-46 borehole ⁴⁰K concentrations were within the range of 0.116 % - 2.822 % (Tables 2 and 3).

Correlation of distribution of ²³⁸U and ²³²Th with selected ore elements

The correlation among concentrations of ²³⁸U/²³²Th (correlation coefficient is -0.30705), ²³⁸U/Cu (correlation coefficient is -0.43582) and ²³⁸U/Ni (correlation coefficient is -0.13461) is negative. Similarly, the correlation relations of ²³²Th/Ni (correlation coefficient is -0.21663) and ²³²Th/Cu (correlation coefficient is -0.54757) are negative. These findings indicate that the direct positive correlation relation does not exist between ²³⁸U and ²³²Th and not even between metal elements (Ni, Cu) accompanying hydrothermal Sb mineralisation and radioactive elements ²³⁸U and ²³²Th.

The correlation between concentrations of ²³⁸U/K (correlation coefficient is -0.258) is negative but between concentrations of ⁴⁰K and ²³²Th there was determined correlation dependency (correlation coefficient is 0.4842).

The preferential binding of ²³²Th to granodiorite indicates that the ²³²Th addition is in connection with granodiorite intrusion into crystalline shale. ²³⁸U is presented in black shale together with Sb mineralisation but its concentrations do not show any positive correlation to metals (Cu, Ni) of hydrothermal mineralisation. This phenomenon is probably connected with ²³⁸U mobilisation from granitic rocks. It is highly presumable that the addition of ²³⁸U and ²³²Th is connected with identical geological event (granodiorite intrusion). Because of Th(IV) is considerably less mobile than U(VI) (Polanski and 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-pyrotite mineralisation.

Even though ²³⁸U 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, the age of intrusion, U/Th mineralisation and Sb mineralisation should be about equal.

Discussion

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

^{238}U and ^{232}Th migrate due to the weathering processes into the soil, water and other land components. Their negative impact in the studied area has not been determined yet. It is mainly because of very low concentrations of these elements in rocks.

CALCULATION OF CONCENTRATIONS OF ^{238}U , ^{232}Th AND ^{40}K
to Bq/kg ACTIVITY

Table 4

| Rock type | ^{238}U mg/kg | Bq/kg | ^{232}Th mg/kg | Bq/kg | ^{40}K % | Bq/kg | Σ Bq/kg |
|----------------|---------------------------|---------|----------------------------|--------|----------------------|-----------|-------------------|
| Granodiorite | 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 |
| Biotite gneiss | 2.274 | 27.288 | 5.563 | 22.808 | 1.734 | 462.388 | 512.484 |
| | 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 |
| Amphibolite | 2.219 | 26.628 | 8.208 | 33.653 | 2.701 | 720.249 | 780.53 |
| | 1.806 | 21.672 | 8.151 | 33.419 | 1.765 | 470.665 | 525.756 |
| Black shale | 1.746 | 20.952 | 7.251 | 29.729 | 1.752 | 467.199 | 517.880 |
| | 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 samples with the highest ^{238}U concentrations, i.e. black shale, are not utilised in the civil engineering. It is satisfactory to handle ^{238}U concentrations in other rocks (granodiorite, amphibolite, biote gneiss) on, i.e. maximum to value 4.080 mg/kg determined in granodiorite in the KV-44 borehole in the depth of 60 – 70 m. The highest ^{232}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 amphibolites.

According to Slovak legislative, it is not possible to take a definite stand to this issue. Sole legislative source on ^{238}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 wastewaters and particular waters, where the recommended concentration is 50 $\mu\text{g/l}$.

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

Half-life of disintegration of ^{238}U is 4.5 billion years. There are 25,381 disintegrations connected with emission of α particles in 1 gram of uranium per 1 second (Greenwood and Earnshaw, 1990; Yousef et al., 2007). For comparison, gas-silicates with radiation effect used in home building and urban planning before the year 1985 had the activity higher than 400 Bq/kg (Klicpera, 2003), whereas nowadays the limit value for building materials is 150 Bq/kg (Philippe, 2007).

If we calculate the radiation effect of the highest measured values at the Pezinok deposit (37.800 mg/kg in black shale), the radiation intensity is 453.6 Bq/kg (Tab. 4). This can be compared with the most used limit values valid in the EU (150 Bq/kg), those 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). The calculation was carried out in case of one anomalous ^{238}U value 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 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, the ^{232}Th activity is 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 realised 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 always contain certain amount of radioactive nuclides (mainly ^{40}K , ^{232}Th and ^{226}Ra) originated by radioactive decomposition of ^{238}U . Mass activities of ^{232}Th and ^{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 originates in the construction materials from radium. The activity of building materials and raw materials for their production is limited. Criterion of utilisation 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.

Based on the above listed ideas, it is possible to assume that ^{238}U concentrations (and obviously as well ^{232}Th concentrations) in the studied rocks are 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 express the negative opinion for their assumed utilisation in the form of building materials. On the other hand, their utilisation for roadwork and similar exterior work does not present any environmental risk.

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 the lowest in black shale.

There was not determined any positive correlation between concentrations of ^{238}U and ^{232}Th . Similarly, correlation between ^{238}U and ^{232}Th concentrations and selected ore elements connected with hydrothermal Sb mineralisation was not verified.

^{238}U and ^{232}Th source is in granodiorite intrusion, but ^{238}U was mobilised from granodiorite during metamorphic process and accumulated together with syngenetic pyrite-pyrhotite and hydrothermal Sb mineralisation in black shale presenting geochemical barrier where the ore precipitation occurred.

Concentrations of ^{238}U and ^{232}Th are very low (^{238}U 0.091 – 37.800, ^{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 land 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 presents the total activity of ^{238}U , ^{232}Th and ^{40}K (80.426 – 1,454.402 Bq/kg).

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