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Article

Characterization of the Main Naturally-Radioactive Geologic Units of Stara Planina

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Abstract: Stara Planina is known for numerous occurrences and deposits of uranium and associated radionuclides. It is also famous for its geodiversity. The geologic framework is highly complex. The mountain is situated between the latitudes of 43° and 44° N and the longitudes from 22°16′ to 23°00′ E. Uranium exploration and radioactivity testing on Stara Planina began back in 1948. Uranium has also been mined in the zone of Kalna, within the Janja granite intrusive. The naturally-radioactive geologic units of Stara Planina are presented in detail in the paper.

Keywords: geology; radioactivity; uranium; sampling; Stara Planina

1. Introduction

The objective of the paper is to provide an overview of the naturally-radioactive geologic units in known areas of the Stara Planina Mountain (also known as the Balkan mountain range). The studied localities include Mezdreja and Gabrovnica (abandoned mines in the Janja granites), graphitic schists of the Paleozoic "Inovo Series", and Early Triassic sedimentary units in the Dojkinci – Jelovica area. These occurrences are known and have been described in papers, reports and books, largely from the perspective of mineral exploration, origin or ecology. The paper aims to characterize naturally radioactive units, with regard to their location, macroscopic and microscopic features, chemical composition, and radioactivity of a specific sample determined both *in situ* and in the laboratory. In other words, the objective is to provide answers to the questions: Which are the particular geologic units, what are their petrologic, mineralogic, geochemical and radiometric characteristics, and how did they come about? The paper presents the outcomes of research conducted in the part of Stara Planina in Serbia.

2. Methodology

1. The samples were collected on pre-determined locations. The goal was to find representative samples of naturally radioactive rocks. The sampling points are shown in the UTM system, zone 34N, ellipsoid WGS84.The weight of the samples was from 2 to 2.5 kg.

2. Thin sections were made from granite and schist samples, and where ore minerals were detected polished sections were also made. The samples were viewed macroscopically and microscopically on a Leitz Ortholux Pol 2 microscope at the Geological Survey of Serbia. The structure of the samples was examined using a Bresser binocular magnifier.

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3. On the ground, the radioactivity of the terrain and at the observation points was measured by a Radiation Detector Explouranium 110 in cps and Gammascout in μSv/h. The results are included in the descriptions of the tested samples. The values were recorded after a period of 10 minutes, when they stabilized on the display and when there were no ±10% fluctuations. The data is presented in the paper in intervals characteristic of the tested location.

4. Chemical analyses of powder were performed on an XRF Niton Xl3t Goldd+ analyzer at the University of Belgrade, Faculty of Civil Engineering. Each sample was tested two or three times, for about 180 to190 seconds in the Soil mode, and checked by Test Allgeo. The samples were ground to 70 μm. Some of the samples were analyzed in their solid state, for example schist; assays were performed on plate and schistosity in resection. The following elements were measured: Mo, Zr, Sr, U, Rb, Th, Pb, Au, Se, As, Hg, W, Cu, Ni, Co, Fe, Mn, Ba, Sb, Sn, Cd, Pd, Ag, Nb, Bi, Re, Ta, Hf, Cr, V, Ti, Ca, K, Sc, S, Cs and Te.

5. The radioactivity of the samples (226Ra, 232Th, 40K and 137Cs) was measured at Vinča Nuclear Institute. Homogenized samples were dried in an oven at 105ºC to constant weight, placed in plastic Marinelli beakers, sealed and left for four weeks to reach radioactive equilibrium [1]. Each prepared sample was placed in an HPGe detector and measured for 90 000s. Gamma background in the laboratory was determined prior to testing, by measuring an empty Marinelli baker under identical conditions. The counting time for background measurement was 240 000s. It was later subtracted from the measured gamma spectra of each sample.

The activity of the samples was measured using a high-resolution coaxial semiconductor detector with high-purity germanium crystal HPGe ORTEC GEM 50 and 50% relative efficiency at 1332 keV. The detector was shielded by lead in order to achieve the lowest possible background level.

Energy and efficiency calibration was undertaken before measurement. The calibration source used was a commercially available gamma standard, with mixed radionuclides-type MBSS 2 in Marinelli geometry of 0.5 l, developed by the Inspectorate for Ionizing Radiation of the Czech Metrological Institute, with the isotopes: 241Am, 109Cd, 57Co, 139Ce, 113Sn, 85Sr, 137Cs, 88Y, 203Hg, and 60Co. The energy of gamma lines of these radionuclides is highly suitable for calibration and covers the region of interest, i.e. from 30 to 3000 keV. Quality assurance of the measurements was carried out by daily efficiency and energy calibration, repeating each sample measurement.

Correction for radioactive decay and background, as well as analysis of the results, were conducted using dedicated software ORTEC Gamma Vision-32 Model A66-B32 Version 6.01.

The 226Ra activity was determined by its decay products: 214Pb (295.22 keV, 351.93 keV) and 214Bi (609.31 keV, 1120.29 keV). In the case of 232Th, two photopeaks of 228Ac (911.20 and 698.97 keV) were used. The activities of 40K and 137Cs were derived from 1460.83 keV and 661.66 keV gamma lines, respectively.

3. Summary of uranium exploration in Yugoslavia (1948-1990) and on Stara Planina

Collection of data on natural radioactivity in the former Yugoslavia began in 1948 at the national Geological Institute (Geoinstitute). Among voluminous data on the radioactivity of rocks, waters (groundwater and surface water resources), soils, alluvions (recent riverine sediments), and air, most are in their original or a certain type of interpreted form (such as statistical data), preserved in annual or periodic geological exploration reports, studies, papers, publications, and the like. They

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are accessible from the archives of Geoinstitute – now the Geological Survey of Serbia, but it is a challenge to unify and covert the data into current units, given that the units have since been changed several times.

Prospecting and exploration of nuclear minerals in Serbia, at different levels of detail, encompassed large areas. The number of data points is of the order of several hundred thousand. So far, the most extensive exploration was conducted in the geographical region of Šumadija (Mt. Bukulja zone), on Stara Planina, and in the areas of Mt. Cer and Mt. Iverak, where uranium deposits have been identified and reserves estimated.

Uranium exploration on Stara Planina began in 1949. Extensive slick probe prospecting and walk-over radiometric prospecting were undertaken from 1949 to 1956. Geologic maps were produced on a scale of 1:50,000, and within the zones of the Aldina River and Mezdreja on a scale of 1:10,000. In late 1956 [2], vein bodies were explored on the Mezdreja locality. Between 1957 and 1966, a geologic-structural map was produced of the Janja granite and exploration conducted of the sediments of the so-called Colorful Series, of the dispersion aureoles on the Mezdreja locality and later, of the geological-mining operations at Gabrovnica and Mezdreja. Exploration was suspended from the early 1970's to 1978, and from 1978 to the early 1990's it was generally conducted within the area of the Colorful Series and in the fault zones of the Janja granite.

Since 2000, there has been non-systematic/thematic exploration, generally of radioactivity and its impact on the environment on certain localities on Stara Planina [3-5] (also methodology in Bai et al. 2017, was considered for future work [6]).

4. Location of Stara Planina and summary of geology

Stara Planina can be viewed from several perspectives, as a nature park and in terms of geography, geology and geodiversity. The present paper addresses areas of interest from the viewpoint of radioactivity. From the east (ridges) and south, the area is bounded by the border with Bulgaria and from the west (north to south) by several rivers: the Beli Timok, the Trgoviški Timok, the Stanjanska, the Klajča, the Temska and the Nišava. In general terms, only a small part of the mountain range is located in Serbia. The remainder is in Bulgaria and extends all the way to the Black Sea (Figure 1).

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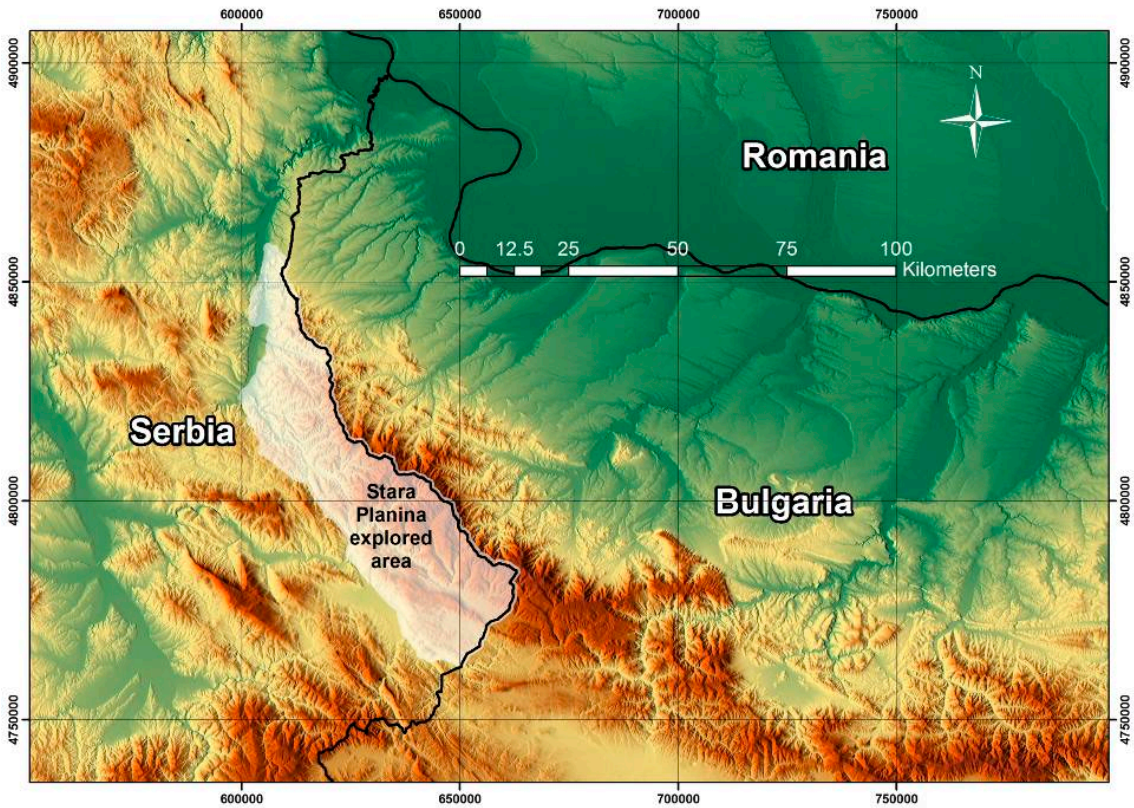

Figure 1. Form of Stara Planina and schematic representation of its extension into Bulgaria (whitish). Raster background is Relief (maps-for-free).

On the base geological map of the former Yugoslavia (scale 1:100,000), the area of interest is depicted in the sections on: Bor, Zaječar, Knjaževac and Belogradcig [7], Pirot and Breznik [8]. On the geological map of the Republic of Serbia, on a scale of 1:200,000 [9], the area of interest is shown in the sections on Knjaževac-Zaječar and Priština-Niš. Both maps were used to produce overview schematic maps of the geologic units discussed in the paper (Figure 2).

Generally speaking, Stara Planina is a complex geologic system, built up of different geologic units (with regard to the composition, characteristics and origin). From the north, where the geologic units are separated by structures and where granite and granodiorite intrusions begin, the area is defined by faults that separate the Late Jurassic in the south from the Early Cretaceous in the north. Towards the south, there is a complex geotectonic assemblage made up of the Janja (Figure 2), Radičevo and Ravno Bučja granites; the Zaglavak gabbro massif; Paleozoic metamorphic rocks: Proterozoic-Cambrian, Silurian-Devonian – the Inovo Series and others; and Permian red sandstones and conglomerates. To the south, there are Mesozoic formations: Triassic (Kopren-Gostuša-Dojkinci), Jurassic (Basara, Odorovci), and Early Cretaceous (Visočka Ržana, Dimitrovgrad). In the southern part of the Mesozoic block the Jurassic and the Cretaceous are intersected by structures running from the northwest to the southeast. The northern boundary of Stara Planina is not clearly defined and can be followed on the Zaječar and Bor maps along Cretaceous formations and intrusions over a length of about 30 km northward and farther via Brusnik and Brestovac to Negotin, but this is not the subject of the present paper.

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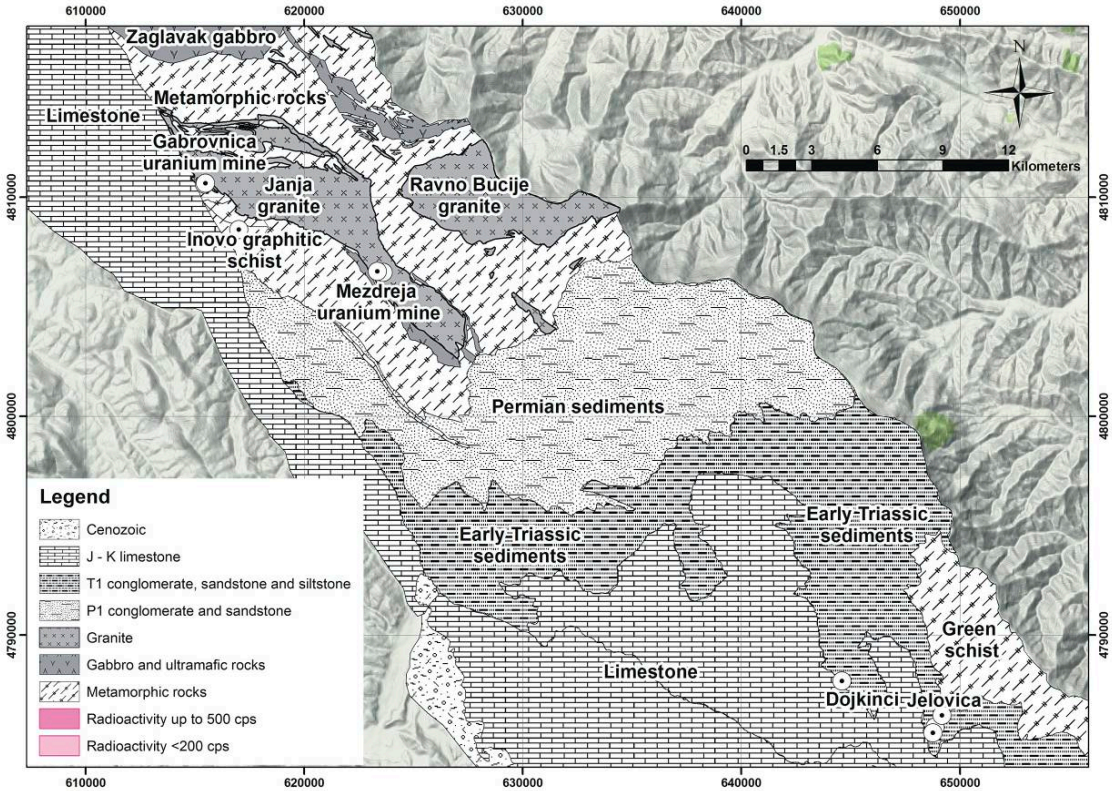

Figure 2. Characteristic geological units and landmarks in the study area on Stara Planina with legend for Figures 2, 3, 4 and 5. Raster background for Figures 2, 3, 4 and 5 is SASlanet, Google w/o names. White circles with dots are observation and sampling points.

In 1997, Stara Planina was designated a nature park, where there are a number of unique examples of geodiversity.

5. Uranium occurrences and deposits on Stara Planina

The following genetic types of uranium deposits and occurrences can be distinguished on Stara Planina after Gertik 2003 [10] and Kovacevic 2006 [2]: 1. Uranium mineralizations in pegmatites, 2. Uranium mineralization related with auto-metasomatic hydrothermal processes in granite, 3. Sedimentary - infiltration deposits and occurrences, 4. Metamorphogenic occurrences.

The maps in Figures 3 and 4 include a schematic representation of the geology and distribution of radioactivity on Stara Planina. In general terms and based on Geoinstitute's activities [2] over several decades, two levels of radioactivity have been identified: (1) about 200 cps, divided into three zones whose total surface area is 307.5 km^2, and (2) greater than 200 and up to 500cps (mostly greater than 200 cps but rarely 500 cps), divided into four zones whose surface area is 70.84 km^2.

In essence, the main sources of radioactivity on Stara Planina can be classified as: 1. Granitic endogenous – syngenetic-epigenetic deposits and occurrences, 2. Metamorphogenic – syngenetic, and 3. Sedimentary, including occurrences of uranium deposition and fluctuation caused by water in different types of sedimentary rocks formed in a continental setting, which could be classified under epigenetic types.

The occurrences described in this paper can also be grouped into two geological-structural blocks [11, 12] (Figure 3): A. an intrusive-metamorphic block, and B. a sedimentary block.

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A. In the intrusive-metamorphic block, the elevated radioactivity is associated with the Janja granite and Aldinac grandiorite porphyritic rocks, as well as graphitic schists of the Inovo Series, over a surface area of about 195 km².

B. The radioactivity in the sedimentary block is associated with both secondary deposition of minerals and reddish Fe-rich cement. Elevated radioactivity has particularly been noted at points of contact between gray and red siltstones, where the gray have been deposited as lenses of different sizes in the basal reddish mass of continental sediments. The surface area is approx. 97 km².

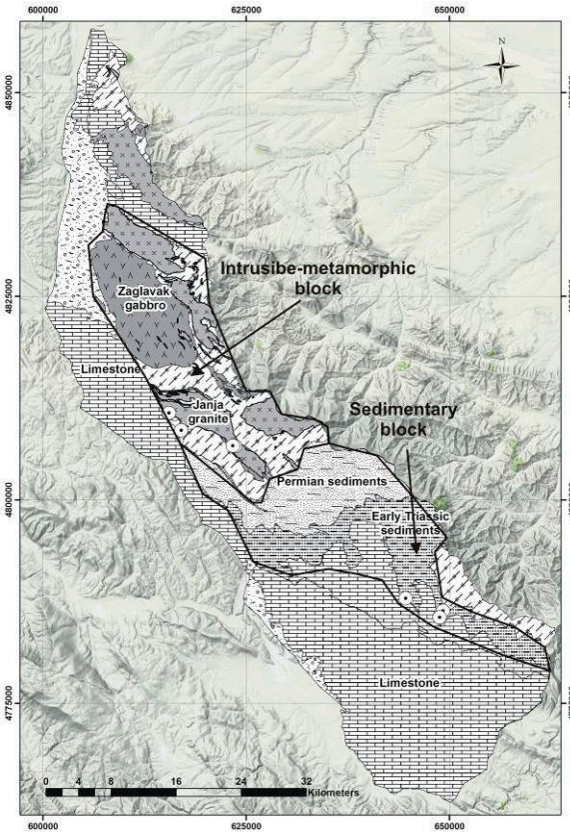

Figure 3. Schematic representation of geologic units and intrusive-metamorphic and sedimentary blocks of Stara Planina.

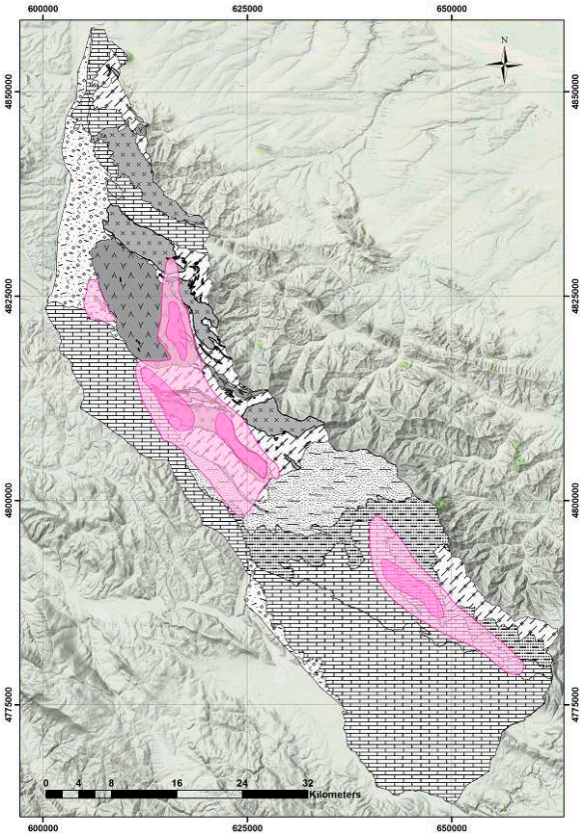

Figure 4. Zones of elevated radioactivity, measured in cps (light pink – 200 cps and above, and dark pink up to 500 cps).

6. Geologic, geochemical and radiometric characteristics of the Janja granite at Mezdreja and Gabrovnica

The Janja granite massif is located south of the Zaglavak gabbro massif and west of the Ravno Bučja granite (Figures 2, 5). It is elongated in the northwestern-southeastern direction. The Janja granite is about 19 km long and 2.5 km wide.

The Janja granite massif is pressed into Late Proterozoic and Cambrian crystalline schists. The crystalline schists feature thermo-contact and metasomatic alterations. The primary structural elements include fractures filled with aplite, pegmatite and quartz veins. In places, the fractures trending NW-SE, concentrated on the fringes of the massif, exhibit sericite crystallization.

In its northwestern part, the massif splits into two masses separated by amphibolites, amphibole schists, gneisses and mica gneisses. Peripherally there are contact alterations manifested by silification, biotitization and local deposition of feldspar [7]. There the massif is contaminated by

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granitoid magma, evidenced by an increasing content of biotite and sphene and decreasing content of K-feldspar and quartz. The Janja granite is generally of the normal calc-alkaline type, which on the fringes turns into the monzonite-akerite type and in the central part into alkaline granite. Deformations and secondary alterations have been noted in the entire massif, particularly on the fringes. They are represented by a schistose texture, crushed minerals and crystallization of secondary minerals. The primary components are quartz, oligoclase, K-feldspar (microcline, rarely orthoclase), and biotite. The accessory components are sphene, apatite, zircon and magnetite, and the secondary components sericite, chlorite, epidote, calcite, limonite and a clayey substance. There are syenite diorites in the periphery of the Janja granite and on its fringes. Their origin is attributed to contact-metasomatic processes in the syenite diorites.

Pegmatite veins are made up of quartz, plagioclase (albite-oligoclase) enriched with U [13], microcline, biotite and muscovite. The accessory components are apatite, zircon, alanite and metallic minerals. There are quartz veins inside and around the massif. Their thickness is up to several meters and they are up to 200 m long. In addition to quartz, they contain tourmaline and metallic minerals.

Typical naturally-radioactive geologic representatives were tested within the Janja granite. Samples of granite, the host rock at Mezdreja and Gabrovnica, were of primary interest. In addition to granite, tailing dump samples from Mezdreja (clayey material with cataclazed granite fragments), silicified batches with limonite stains and fragments of contact gabbroid with coarse (1.5 cm) K-feldspar were examined.

Detail information about granite and radioactivity in general are in [14-16].

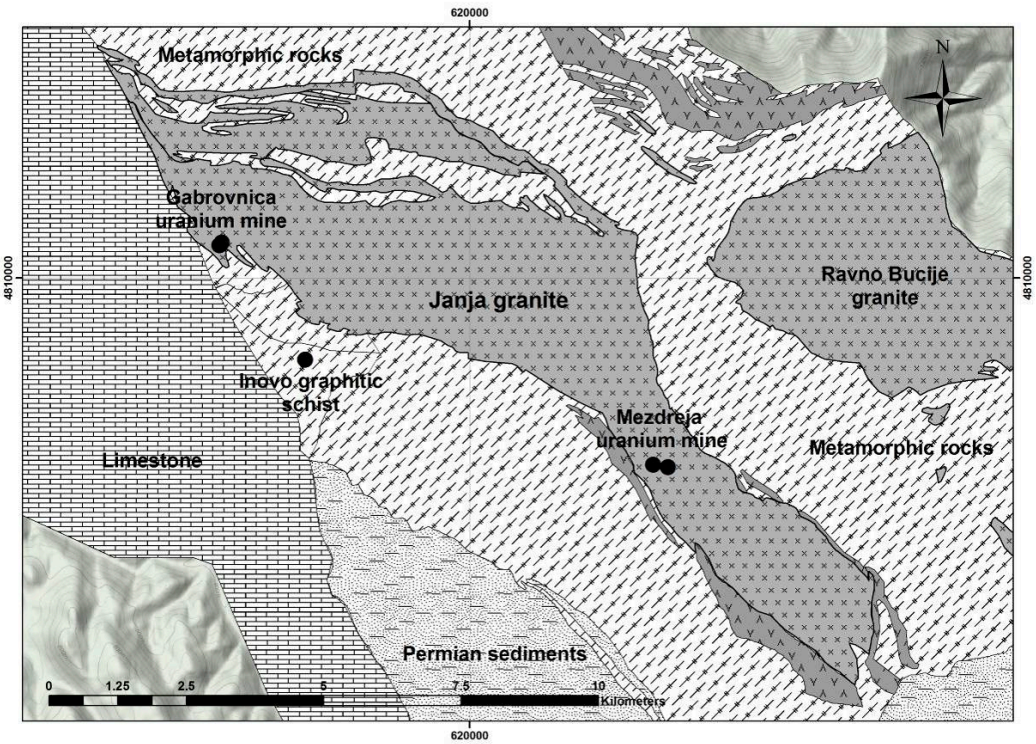

Figure 5. Map of Mezdreja and Gabrovnica (including the Inovo metamorphic rocks area) within the Janja granite, along with control points (black dots).

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Mezdreja mine area

Mezdreja is located in the southern part of the Janja igneous metamorphic complex. It is defined by two fault zones, so-called zones 0 and 1 [10].

Fault zone 0 trending NW-SE is 1300 m long and has vertically been explored from 200 to 600 m. The following zonality has been noted in the vertical profile: kaolinized, sericitized and chloritized zones in the upper parts, and silification, pyritization and hematitization in the lower parts. The ore is developed in the form of lenses that locally form columns. Uranium mineralization is finely dispersed in crushed and hydrothermally altered granite or in the form of veinlets, coatings and stains of pitchblende visible to the eye. Non-uranium-bearing parts of the fault zone are filled with sericite and chalcopyrite. Fault zone 1 is developed adjacent to metagabbroid rocks (Figure 10). The form and extent are similar to those of Zone 0. Mineralization is of the vein/lens type at the point of contract with the metagabbros. Along Zones 0 and 1 there are biotite granites and metamorphic gabbros. Uranium is mineralized in the form of impregnations of veinlets and stains, and is represented by pitchblende and secondary pitchblende.

Four samples were acquired from the Mezdreja site:

1. A granite sample was collected near the pit (Figure 6) and radioactivity measured by GR110 *in situ* was 520 cps at the sampling point and 420 cps and 0.322 μSv/h at the mine portal. The pit has caved and could not be accessed. The rock is partially fractured. The predominant components are pink K-feldspar and white plagioclase, both fractured and sericitized and kaolinized to different degrees. The dimensions were up to 0.5–1.5 cm (Figure 7). There was also chloritization, occasionally accompanied by magnetite grains developed at a later date during short hydrothermal or auto-metasomatic episodes.

Figure 6. Granite sample collected near the Mezdreja mine portal.

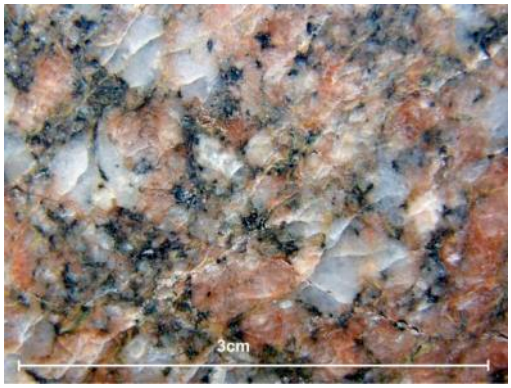

Figure 7. Macro image of a polished granite sample collected at the Mezdreja mine portal, including pink K-feldspar and white plagioclase.

2. In the area between the mine portal and dump, there were small outcrops of silicified material with occurrences of ore impregnation and limonitization (Figure 8). Radioactivity measured 320 cps and 0.182 μSv/h.

3. The mine dump contained crushed granite material – clayey, kaolinized and chloritized (Figure 9). Radioactivity measured up to 1250 cps and 0.421 μSv/h.

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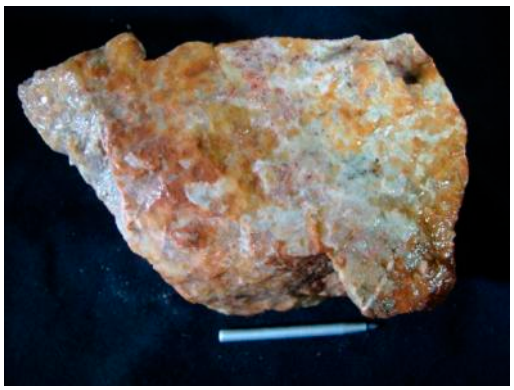

Figure 8. Silicified rock (vein) with ore minerals and alterations.

Figure 9. Fragments of granite and clayey material from the Mezdreja mine dump.

4. A sample with large pink K-feldspar was collected from the point of contact between granitic and gabbroid rocks. Radioactivity measured 120 cps and 0.192 μSv/h. The K-feldspar shown in Figure 11 was separately tested by XRF. The results are shown further below.

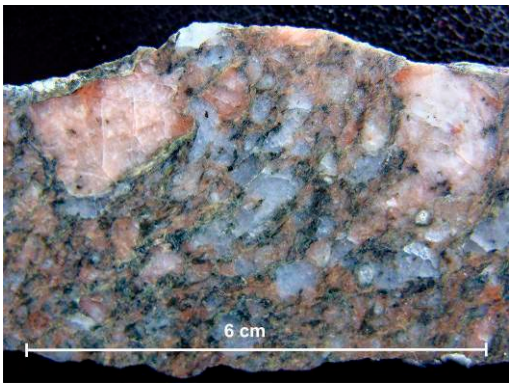

Figure 10. Macro image of a polished sample of a gabbroid outcrop from Mezdreja.

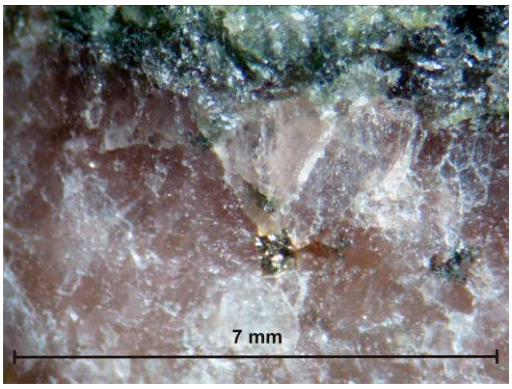

Figure 11. Gabbroid K-feldspar – pinkish; the metallic yellow in the middle is an idiomorphic grain of pyrite.

Gabrovnica mine area

The origin of the deposits is similar to that of Mezdreja. The only difference is that there are eight fault zones that can be divided into two groups: (1) diabase dikes in granites and milky white quartz, and (2) crushed granites. Uranium ore is developed in chloritized phyllonites and crushed granites. Solid and non-tectonized batches are sterile or contain little ore. The fault zones are highly tectonized by post-ore tectonics. The origin of the uranium is similar to that at Mezdreja.

Fresh granite near the pit and granite (Figure 13) from the mine dump were sampled as representative of the locality. Radioactivity measured 240 cps and 0.210 μSv/h at the mine portal (Figure 12) and 360 cps and 0.248 μSv/h at the mine dump.

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Figure 12. Gabrovnica mine portal.

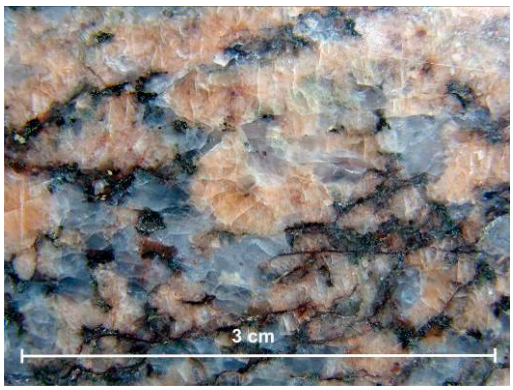

Figure 13. Macro image of a polished granite sample from Gabrovnica, containing pinkish K-feldspar and white plagioclase.

Origin of uranium in Mezdreja and Gabrovnica mines

In the endogenous group, specifically in the case of the Mezdreja and Gabrovnica granites and ore deposits, feldspar and mica minerals are the most important in terms of uranium concentrations. Given that the concentrations of uranium in the main petrogenic minerals are rather low, and the total amounts of such minerals and their spread large, they represent sources from which "hot" granites leach considerable concentrations of uranium. Uranium occurs as U^{4+} in biotite, muscovite and minerals from the feldspar group. If these minerals have been altered under the influence of oxygen-rich hydrothermal or meteoric waters [17], uranium in the form of U^{6+} (as the $U^{6+}O_2$ ion) might be present in them, as well as in accessory minerals: sphene, zircon, monazite, ortite, xenotime, apatite, tourmaline, apatite [18] and others.

Since uranium is remobilized from the primary granite at Mezdreja and Gabrovnica, it should be noted that in the presence of water and the H^+ ion: (1) kaolinite, the K^+ ion, U^{4+} – uranium ion and orthosilicilic acid are created from the primary "uranium-bearing" K-feldspar, and (2) sericite, K^+ ion, UO_2^{2+} – uranyl ion and again orthosilicilic acid might be formed. Sericitization has been observed in petrologic samples from Mezdreja and Gabrovnica (Figures 14 and 15). In the samples collected as part of the present research, sericitization was more pronounced at Mezdreja than at Gabrovnica.

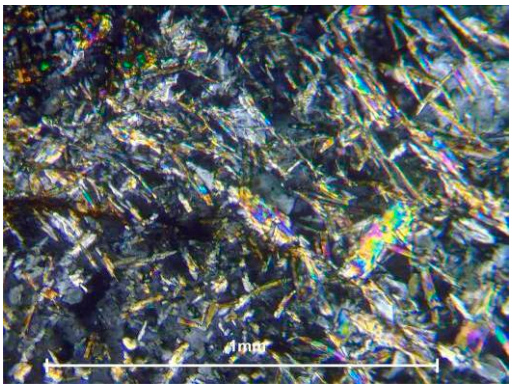

Figure 14. Microscopic image of the sericitization of a sample from Mezdreja.

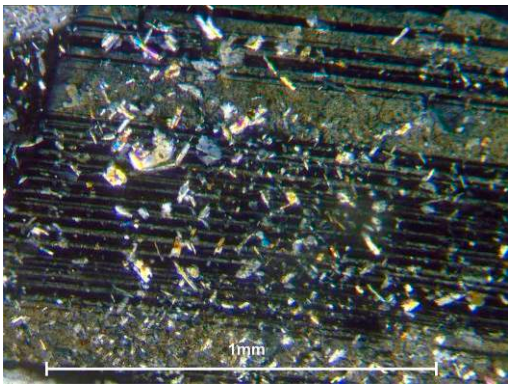

Figure 15. Microscopic image of the sericitization of a sample from Gabrovnica.

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Biotite, another primary "uranium-bearing" mineral in granite, can also be transformed in two ways: (1) when the negative OH^- ion is present, creating sericite, silicon dioxide, water, aluminum silicate (which may occur as andalusite, kyanite or sillimanite), K^+ ion and U^{4+} uranium ion, and (2) in the presence of water and the H^+ ion creating sericite, aluminosilicate, K^+ ion and UO_2^{2+} – uranyl ion.

7. Geological, geochemical and radiometric characteristics of samples of black graphitic schists from the Inovska River

The Inovo Series transgresses the southwestern part of the Janja granite-metamorphic system. Metaconglomerates and metasandstones are the base of the metamorphic-sediment batch. They are overlain by metasandstones containing argillophyllites, with schists in the upper part. The sequence is built up of chlorite-phyllite schists, green schists, amphibolites, graphitic schists, greywackes and conglomerates [7].

The Inovo Series graphite-bearing schist is located in relative proximity to the Gabrovnica mine, 2.5 km southeast and 1.3 km southwest of the closest mapped point of the Janja granite (Figures 2 and 3).

The Inovska River occurrence is situated in the river (on the riverbanks), developed in fractured and altered brecciated metasandstones with interbeds and lenses of black graphitic schists (Figure 16), 50 to 70 m thick.

The upper part of the batch contains layers of coarse-grained and fine-grained metasandstones with black clayey schist intercalations. In the lower part there are brecciated arkose metasandstones. The package dips to the northeast at an angle of 70 to 80°.

Uranium is mineralized in the form of elongated lenses in the direction of the dip, following layers of metasediments between coarse-grained metasandstones and black clayey schists [10]. The lens-like ore body runs along the dip to about 30m. Ore bodies are built up of carbonitized, pyritized, chloritized and sericitized microconglomerates to arkose sandstones with traces of chalcopyrite and galenite.

A number of samples were collected. Those shown here contain a little and a lot of graphitic material. Niton XRF Goldd+ analyses showed that the sample with more graphitic material carried a larger amount of uranium. Also, that sample was brittle, with limonitic stains (Figure 17) along the directions of shearing. Radioactivity at the sampling site measured 650 cps and 0.279 μSv/h.

Figure 16. Outcrop of graphitic schist at the Inovska River.

Figure 17. Limonitized batches (brownish) and quartz veins (top right next to the hammer).

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With regard to the thin sections, the lighter and harder variety had more petrogenic minerals and less graphitic material, and also contained limonitic stains (Figures 18 - 21).

Figure 18. Graphitic schist of the Inovo Series, with less organic material. The break is sharp. Limonitic stains can be noted on tectonized parts. In the upper part of the sample there is a lens with quartz and silicified material.

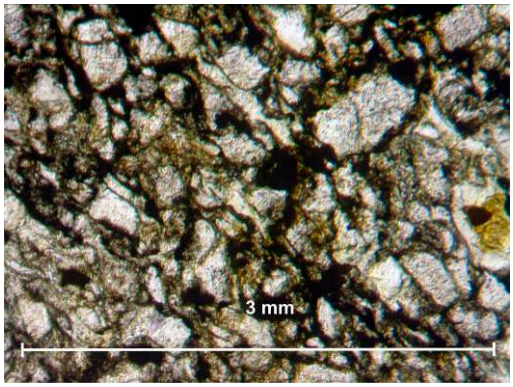

Figure 19. Thin section of the sample with less organic material. Obj.8x//N.

Figure 20. Graphitic schist of the Inovo Series, with more organic material, showing obvious stratification and limonitization.

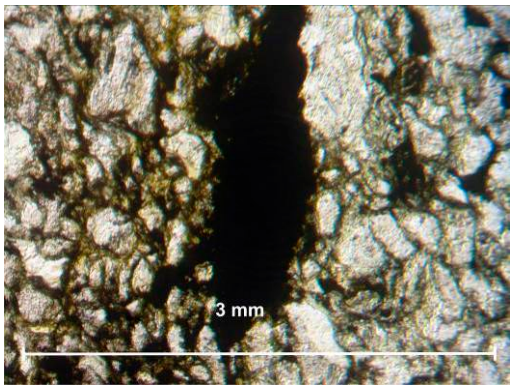

Figure 21. Thin section of the sample with more organic material. Graphitic material is concentrated in the middle (black). Obj.8x//N.

Elevated concentrations of uranium in these metamorphic rocks are a result of redistribution of ore components under dynamic-thermal metamorphism conditions.

Since these two samples were collected in relative proximity and their alterations varied at a decimeter level, radioactivity was measured at the Vinča Institute lab, using homogenized samples of the two varieties of graphitic schists of the Inovo Series.

8. Geological, geochemical and radiometric characteristics of the Colorful Series

The observation points within the Colorful Series are located in an area defined as Early Triassic. Known places where elevated uranium concentrations have been detected are in the part of the terrain called Dojkinci – Jelovica (Figure 2). The area is known as that of "clastic rocks of Stara Planina", a formation that features clearly defined continuous sedimentation in continental warm and humid climate conditions. The geology is represented by continental formations built up of fragments of crystalline schists and granites, light-red quartz conglomerates, red and gray sandstones, and gray to grayish-pink siltstones [8]. The upper part of the Colorful Series includes Middle Triassic marls and sandy limestones. Uranium mineralizations are usually found in the form

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of pitchblende [2]. The color of the sandstones varies from red – usually (Figures 24 and 25) to greenish – rarely. All siltstones exhibited elevated concentrations of uranium. From the north, the Early Triassic (Permo-Triassic) sediments of the Colorful Series are in contact with Ripheo-Cambrian schists. The regional metamorphism of these rocks corresponds to a green schist facies. There is distinct foliation and the color is typically grayish-green (Figures 22 and 23). The alterations have been influenced by granodiorites, a small portion of which are in Serbia and the majority in Bulgaria [8]. In particular, samples of quartz veins form this unit measured 6 ppm of gold. A low/insignificant level of radioactivity was detected.

Figure 22. A block of green schists 300 m northeast of the sampling point Sandstone_red1 from T1 (Table 4).

Figure 23. Typical appearance of the green schists from Fig. 22. Whitish are quartz veins.

Microscopic examination of thin section as part of the present research revealed that a typical sample of the Colorful Series sandstone was dark "hematite" red to pinkish-gray, with a psammitic structure, built up of quartz, orthoclase, plagioclase, muscovite, biotite, apatite, epidote, chlorite and fragments of metamorphic rocks. The grains were several tens to 100 and exceptionally 300 μm. There is more orthoclase than plagioclase. The grains were highly altered into clay minerals and sericitized. The plagioclases are sericitized as well as calcitized. The quartz, orthoclase and plagioclase are angular. The micas exhibited linear orientation and locally built nest-like forms. The apatite was rounded. Zircon was noted locally in the quartz. The epidote was developed as independent entities. The cement are of the iron-carbonate type. The sample was collected as a "representative" from the direction of contact with metamorphic rocks, before the gray siltstones. The sampling point measured 120 cps and 0.172 μSv/h.

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Figure 24. Typical outcrop of Early Triassic red sandstone from Jelovica.

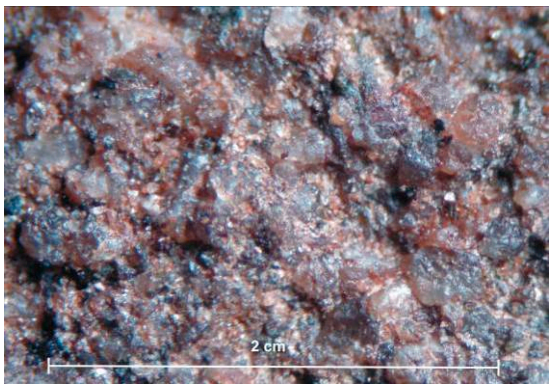

Figure 25. Macro image of a freshly broken Early Triassic red sandstone from the Dojkinci-Jelovica area. Visible are mostly quartz grains and a reddish matrix.

By way of an explanation of the uranium concentrations in the red members of the Colorful Series, it should be noted that the reduction of mobile uranium (U^{6+}) to insoluble uranium (U^{4+}), such as uraninite, takes place when the fugasity of oxygen in solution drops. This reaction occurs on account of iron or sulfur oxidation. When the solution (water) is rich in oxygen, bivalent iron will oxidize into trivalent iron, but if there is an excess of Fe^{2+} relative to the oxygen, the oxygen will be spent and the uranyl ion is the one to convert bivalent iron into trivalent, or sulfides to sulfates, and is itself precipitated as uraninite. It is known in geology that iron oxidation in nature can result in uranium-bearing hematite [19]. The typical red color is attributed to Fe hydroxides, largely deposited as cement. Their widespread presence suggests considerable incoming Fe from the Zaglavak gabbroids (granites carry a much smaller amount of Fe).

The sample of the gray siltstone is pelitic, fine-grained and compact. It is built up mainly of clay-sericitic material. There was also fine sharp-edged quartz with thin plates of muscovite and biotite, turning into an iron substance and chlorite. Rare metallic minerals and fragments of coaly-organic material (Figure 27) were also found. The amounts of the gray siltstone were not large and they were likely created from the sediments of small local lakes and wetlands. The sample of gray siltstone was collected at the redox contact between the red siltstone and reddish sandstone (Figure 26), where the grain sizes of the fragments increased from the sampling point to the substrate (road level). Radioactivity in the redox zone measured 280 cps and 0.429 μSv/h.

Figure 26. Redox contact, elevated radioactivity of red and gray siltstones in the Dojkinci-Jelovica area.

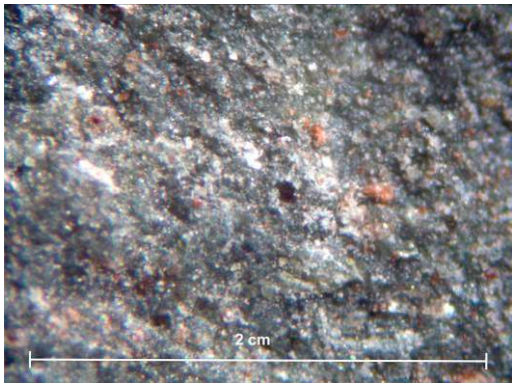

Figure 27. Macro image of gray siltstones from the redox zone of the Early Triassic at Jelovica (black in the center is organic-coaly material).

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Uranium concentrations in this case are attributable to adsorption to clays and organic-coaly material (well described in Wang et. al 2015 [20]). This process takes place in the presence of specific adsorbents such as clay minerals, limonite, carbonate sediments or organic substances – humic acid or caustobiolites, with which the uranium-bearing solution comes into contact. Muto *et al.*, 1968, tested uranium adsorption to the clays commonly found in nature: montmorillonite, haloizite and kaolin [21]. The results they reported show that uranium is fixed most efficiently at pH from 6.1 to 6.2.

In the Dojkinci area, pH measured about 7, locally 7.4. In addition, in the Dojkinci – Jelovica area uranium migrativity and a reduction environment have been noted [22]. Uranium is being deposited in a reduction environment, after the change of redox conditions. Organic substances are the major reducers of uranium, followed by iron compounds and clay minerals [23]. In the zone of the geochemical barrier in Permo-Triassic sediments, pH levels of water recently measured about 7 and Eh about 140 mV.

9. Discussion and results

The concentrations of U, Th, Pb, as Sr, Rb and K are presented in a from-to form, given that measurements were repeated several times to obtain concentration ranges of powdered and solid samples and to also check for any large variations. Before the results of chemical XRF analyses, the Table 1 below shows the measured radioactivity of typical petrologic representatives.

Table 1. Radioactivity of characteristic petrologic samples from Stara Planina

Label	Mass [g]	Activity concentration [Bq/kg]			
		226Ra	232Th	40K	137Cs
Mezdreja_granite_mine1	524.30	142 ± 7	250 ± 10	1420 ± 60	< 0.4
Mezdreja_silicified_lim1	359.84	400 ± 20	188 ± 9	600 ± 30	< 0.6
Mezdreja_granite2	459.73	116 ± 5	230 ± 10	1020 ± 50	< 0.4
Mzdreja_clay_tailings1	554.85	2600 ± 100	169 ± 8	1240 ± 60	10.8 ± 0.5
Schist_graphitic_silicified1	505.77	220 ± 10	141 ± 7	1420 ± 60	< 0.4
Schist_graphitic2	439.11	380 ± 20	169 ± 8	900 ± 40	3.7 ± 0.2
Gabrovnica_mine1	552.72	58 ± 3	163 ± 8	1700 ± 80	2.3 ± 0.1
Gabrovnica_tailings1	603.55	206 ± 9	250 ± 10	1690 ± 80	4.8 ± 0.3
Siltstone_gray1	465.30	102 ± 5	97 ± 5	2080 ± 90	< 0.5
Sandstone_red2	495.80	28 ± 1	52 ± 3	1270 ± 60	1.6 ± 0.1

Before proceeding with the discussion of the results, the outcomes of the chemical tests are presented in tabular form to show the geologic and radiometric characteristic of the tested petrologic units.

9.1. Samples and assays of igneous rocks

The concentrations of uranium in the granite samples from Mezdreja and Gabrovnica are presented in Table 2.

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Table 2. Assays related to igneous rocks (values are in ppm)

Assays_igneos rocks	U	Th	Pb	Sr
Mezdreja_granite_mine1	12.37	36.63	53.03	636.69
Mezdreja_granite_mine2	14.39	60.27	42.39	827.62
Mezdreja_granite1	12.85	37.01	54.15	634.69
Mezdreja_granite2	12.21	55.44	44.68	840.98
Mezdreja _K-feldspar_plate	6.5	4.56	61.74	655.11
Mezdreja_K-feldspar_section	6.99	9.72	46.64	665.36
Mezdreja _silif_lim1	0	30.25	104.22	1962.7
Mezdreja _silif_lim2	0	28.42	94.31	1850.88
Mezdreja _clay_tailings1	76.54	52.91	97.48	590.66
Mezdreja _clay_tailings2	77.65	43.17	103.06	749.37
Gabrovnica_granite_mine1	13.8	32.99	67.75	308.1
Gabrovnica_granite_mine2	11.61	30.82	64.27	288.82
Gabrovnica_granite_tailings1	20.69	31.84	74.66	186.94
Gabrovnica_granite_tailings2	21.09	38.66	69.47	189.56

The concentrations of uranium in the granite samples from Mezdreja and Gabrovnica were always lower by a factor of 3 to 4 than those of thorium. At Mezdreja, the uranium concentrations varied from 12.21 to 14.39 ppm and those of thorium from 36.63 to 60.27 ppm. Radioactivity (226Ra in Bq/kg) of the granites near the Mezdreja mine and at the mine portal measured 116 ± 5 and 142 ± 7, while 232Th was 230 ± 10 to 250 ± 10 Bq/kg. At Gabrovnica, the concentrations of uranium were from 11.61 to 21.09 ppm and of thorium from 30.82 to 38.66 ppm. Here the radioactivity (226Ra) of the granite samples from the mine portal area were 58 ± 3 and of the granite samples from the mine dump 206 ± 9. The measured 232Th radioactivity of the mine portal granite was 163 ± 8 Bq/kg and of the mine dump granite 250 ± 10 Bq/kg. Hence, in both cases (Mezdreja and Gabrovnica), the thorium concentrations and radioactivity were higher than those of uranium. It should be noted that the concentrations of Pb at Gabrovnica were somewhat higher – 64.27 to 74.66 ppm than at Mezdreja – 42.39 to 54.15 ppm.

Assays of coarse-grained pink K-feldspar sampled at Mezdreja, from the point of contact between the gabbroids and granites, showed that the concentrations of uranium were low – 6.5 to 6.99 ppm, while those of Th varied from 4.56 to 9.72 ppm. The sample was a 2 cm solid grain, tested at the basis and section. A high Th concentration was measured at the section. The lead (Pb) concentrations were similar to those in the granite samples.

The concentrations of uranium in the clayey and kaolinized material from the Mezdreja mine dump were higher than in fresh granites, but still lower than in the graphite-rich schists. The values ranged from 76.54 to 77.65 ppm of U. In this case there was less Th than U; Th concentrations were from 43.17 to 52.91 ppm. The concentrations of lead were nearly double those in granites, from 97.48 to 103.06 ppm. With regard to radioactivity, this material measured the highest equivalent values for uranium 226Ra – 2600 ± 100 Bq/kg. The radioactivity of 232Th was 169 ± 2 Bq/kg and correlated with the values measured in the Mezdreje and Gabrovnica granites. This particular sample exhibited the highest radioactivity of 137Cs – 10.8 ± 0.5 Bq/kg, compared to all the other samples tested in the research. In the granites, 137Cs measured 2.3 ± 0.1 at the pit and 4.8 ± 0.3 Bq/kg at the mine dump. The values of 137Cs at Mezdreja were low – less than 0.6 Bq/kg. In clay minerals, U enrichments are

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in illite bearing uranium ore from Baiyanghe [24], the uranium mineralization is located near the fracture zone, which represents the center of hydrothermal fluid activity or mineralization as is similar in case of Mezdreja mine.

No uranium (LOD) was found in a sample of silicified material from Mezdreja. The concentration of thorium was from 28.42 to 30.25 ppm, and of lead from 94.31 to 104.22 (i.e. higher than in the other endogenous products tested). It is interesting to note that this sample measured the highest concentrations of cadmium (311.72 – 352.69 ppm) and palladium (5.5 – 6.2%). The radioactivity of 226Ra was 400 ± 20 Bq/kg and of 232Th 188 ± 9.

A highly-silicified sample from Mezdreja (Fig. 18) measured the highest concentration of strontium – from 1850.9 to 1962.7 ppm. In the samples from Mezdreja and of the monomineral pink K-feldspar, the concentrations were from 634.69 to 840.98 ppm and from 655.11 to 665.36 ppm, respectively. The Sr concentrations in the Gabrovnica granites were lower and ranged from 186.94 to 308.1 ppm.

9.2. Samples and assays of graphitic schists

The concentrations of U, Th, Pb and Sr in graphitic schists from Inovo series are presented in Table 3.

Table 3. Assays related to graphitic schists (values are in ppm)

Assays graphite schist	U	Th	Pb	Sr
Schist_graphitic1	99.47	42.01	107.69	88.88
Schist_graphitic2	20.99	19.29	51.55	115
Schist_graphitic_ silicified1	27.31	14.35	51.11	119.65
Schist_graphitic_ silicified2	14.69	27.06	47.33	244.78
Schist_graphitic_compopowder	12.52	20.66	50.42	237.61

The highest concentration of uranium was measured in the graphitic schist of the Inovo Series, rich in graphitic (organic) material, and it amounted to 99.47 ppm, as opposed to the schist samples from the same sequence that were richer in silicate material, which measured less uranium by a factor of nearly 4 (20.99 to 27.31 ppm). The concentration of Th was generally lower than that of U. The graphite-rich samples had nearly half the Th.

The samples that contained more silicate material had Th concentrations varying from the ratio 1:2 in favor of uranium to the same ratio in favor of thorium. The highest measured concentration of Th was 42.01 ppm in a graphite-rich sample. The concentration of lead varied from 47.33 to 51.55 ppm and was similar to the lead concentrations in the granites, particularly at Mezdreja where 107.69 ppm of Pb was exceptionally measured in graphitic schists (which exhibited the highest uranium concentrations). Radioactivity was measured in both cases. In the graphite-rich schist 226Ra was 380 ± 20 and in the graphite-poor schist 220 ± 10 Bq/kg, which correlated with the concentrations of U measured by XRF. The radioactivity of 232Th in the graphite-rich schist was 169 ± 8 and in the graphite-poor schist 141 ± 7 Bq/kg. The radioactivity of 137Cs was 3.7 ± 0.2 in the graphite-poor sample.

It should be noted that home water well is 200 m approx. from observation point, in vicinity of river and water should be tested for uranium as it was carried out in Montana [25].

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The highest Sr concentrations were noted in the graphitic schists of the Inovo Series with less organic material and the grade was 244.78 ppm.

9.3. Samples and assays of sedimentary rocks

The concentrations of U, Th, Pb and Sr in sedimentary rocks - colorful series from Jelovica area are presented in Table 4.

Table 4. Assays related to sedimentary rocks (values are in ppm)

Sample	U	Th	Pb	Sr
Siltstone _gray1	49.36	11.83	11.85	95.84
Siltstone _gray2	49.94	12.46	11.59	92.71
Siltstone _redox1	54.43	13.13	12.34	96.74
Siltstone _redox2	52.02	12.88	16.13	93.59
Siltstone_redox_gray1	22.93	10.77	18.18	117.28
Siltstone_redox_gray2	29.31	13.7	16.45	110.23
Sandstone_red1	7.78	3.56	11.81	91.08
Sandstone_red2	12.64	4.76	10.35	51.46
Sandstone_red_orange1	8.7	3.42	10.94	47.29
Sandstone_red_orange2	9.15	9.25	8.42	97.77
Sandstone_orange	9.73	7.65	10.79	94.71

All the gray siltstones of the Colorful Series measured uranium concentrations from 49.36 to 54.43 ppm. In this case the concentrations of thorium were lower by a factor of about 4 – from 11.83 to 13.13 ppm. Lead concentrations were similar to those of Th and ranged from 11.59 to 18.18 ppm. These samples exhibited somewhat elevated concentrations of Ba – from 590.14 to 603.42 ppm. The radioactivity of 226Ra was relatively low (102 ± 5 Bq/kg) and 232Th measured 97 ± 5 Bq/kg. The radioactivity of 40K was relatively high – 2080 ± 90 Bq/kg. The values of 40K of the other samples were lower and ranged from 900 ± 40 to 1700 ± 80 Bq/kg (the lowest in the case of a highly silicified sample with limonite stains collected near Mezdreja).

The red sandstones of the Colorful Series measured relatively low concentrations of uranium, from 7.78 to 12.64 ppm, and of thorium from 3.42 to 9.25 ppm. Lead concentrations varied from 8.42 to 11.81 ppm. These samples measured the lowest radioactivity of 226Ra – 28 ± 1, and 232Th was 52 ± 3 Bq/kg.

In all sedimentary units the concentrations of strontium were much lower (in relation to granite and graphite schist samples) and generally varied from 90 to 120 ppm.

10. Note

One of the major causes of elevation of naturally-occurring radionuclide material concentrations on the Earth's surface is mining [26]. All the above-mentioned occurrences can conditionally be deemed natural. Still, the Mezdreja and Gabrovnica mine dumps carried non-processed material. It is also a fact that these areas are relatively large and that the radioactive material of the described samples is continuously drained into watercourses. Acoording Dragović et

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al., 2007 [27], the total gamma dose rate in areas of Mezdreja and Gabrovnica is two times higher in relation to the world average.

The samples shown in Figures 24 - 27 were collected next to a road. In Peng et. al 2016 [28] is shown that the groundwaters from the oxidizing aquifer with high dissolved oxygen concentration (O_2) which is case for Jelovička and Dojkinčka rivers, and oxidation-reduction potential (Eh) are enriched in U. The material from this and similar outcrops is regularly washed out by runoff after heavy rainfall or snowmelt, into the Jelovička River (a tributary of the Dojkinačka).

There is widespread contamination of the environment due to natural and anthropogenic enrichment of radionucleides in the world. In soil samples and alluvial deposits in Gabrovnica and Mezdreja deposits, an increased concentration of uranium in relation to natural background values were noted [29]. Also in Niger Delta [30] the highest activity concentration in all fish species of gamma emitting radionuclides was observed for ^{40}K, followed by ^{238}U, ^{232}Th and ^{226}Ra. Exploring the Gawib River floodplain in Namibia, Abive and Shaduka 2017 concluded that the radioactive contaminants can spread into the deeper aquifer system through the major structures such as joints and faults [31].

The study area was well known for livestock breeding and the production of cheese and meat, especially between the two world wars. However, since the 1970's the population has been migrating to industrial centers. Now some of the villages are completely abandoned and the average age of the sparse population of others is above 60. There has never been any systematic monitoring of the impact of naturally elevated radioactivity on human and animal health, such that no data has been compiled.

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