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Geology

The First Data on U-Th Mineralization in the Shkhara Paleozoic Crystalline Massif, the Greater Caucasus

Avtandil Okrostsvaridze[*], Karlo Akimidze[**], David Bluashvili[§], Salome Gogoladze[*], Rabi Gabrielashvili[*]

[*]*Institute of Earth Sciences, Ilia State University, Tbilisi, Georgia*
[**]*Faculty of Natural Sciences, Tbilisi State University, Tbilisi, Georgia*
[§] *Mining Geological Faculty, Georgian Technical University, Tbilisi, Georgia*

(Presented by Academy Member David Shengelia)

A granite vein with a thickness of ~2-3 m exposed in the headwaters of the Enguri River, with elevated radiation (μSv/h fluctuates in the range of ~1-3) has been studied in detail. It is located along the Main Thrust of the Greater Caucasus, in the Upper Paleozoic biotite-bearing migmatites of the Shkhara massif. The vein represents hydrothermally altered rock composed of a biotite-quartz-plagioclase assemblage, whose zircon LA-ICP- ^{206}Pb/^{238}U age was determined to be late Variscan (310.2±7). It is slightly fragmented and fractured, where the existing fractures and nests are filled with quartz and thorianite-uraninite veins. According to ICP-MS-ES multielement analysis, in this vein, the Th content varies from ~26 ppm ~50 ppm, the U - varies between ~55 ppm and ~290 ppm, while the content of all other chemical elements is within the normal concentrations. Of particular interest in this vein is an elevated concentration of uranium, as it is almost 100-200 times higher than normal. Those are industrial contents for the vein-type deposits. Based on the conducted research, it has been found that there is full correlation between the studied vein and of U-bearing granitic veins of different regions of the world, by genesis, composition, localization and age. Based on these data, we suppose that the Late Variscan hydrothermal plagiogranite veins, which are localized in the shear zones of the Shkhara massif granite-migmatite complex and entirely the Main Range Zone of the Greater Caucasus, may be potentially U-bearing. *© 2021 Bull. Georg. Natl. Acad. Sci.*

Greater Caucasus, Shkhara massif, plagiogranite vein, U-Th mineralization

As is known, thick felsic melts that are formed in subduction zones and experience postmagmatic hydrothermal action in the upper part of these structures is often enriched with economic deposites of metals [1-4]. These types of geodynamic regimes also form hydrothermal uranium- vein ore deposits, which make up ~ 30% of the global uranium reserves. Two main types of these uranium ore deposits are distinguished: granitic vein-like and breccia complex [5]. Breccia complex-type uranium ore deposits are mostly related to Proterozoic rocks (Ukraine, Australia, Africa), while vein type are related to the Upper Paleozoic and Mesozoic granitoids (Spain, France, Germany, Namibia, south China) [6-8]. Uranium concentration in the vein-type deposits is typically within ~200 ppm and, as a rule, their formation is associated with the late orogenic activities of magmatism [5, 8].

The dominant part of the Uranium deposits in granites is associated with the Late Carboniferous peraluminous veins of the Variscan orogeny. These veins that are localized in brecciated or fault zones occur in the center of granitic massifs as well as in their peripheries. In Europe such types of uranium deposits are identified in Iberian massif, Spain [9]; in Armoric and Central Massifs, France [10]; in Schwarzwald massif, Germany [11]; and in Bohemian massif, the Czech Republic [e.g. 12]. In Canada, the important uranium vein-type deposits of late orogenic activity are associated with the Proterozoic granites (northern Saskatchewan) [13], while in the Namibia (Damara orogeny) [7] and southern China (Yanshanian orogeny) [14] – with the Jurassic granites.

In 2020, during the field investigation, high concentrations of thorium and uranium were discovered in one of the plagiogranite veins of the Skhara massif. This paper considers primary results of research on this vein, which will enrich general knowledge on uranium and thorium hydrothermal mineralization. We believe that the results of this study will be used in the future in the search for new uranium ore occurrences in the Greater Caucasus.

A Brief Overview of the Geology of the Greater Caucasus

The Greater Caucasus fold-and-thrust belt is the northernmost expression of the Caucasus and is linked to the southern margin of the Precambrian Scythian platform. This belt extends in a NW-SE direction from the Caspian to the Black Sea, a distance of more than 1100 km. In the structure of the Greater Caucasus two major formations are distinguished: pre-Jurassic crystalline basement and Meso-Cenozoic magmatic and sedimentary formations. It has been interpreted that the pre-Jurassic basement in Paleozoic was an active continental margin, along which Paleo-Tethys oceanic crust was subducting to the north [15-20].

The basement complex along the Main Thrust of the Greater Caucasus (MTGC) is thrust over the lower Jurassic formations. In the construction of the basement complex four regional structural-tectonic zones are recognized from south to north: Southern Slope, Main Range, Fore Range and Bechasyn [20].

The Main Range zone is the best exposed part of the basement complex. Because of differences in structure; and composition it is divided into two sub-zones: the Pass and the Elbrus. They are in tectonic contact along the Alibek-Urukh regional fault, where the northern part of the zone is built with the Elbrus sub-zone and in the southern part by - Pass sub-zone [20].

In the crystalline basement of the Greater Caucasus, the Variscan plutons are localized in both the Pass and the Elbrus sub-zones of the Main Range zone. In the pass subsection, the plutons are mainly represented by the I-type quartz-diorites and granodiorites, while the Elbrus subsection is characterized by the S-type two-mica-granites. In both subsections, these plutons cut through the Paleozoic gneiss-migmatite infrastructure. It is noteworthy that in this infrastructure and in the intersected plutons the ~0.3-4.5 m thick plagiogranite veins are developed. These veins are not usually overprinted by the regional microclinization, which is one of the pieces of evidence that they are late orogenic formations [18].

Shkhara Massif

The Shkhara crystalline massif is located in the highest part of the Greater Caucasus orogen, in the Svaneti historical province. The province is located in the central, highest elevation portion of the Greater Caucasus and covers more than 7,000 km^2 area. Crystalline basement is exposed here, underlying the Mesozoic sedimentary cover and plutons. The Shkhara massif is exposed in the eastern part of the province, at the headwaters of the Enguri River and creates a ~15 km long and ~5 km high ridge (Fig. 1).

experienced intense microclinization, microcline granites formed in some areas.

Zircons in granodiorites of the main phase of the Shkhara pluton and enclosing biotite-gneisses were

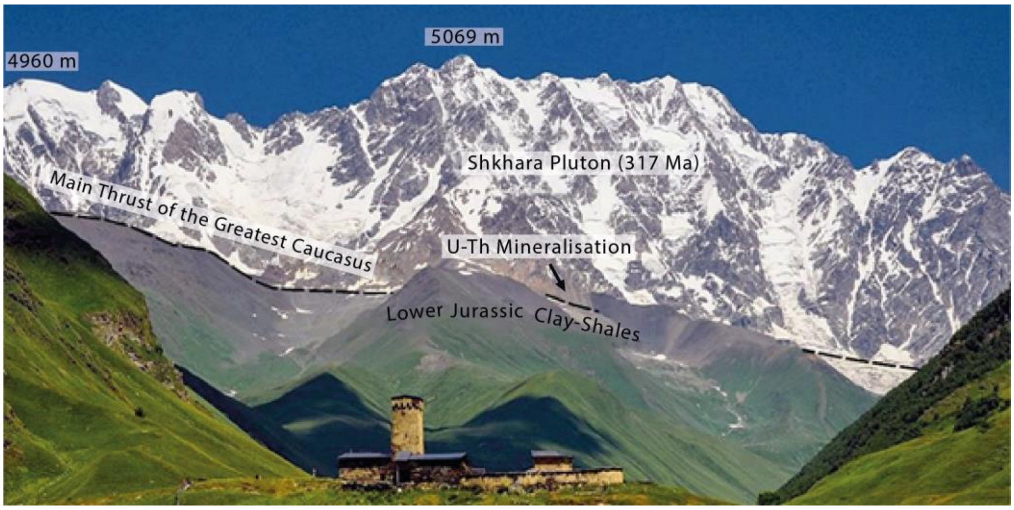

Fig. 1. Exposed parts of the Shkhara massif, viewed from the south. In the foreground: the Svanian tower and the medieval Georgian Orthodox church.

The massif composed by the Early and the Middle Paleozoic biotite crystalline schists, gneisses and migmatites, cut by the thick granitoid pluton of the Variscan orogeny generation. It is in active tectonic contact with the Lower Jurassic clays-shales and it is thrust over these rocks to the south.

According to available studies, the Shkhara pluton is interpreted as a formation of mantle-crustal generation, which formed under the geodynamic setting of an island arc [19]. The pluton is mainly composed of granodiorites, with lesser amount of granites and quartz-diorites. SiO_2 content in granodiorites varies between ~67% and 71%, with Al_2O_3 content of – ~14 to – 16%; Fe_2O_3 content – of ~3-6 %; MgO content of – ~ 0.5 to-1%; Na_2O content of of – ~2.5 to-3.5 %; and K_2O content of –3 to -4%.

The Shkhara massif is characterized by numerous enclaves of biotite-migmatites and gneisses, the volumes of which sometimes reach several cubic meters. Because the entire complex

dated by the LA-ICP-MS method [19]. This study found a weighted mean $^{206}Pb/^{238}U$ age of 316.9±8.8 Ma for zircons of the Shkhara pluton, compared to a weighted mean $^{206}Pb/^{238}U$ age of 488.5±8.5 Ma from zircons of the biotite gneiss.

Plagiogranite veins of different thicknesses (~0.5-4 m) cut the Shkhara massif. We detected the anomalous uranium and thorium concentration in one of these types of veins. In this paper, we provide the results of detailed investigation of this vein.

Materials and Methods

During the field investigation, we studied the background radiation of the Shkhara plagiogranite vein using the FAG-FH40F2 dose – rate meter. We took 12 samples for chemical analyses of the vein and its surrounding rocks, each sample with an average weight of 3-4 kg. The whole-rock chemical compositions of these samples were measured using the different spectrometers in different laboratories: 1) An X-ray fluorescence spectrometer (XRF 2000) at the Geological Institute, Georgia (samples #20Sv1 to 20Sv12); 2) ICP-MS analysis for 51 elements conducted by a laboratory contracted by the U.S. Geological Survey of (USGS) (samples #20Sv1 to 20Sv5); and 3) ICP-ES analyses for 48 elements conducted by MS – Analytical laboratory (MSALABS), Canada (samples #20Sv6 to – 20Sv12).

One sample (20Ge15) weighing ~5 kg was taken from the Shkhara massif plagiogranite vein for U-Pb zircon geochronology. A total of 25 zircon grains were separated and dated from this vein. The U-Pb zircon age determination analyses was conducted at the Department of Earth and Environmental Sciences, National Chung-Cheng University, Taiwan, via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) equipped with an Agilent 7500s quadrupole and a New Wave UP213 laser ablation system. Calibration was performed using the GJ-1 zircon standard [21] and Plešovice zircon [22] to assess data quality. All U-Th-Pb isotope ratios were calculated using GLITTER 4.4.2 (GEMOC) software, and the isotope ratio of common lead was corrected using the approach proposed by T. Andersen [23]. (2002). Isoplot v. 3.0 [24] was used to calculate weighted mean U-Pb ages and probability density curves. The detailed analytical procedure has been described by G. Chiu et al. [25].

The Results of Investigation of the Shkhara Plagiogranite Vein

In 2020, under a project of the Rustaveli National Science Foundation (Thorium – Future Energy: Investigation of Thorium Occurrences and Geologic Settings in Georgia; # FR-18-8122), we conducted fieldwork in the headwaters of the Enguri River. The radioactive vein discovered by this study is located in the southern contact area of the Shkhara pluton [Lat (^{0}N) 42. 5845; Long (^{0}E) 43.3027] in a biotite gneiss-migmatite complex, in the area of the Main Thrust of the Greater Caucasus. The vein has, a thickness of ~2 to – 3 meters, dipping ~ 55 to 60^0 to the south, and extending in NW-SE direction.

Radiation dose. The radiation dose of plagiogranite vein of the Shkhara pluton was measured on the outcrop using a FAG-FH40F2 dosimeter. It measures the gamma radiation in microSievert (μSv), which is a derived unit of ionizing radiation dose in the International System of Units (SI). This parameter is rated as a microSievert/hour (μSv/h); according to this parameter the normal safe radiation dose for human health is 0.17 [26].

The radiation dose varies from 1.5 up to 2.0 μSv/h on the surface of the Skkhara plagiogranite vein. In some places along the vein this parameter increases to 2.7 to 3.0 μSv/h, but in some areas the radiation decreases from to 1.2 to 1 μSv/h. These values are almost 15 times higher than natural radiation. For this reason, we took eight samples from the vein for more detailed analyses. Moreover, we took four samples from the country rock adjacent to the vein, because here the background radiation is two times higher than the normal value (μSv/h >0.30).

Petrography and petrochemistry. The Shkhara plagiogranite vein with elevated radiation has a milky color, massive structure, and is composed of medium and fine-grained crystals. It is localized in biotite-migmatites and gneisses and, unlike other rocks of the Shkhara massif, did not undergo regional microclinization. The vein is mainly composed of quartz and plagioclase, with microcline, biotite, muscovite, chlorite and epidote present in minor amounts. Accessory minerals are allanite, zircon, and sphene. This assembly of the minerals is slightly fractured and these cracks are filled with younger quartz veins. The youngest component of the rock are the ore minerals, which in some precincts impregnations occur in quartz-plagioclase masses (Fig. 2). Based on the results of microscopic and geochemical studies of this vein, we consider that this ore mineral is uraninite.

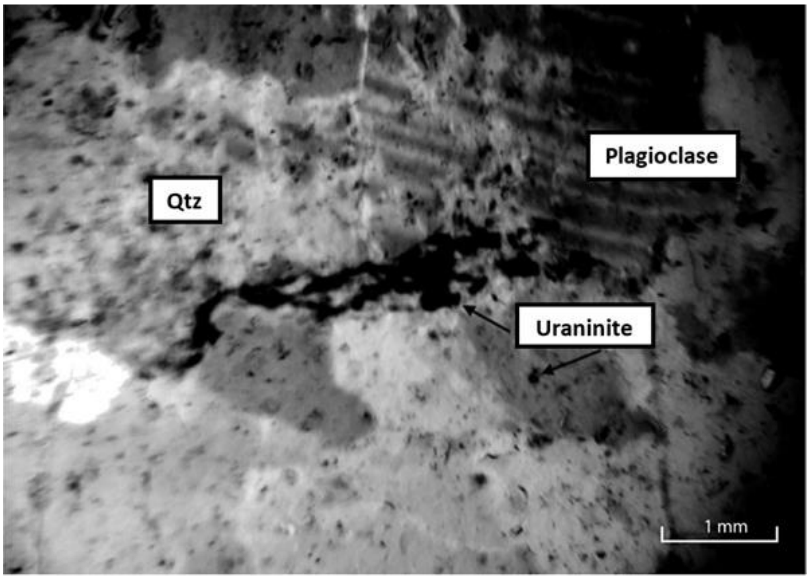

Fig. 2. Typical mineralogy of the thorianite-uraninite veins in plagiogranite of the Shkhara massif in plane polarized light (sample 21Sv8).

According to a petrochemical study the Shkhara plagiogranite vein is a felsic formation, in which SiO_2 content varies from 74.9% to 84.5%. The other chemical elements are represented with lesser amounts and create the following variations: Al_2O_3 - 10.2-11.3%, Fe_2O_3 – 1.8-2.6%, MgO – 0.8-2.0%, Na_2O – 3.1-3.5%, while K_2O – 1.4-1.7%. According to the chemical composition, this vein corresponds to the quartzitized plagiogranite.

Geochemistry and Isotopic Geochronology

According to the geochemical study, in the samples from the Shkhara plagiogranite vein, the whole range of elements (48 elements) shows the normal concentrations, whereas thorium and uranium content is anomalously high (Table).

In four samples of country rocks, Th and U content varies from 1.7 ppm to 19.7 ppm and from 0.5 ppm to 1.5 ppm, respectively. These values are not unusual for unaltered gneiss. The concentrations of these radioactive elements drastically increase in the plagiogranite vein, which is displayed in Fig. 3.

In eight samples taken from this plagiogranite vein, Th concentrations vary in the range of 26.5 to 50.1 ppm, whereas the U content ranges from 54.7 ppm to 290.9 ppm. As we can see from Fig. 3, in these samples, the Th content in the vein is 7 to 10 times higher than average crustal concentration, and the U content is 100 to 290 times higher. From these data, the U mineralization deserves special interest, since for granite veins of this type and age, as mentioned above, deposits with such U concentrations are mined elsewhere.

One sample of ~5 kg (20Geo15) was taken from the uranium-bearing plagiogranite vein from the Shkhara massif for the dating of zircons using the U-Pb method. It is medium grained, massive quartz-plagiogranite rock with the following mineral composition: quartz +plagioclase+ +microcline+biotite+muscovite±chlorite±allanite± zircon.

We separated and dated 25 zircon grains from this sample. The grains make small (~120μmX~60 μm) crystals, where two zones can be observed: a small number of inherited older zircon core and rim. Inherited zircon cores ages varies between ~ 407-433 Ma, while rim ages are in ~301-311 Ma range. Zircons weighted mean $^{206}Pb/^{238}U$ age of Shkhara massif plagiogranite vein corresponds to 310.2±7 Ma (MSWD=2.5, probability = 0.003).

Table. U, Th, and selected trace elements (in ppm) as determined by ICP-ES chemical analyses of the Shkhara massif plagiogranite vein and adjacent country migmatites

Sample	Rb	Ta	Hf	Th	Nb	Tl	U	V	W	Y	Zn	Pb
20Sv1	61	0.38	0.2	**3.5**	4.4	1.20	**0.5**	262	0.3	16.9	39	5.5
20Sv2	110	0.72	0.4	**19.7**	8.5	0.69	**1.5**	12	2.6	19.2	22	26.2
20Sv3	201	1.3	4	**26.5**	13.1	1.2	**121**	26	<1	18.2	21	35.3
20Sv4	114	1.5	10	**40.5**	16.3	0.7	**273**	37	<1	12.1	30	42.4
20Sv5	78.1	0.9	3	**37.1**	7.6	<0.5	**183**	9	<1	9.7	9	30.5
20Sv6	492	2.8	7	**40.6**	42.9	3.2	**54.7**	120	2	7.1	101	31.5
20Sv7	185	1.28	0.3	**29.4**	17.5	1.07	**105.6**	32	0.4	15.0	27	35.7
20Sv8	114.2	1.59	0.4	**50.1**	8.0	0.67	**290.9**	37	0.4	10.3	36	47.78.
20Sv9	79.8	0.95	0.1	**37.7**	44.1	0.41	**174.3**	13	0.3	7.9	14	41.5
20Sv10	334.7	3.04	0.1	**47.5**	3.5	2.77	**62.4**	124	2.1	5.0	112	53.4
20Sv11	43,2	0.27	0.6	**3.1**	3.5	0.32	**0.7**	42	0.7	5.9	146	125.8
20Sv12	27.2	0.17	0.3	**1.7**	1.8	0.08	**1.3**	17	0.3	37.5	35	89.5

Samples: 20Sv1, 20Sv2, 20Sv11 and 20Sv12 from country migmatites; Samples: from 20Sv3 to 20Sv10 from plagiogranite vein.

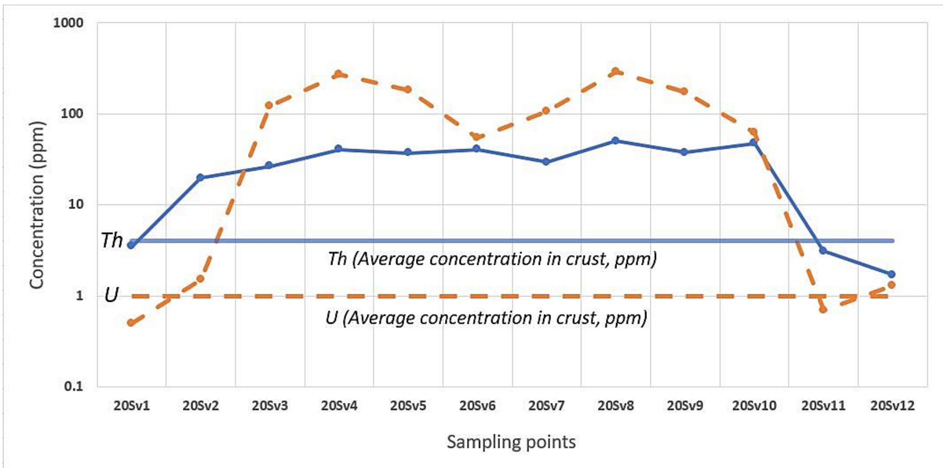

Fig. 3. The variation diagram of U and Th concentrations (ppm) in the plagiogranite vein of the Shkhara massif (from 20Sv3 – to Sv10) and country migmatites (20Sv1, 20Sv2, 20Sv11, 20Sv12).

Discussion

Due to the difficult terrain of the Shkhara massif, we had problems in determining its exact contours and scale of the study plagiogranite vein. For the same reason, it is also impossible to prospect properly for similar veins in the central segment of this massif. Because of this, we consider that future research of U should be carried out on the western periphery of the massif, namely in the headwaters of the River Khalde, where the terrain is relatively soft.

Based on the analysis of the obtained results, we recommend the field investigation of uranium should be carried out entirely in the late orogenic plagiogranite veins of the granite-migmatite complex in the Main Range Zone of the Greater Caucasus.

Based on the microscopic and geochemical studies, we consider that U and Th occur in minerals of the thorianite-uraninite series (ThO_2 - UO_2). Within the crystalline structure of uraninite, U is easily replaced with Th, and in most cases, it is represented as a solid solution of uraninite and thorianite [27].

Regarding the age of radioactive minerali-zation, the microscopic research shows that the U-Th deposition is the youngest process that follows the rock formation. However, at this stage of research, it is impossible to determine whether it is late Variscan or younger.

As the title of this publication shows, this paper is the first study on U and Th mineralization in the Shkhara massif and, generally, in the crystalline basement of the Caucasus. Thus, there is still a lot of work to be done and many issues to be clarified, such as the age of U-Th mineralization, identification of their source, and the scale of their distribution. We hope that in the near future it will be possible to answer these questions.

Conclusions

1. In the headwaters of the River Enguri, on the southern slopes of the Shkhara massif, one of the outcropping veins of plagiogranite, ~ 2-3 m thickness, is characterized by elevated radiation, which ranges from ~1 to 3 μSv/h.
2. This vein is localized in the Upper-Middle Paleozoic biotite migmatites, in the contact area of the late Variscan Shkhara granitic pluton in the Greater Caucasus Main Trust zone.
3. Petrographicaly, this vein is hydrothermally altered, biotite plagiogranite, in which the SiO2 content varies from ~75 to 85%. The U-bearing mineral is Th-rich uraninite, which is the main ore mineral for vein type uranium deposits.
4. According to the ICP-MS analysis of vein samples, the Th concentration in this vein ranges from ~26 ppm to ~50 ppm, whereas U concentrations vary from ~55 ppm to 290 ppm. It should be noted that, these concentrations of U have been mined from vein-type deposits in other countries.
5. Using LA-ICP-MS analysis, 206Pb/238U age of zircons from the vein indicate an age of 310.2±7.5 Ma that corresponds with the Variscan late orogenic activity.
6. According to the genesis, composition, age, localization, and type of U mineralization, the studied vein is in full correlation with the same type of U-bearing granitic veins in different regions of the world. Based on these data, we suppose that the Late Variscan hydrothermal plagiogranite veins, which are localized in the shear zones of the Shkhara massif granite-migmatite complex, indicate the potential for U-bearing veins in this massif.
7. In the Late Variscan plagiogranite veins of the granite-migmatite complex of the Greater Caucasus, which are localized in the shear zones and in the surrounding sediments, should be a focus of detailed investigation for U-Th-vein mineralization. According to all forecasts, the demand for these elements will sharply increase in the future [28, 29].

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გეოლოგია

U და Th მინერალიზაციის პირველი მონაცემები შხარის პალეოზოურ კრისტალურ მასივში, კავკასიონი

ა. ოქროსცვარიძე*, კ. აქიმიძე**, დ. ბლუაშვილი§, ს. გოგოლაძე*, რ. გაბრიელაშვილი*

*ილიას სახელმწიფო უნივერსიტეტი, დედამიწის შემსწავლელ მეცნიერებათა ინსტიტუტი, თბილისი, საქართველო

**ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, საბუნებისმეტყველო ფაკულტეტი, თბილისი, საქართველო

§საქართველოს ტექნიკური უნივერსიტეტი, სამთო-გეოლოგიური ფაკულტეტი, თბილისი, საქართველო

(წარმოდგენილია აკადემიის წევრის დ. შენგელიას მიერ)

დეტალურადაა შესწავლილი მდ. ენგურის სათავეებში გაშიშვლებული ~2-3 მ სიმძლავრის გრანიტული ძარღვი, რომელსაც მაღალი რადიაცია გააჩნია (μSv/h მერყეობს ~1-3 ინტერვალში). იგი ლოკალიზებულია კავკასიონის მთავარი შეცოცების გასწვრივ, შხარის კრისტალური მასივის ზედაპალეოზოურ ბიოტიტიან მიგმატიტებში. ძარღვი წარმოადგენს ჰიდროთერმულად შეცვლილ ბიოტიტიან კვარც-პლაგიოკლაზიან ქანს, რომლის ცირკონების იზოტოპური LA-ICP-MS 206 Pb/238U ასაკი გვიანვარისკულით დათარიღდა (310.2±7.5 მლნ. წ.). იგი სუსტადაა დამსხვრეული და დანაპრალიანებული, ხოლო ნაპრალები და ბუდობები ამოვსებულია კვარცისა და ურანიტიტის ძარღვაკებითა და ბუდობებით. მულტიელემენტური ICP-MS -ES ქიმიური ანალიზის მიხედვით შხარის პლაგიოგრანიტულ ძარღვში თორიუმის კონცენტრაცია მერყეობს ~26 გ/ტ-დან ~50 გ/ტ-მდე, ურანის - ~55 გ/ტ-დან ~290 გ/ტ-მდე ინტერვალში, ხოლო ყველა დანარჩენი ქიმიური ელემენტის შემცველობა ნორმის ფარგლებშია. ამ ძარღვში განსაკუთრებულ ინტერესს იწვევს ურანის ამაღლებული კონცენტრაცია, ვინაიდან იგი ნორმულთან შედარებით თითქმის 100-200-ჯერაა გაზრდილი, რაც ძარღვული ტიპის საბადოებისათვის სამრეწველო შემცველობებია. ჩატარებული კვლევის შედეგად დადგინდა, რომ შესწავლილი ძარღვი გენეზისის, შედგენილობის, ასაკისა და ლოკალიზაციის მიხედვით სრულ კორელაციაშია მსოფლიოს სხვადასხვა რეგიონის ურანის ძარღვული ტიპის საბადოებთან. ამ მოცემულობიდან გამომდინარე ვუშვებთ, რომ შხარის მასივის და მთლიანად კავკასიონის მთავარი ქედის ზონის გვიანვარსკული ჰიდროთერული პლაგიოგრანიტული ძარღვები, რომლებიც ლოკალიზებული არიან რეგიონული რღვევის ზონებში, პოტენციურად შესაძლებელია ურანის შემცველი იყოს.

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