RADIOACTIVITY OF ROCK SAMPLES IN THE SHIDA KARTLI REGION (GEORGIA)

Nodar Kekelidze[1, 2, 3], Teimuraz Jakhutashvili1, Bezhan Tutberidze[1], Eremia Tulashvili[1], Mariam Akhalkatsishvili[1], Lela Mtsariashvili[1]

[1] Ivane Javakhishvili Tbilisi State University, 13 Chavchavadze av., 0179, Tbilisi, Georgia

[2] Ferdinand Tavadze Metallurgy and Materials Science Institute, 10 Mindeli str., 0186, Tbilisi, Georgia

[3] Georgian Technical University, 77 Kostava str., 0175, Tbilisi, Georgia

ABSTRACT

This study investigates the distribution of natural and technogenic radionuclides in rock samples within the territory of the Shida Kartli region, which is located within the tectonic structure of the Transcaucasian intermountain area. This area is characterised by a complex geological structure, and the radioactivity of soil and rocks has not been investigated from a practical perspective. Eighteen samples of rocks of various types, including magmatic, sedimentary and metamorphic, were investigated with the gamma-spectroscopic method. Up to 21 naturally occurring radionuclides and one technogenic radionuclide were identified in these samples. The average activity concentration of the Th-232 family radionuclides varied between 1.2 and 64.8 Bq/kg; that of the U-238 family varied between 4.5 and 47.3 Bq/kg; and that of the U-235 family between 0.22 and 2.3 Bq/kg. The highest activity concentration was observed for K-40 (with a maximal value of 1263 Bq/kg). Activity of the technogenic radionuclide Cs-137 was measured in several samples as being between 0.1 and 0.6 Bq/kg. Several features of the radionuclide distribution were observed to depend, in particular, on the type of rock, the tectonic zone and age. Several radionuclide activity ratios were also considered, including U-238/U-235, U-238/Th-232, Ra-226/U-238, and Pb-210/Ra-226, and a comparison was carried out with existing data in the literature.

Keywords: Radionuclides, rock, radioactivity, activity ratios.

INTRODUCTION

Investigations of the natural and technogenic radioactivity in different environmental structures form one of the topical problems of ecology. Natural radioactivity in the environment is caused by radionuclides of the three families of Th-232, U-238, and U-235, and also K-40; these are referred to as alpha-, beta-, and gamma-emitters. The long-lived radionuclides Cs-137 and Sr-90 are the most widespread among the technogenic radionuclides. The radioactivity of rocks is the subject of numerous research studies.

For example, the distribution of natural radionuclide γ-ray activities was determined for igneous rock samples collected along the road between Idfu and Marsa Alam in eastern desert of Egypt [1]. This subject is important in environmental radiological protection, since igneous rocks are widely used as building material. The radium equivalent activities of samples under investigation were calculated, and the average Ra_{eq} value for the studied area 65.51 Bq/kg are below the internationally accepted value 370 Bq/kg [2], [3]. It was also studied some radionuclide activity ratios, in particular U-238/Ra226, Th-232/Ra-228.

Another study [4] carried out comparative research of radioactivity content in samples of igneous rocks from various deposits in Egypt and Germany. Concentration of Th-232 in igneous samples collected in Egypt varied from 3.2 to 53.4 Bq/kg, and in samples from Germany from 5.8 to 70 Bq/kg. Concentration of Ra-226 in Egyptian igneous samples rangeв from 3.9 to 57.4 Bq/kg and in samples from Germany from 11.2 to 76.1 Bq/kg. Activity of K-40 ranged from 203 to 1041 Bq/kg in samples from Egypt and from 177 to 1465 Bq/kg in samples from Germany. The authors noted that even though these radionuclides are widely distributed, their concentrations depend on the local geological conditions.

The aim of study [5] was to investigate the specific activity of radionuclides in charnockite rocks of Kalrayan Hills, India. Besides specific activity, the activity ratios (U-238/Th-232, U-238/K-40, Th-232/U-238, Th-232/K-40, K-40/U-238 and K-40/Th-232) were calculated. U-238/Th-232 ratio varied from 0.25 to 1.49 with an average of U-238/Th-232 of 0.8. This average is equivalent to the upper crust value (0.8). This shows that the concentration of uranium and thorium in the present study area rock samples is more or less equal to the concentration of uranium and thorium in the upper crust value.

Shivakumara et al. [6] studied radionuclides content and activity concentration for rock samples collected in Mandya District, Karnataka state, India. In the study area, unclassified crystalline rocks mainly carbonate and gneisses types of rocks and in some areas igneous rocks of granitic composition were found. The concentrations of radionuclides in the study area are slightly higher than Indian average and world average values.

Research has been carried out in the past into the radioactivity of various environmental objects in Georgia, prompted by the meltdown at the Chernobyl atomic power station in 1986. Elevated concentrations of various technogenic radionuclides (up to several thousands of Bq/kg) have been observed, especially in the soil of the western Georgian coastal region [7], although rocks have not studied. The present work therefore analyses the natural and technogenic radioactivity of rocks in the territory of Georgia, in the Shida Kartli region.

2. MATERIALS AND METHODS

2.1. Study area

2.1.1. Area geology

The Shida Kartli region is located towards the south of the Caucasus fold system (I), within the Transcaucasian intermountain area (II) (the left-hand bank of the depression of the Mtkvari River) and the Lesser Caucasus fold system (III) (the right-hand bank of the depression of Mtkvari River). According to tectonic characteristics, it is possible to distinguish several areas within this region [8]:

- The central raising zone (II_2), a tectonic unit formed of massive Bajocian volcanogenic formations, shallow-water Cretaceous carbonate sediments, etc.;
- Part of the molassic subzone of Kartli (II_3^1) of the eastern immersion zone or Georgian Block (II_3), which is almost completely formed of massive molasses of the Oligocene-Miopliocene;
- The Achara-Trialeti folded zone (III_1), a mountainous area (600–1000 m above sea level) to the southwest of the city of Mtskheta; two subzones are contiguous in this region:
    - A rather depressed northern subzone (III_1^2);
    - The raised central (axial) subzone (III_1^3).

Sedimentary rocks (limestone, sandstone, argillite, clay, and slate) are predominant in these areas.

It should be noted that the region investigated here is also characterised by a complex hydrological system. Subzones II_2 and II_3^1 are located in the territory of the Kartli artesian basin of pore, fissure and fissure-cavern waters. Non-confined waters are developed here, both in modern and Quaternary sediments, and also in the upper parts of pre-Quaternary rocks. Subzones III_1^3 and III_1^2 are mostly located within the territory of the Tbilisi artesian basin, a water-pressure system of fissure and fissure-cavern waters. Ground pore waters and underground waters of deep circulation are developed here, and are mainly developed in volcanogenic-sedimentary rock series of the Middle Eocene and carbonate rock series of the Upper Cretaceous [9].

2.1.2. Locations and samples

Eighteen rock samples (Table 1) were collected from 18 locations within the investigated area (located near Grakliani hill (Gr), Uplistsikhe cave town (Up), Surami (Sr) settlement, Rikoti pass (Rk), Saskhori (Ss), Khekordzi (Kk), Kvemo Nichbisi (Nb), Telatgori (Tg), Khidistavi (Hd), Didi Ateni (At) settlements). In particular:

- In subzone II_3^1: three samples (36, 153, 152) were collected from three locations;
- In zone II_2: three samples (34, 33, 31) were collected from three locations;
- In subzone III_1^3: eight samples (78, 76, 77, 74, 80, 82, 144, 146) were collected from eight locations;
- In subzone III_1^2: four samples (159, 155, 156, 158) were collected from four locations.

The types of samples collected were as follows:

- Magmatic (intrusive) – one sample (31), granite, acid rock;
- Sedimentary – fifteen samples:

- o Carbonate (limestone): five samples (33, 144, 146, 74, 80);
  - o Sandstone: six samples (carbonate sandstone: 158; arkosic sandstone: 34, 159, 153; tuff sandstone: 78, 82);
  - o Clay: one sample (155, argillite);
  - o Tuff breccia: one sample (156, volcanogenic, sedimentary);
  - o Conglomerate, breccia – two samples (carbonate: 36; arkosic breccia and conglomerate: 152);
- Metamorphic volcanic: two samples (tuff: 76, 77).

Figure 1 shows the layout of these locations.

Table 1

List of locations (L), sample numbers (SN) of investigated samples, their types (ST), and age (T)

#	Tct	L	SN	Lt(N); Ln(E)	ST	T
1	II$_3$ ^{1}	Gr-1	36	41.99663; 44.40515	Conglomerate, breccia (carbonate) [Cg-Bc (Cr)]	Quaternary
2	-"-	Up-2	153	41.96735; 44.21124	Sandstone (arkosic, fine-grained and medium-grained, tan) [Ss (Ak, Fg, Mg, Tn)]	Neogene
3	-"-	Up-1	152	41.96763; 44.21116	Conglomerate, breccia (arkosic, grey) [Cg-Bc (Ak, Gr)]	-"-
4	II$_2$	Sr-2	34	42.02705; 43.56042	Sandstone (arkosic) [Ss (Ak)]	Paleogene
5	-"-	Sr-1	33	42.03711; 43.51845	Carbonate, limestone [Cr-Ls]	Cretaceous
6	-"-	Rk-5	31	42.04650; 43.49669	Granite [Gn]	Jurassic
7	III$_1$ ^{3}	Ss-2	78	41.83731; 44.56759	Sandstone (tuff) Ss (Tf)	Paleogene
8	-"-	Kk-1	76	41.83588;	Tuff zeolitic (greenish) (Tf-Zl (G))	-"-

				44.56786		
9	-"-	Kk-2	77	41.83575; 44.56819	Tuff zeolitic (whitish) (Tf-Zl (W))	-"-
10	-"-	Kk-3	74	41.83063; 44.56346	Carbonate, limestone [Cr-Ls]	Cretaceous
11	-"-	Ss-3	80	41.83779; 44.54783	Carbonate, limestone [Cr-Ls]	-"-
12	-"-	Nb-1	82	41.82472; 44.52665	Sandstone (tuff) [Ss (Tf)]	Paleogene
13	-"-	Tg-1	144	41.84663; 44.51311	Carbonate, limestone (whitish, thinly laminated and thick laminated) [Cr-Ls (W, Tl, Tc)]	Cretaceous
14	-"-	Tg-3	146	41.84697; 44.47353	Carbonate, limestone (tan, fine-grained and medium-grained) [Cr-Ls (Tn, Fg, Mg)]	-"-
15	III$_1^2$	Hd-1	159	41.96549; 44.12175	Sandstone (arkosic, grey) [Ss (Ak, Gr)]	Paleogene
16	-"-	At-1	155	41.91164; 44.09427	Argillite (black) [Ar (Bk)]	-"-
17	-"-	At-2	156	41.90998; 44.09496	Tuff breccia (grey, fine-grained and medium-grained) [Tf-Bc (Gr, Fg, Mg)]	-"-
18	-"-	At-4	158	41.90473; 44.09589	Sandstone (carbonate, laminated) [Ss (Cr, Lt)]	-"-

Notes: Tct – tectonic zone; Lt(N) – latitude (north); Ln(E) – longitude (east).
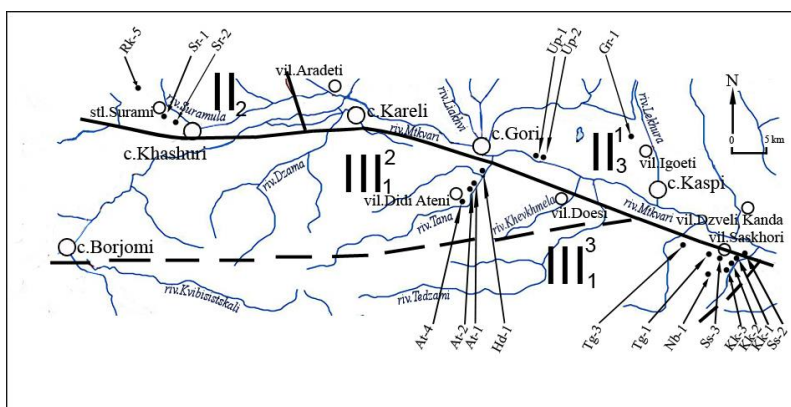
Figure 1. Layout of locations

2.2. Sampling and analysis

2.2.1. Sampling

Samples were collected from the outcrops and placed directly into plastic containers; under laboratory conditions, the samples were broken and then crushed using special equipment (a Retsch jaw crusher) to sizes of less than 1 mm. The samples were then dried, and their bulk density and weight were determined. They were then sealed in Marinelli beakers (polyvinyl chloride adhesive tape was used for hermetic sealing) and stored for more than four weeks to achieve a secular equilibrium between Ra-226 and Rn-222.

2.2.2. Measurement of gamma radiation activity

Measurements were carried out using a Canberra GC2020 gamma spectrometer with a semi-conductor germanium detector, with a relative efficiency of 24%. The acquisition time for gamma spectra was 72 hours. For analysis, Genie-2000 S500 software was used with additional modules, in particular the S506 Interactive Fit Program. Activity concentrations were determined for Th-232 (average values were reported for Ac-228, Ra-224, Pb-212, Bi-212, and Tl-208, for which the determination error varied between 3.4% and 6.5%), U-238 (using the Th-232 line at 63.3 keV with an error in the diapason varying between 13.3% and 24%), Ra-226 and U-235 (using the line at 186 keV, which was divided using the S506 program with an error of between 11.2% and 27% for Ra-226, and 6.5% and 18.1% for U-235), Pb-214 and Bi-214 (with an error of between 2.4% to 5.9%), and Pb-210 (using the line at 46.54 keV with an error from 14.3% to 20.0%). Also identified were Be-7, K-40, and the technogenic radionuclide Cs-137.

Taking into account the influence of matrix composition on the gamma attenuation, the chemical compositions of the samples were determined on the basis of reference data [10], [11] and were

then input into LabSOCS software to carry out an efficiency calibration for the activity concentration calculation. The NuDat database [12].was used to create the radionuclide library.

An assessment of the radium equivalent activity, Ra$_{eq}$, (Bq/kg) was carried out using the formula [13]:

$Ra_{eq} = A_U + 1.43\,A_{Th} + 0.07\,A_K$

where A_U, A_{Th}, and A_K are the activity concentrations (Bq/kg) of U-238, Th-232, and K-40, respectively.

To characterise the samples by radioactivity, taking into account the accepted limit for Ra_{eq} of 370 Bq/kg (equivalent to an annual gamma-radiation dose of 1.5 mSv/y [14]), some groups were established using the value of equivalent activity. The first group included nonradioactive samples with activity not exceeding 30 Bq/kg; the second included those with low radioactivity, within the range 30 to 100 Bq/kg; the third included those with a medium level of radioactivity within the range 100 to 300 Bq/kg; and the fourth included those with high radioactivity within the range 300 to 1000 Bq/kg)[1]. This technique is described in more detail in [15], [16].

3. RESULTS

Using the results of the gamma spectra analysis, up to 22 radionuclides were identified in the rock samples: the Th-232 family (Ac-228, Th-228, Ra-224, Pb-212, Bi-212, and Tl-208: six radionuclides in total); the U-238 family (Th-234, Pa-234, Th-230, Ra-226, Pb-214, Bi-214, and Pb-210: seven radionuclides in total); the U-235 family (U-235, Th-231, Th-227, Ra-223, Rn-219, and Pb-211: six radionuclides in total); and other natural radionuclides (Be-7, K-40), and the technogenic radionuclide Cs-137. Certain specific gamma lines were also identified, which originated as a result of cosmic rays interacting with the material of the detector or the sample. The average activity of the identified radionuclides of these families varied over a wide range, from 0.22 Bq/kg (for the U-235 family) to 64.8 Bq/kg (for the Th-232 family). Of the individual radionuclides, K-40 had the highest activity (1263 Bq/kg). For some samples, the activity of certain radionuclides (primarily in the U-235 family) was lower than the minimal detectable activity (MDA).

The results of measurements of the activity concentration of the main radionuclides in the investigated samples, their equivalent activity, activity ratios, average (*av*), minimal (*mn*) and maximal (*mx*) values and other data are given in Tables 2 to 6.

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[1] Such samples were not observed in this work.

Table 2

Activity concentration (Bq/kg) of radionuclides of families Th-232, U-238 (Th-234), U-235, Ra-226, Pb-210, radionuclides Be-7, K-40, and Cs-137; the radium equivalent activity (Ra_{eq}, Bq/kg), activity ratios U-238/U-235; U-238/U-235, Ra-226/U-238, and Pb-210/ Ra-226; and their average (*av*), minimal (*mn*) and maximal (*mx*) values

#	Tct	L	SN	ST	Th-232	U-238	Ra-226	Pb-214	Bi-214	Pb-210	U-235	Be-7	K-40	Cs-137	Ra_{eq}	U-238/ U-235	U-238/ Th-232	Ra-226/ U-238	Pb-210/ Ra-226
1	II₃[1]	Gr-1	36	Cg-Bc (Cr)	5.4	6.6	7.2	7.3	7.0	<M	0.32	—	89.3	<M	21.2	21.0	1.22	1.08	—
2	-"-	Up-2	153	Ss (Ak, Fg, Mg, Tn)	16.9	19.2	17.4	17.8	17.0	<M	0.89	<M	571	—	81.6	21.6	1.14	0.91	—
3	-"-	Up-1	152	Cg-Bc (Ak, Gr)	7.4	25.2	28.8	29.0	28.6	19.5	1.18	—	587	0.6	80.4	21.3	3.42	1.14	0.68
4	II₂	Sr-2	34	Ss (Ak)	9.7	6.3	6.7	7.0	6.4	<M	0.28	—	947	—	86.8	22.4	0.64	1.08	—
5	-"-	Sr-1	33	Cr-Ls	3.6	24.2	33.3	30.5	31.0	27.7	1.15	<M	261	—	56.7	21.0	6.78	1.38	0.83
6	-"-	Rk-5	31	Gn	58.8	39.7	27.0	28.4	27.8	22.6	1.75	—	1263	—	199	22.6	0.68	0.68	0.83
7	III₁₃	Ss-2	78	Ss (Tf)	5.8	5.8	4.9	4.8	4.5	<M	0.28	<M	184	0.1	26.1	20.3	0.98	0.85	—
8	-"-	Kk-1	76	Tf-Zl (G)	23.5	27.9	25.6	23.8	22.8	21.1	1.22	—	746	—	111	22.9	1.19	0.92	0.82
9	-"-	Kk-2	77	Tf-Zl (W)	30.8	35.5	17.4	18.3	17.2	19.3	1.6	—	416	0.2	90.5	22.7	1.15	0.49	1.11
1	-"-	Kk	74	Cr-Ls	13.	10.	15.	11.	10.	<M	0.47	—	551	—	73.9	22.9	0.77	1.46	—

0		-3			8	7	6	0	5										
11	-"-	Ss-3	80	Cr-Ls	4.5	4.5	4.8	5.2	5.1	<M	0.22	<M	89.0	<M	17.6	20.9	0.99	1.07	—
12	-"-	Nb-1	82	Ss (Tf)	18.4	16.3	14.8	14.1	13.5	16.6	0.75	—	454	—	72.9	21.6	0.88	0.91	1.12
13	-"-	Tg-1	144	Cr-Ls (W, Tl, Tc)	6.0	7.5	6.8	6.5	5.7	<M	0.35	<M	146	—	25.6	21.2	1.26	0.90	—
14	-"-	Tg-3	146	Cr-Ls (Tn, Fg, Mg)	1.2	5.7	6.1	5.8	5.3	12.9	0.27	3.9	22.0	—	9.4	20.9	4.64	1.06	2.11
15	III_1^2	Hd-1	159	Ss (Ak, Gr)	14.1	9.5	10.6	10.9	10.3	<M	0.43	<M	598	—	72.7	22.3	0.67	1.12	—
16	-"-	At-1	155	Ar (Bk)	42.7	39.9	41.8	38.9	38.0	30.3	1.8	<M	732	<M	154	21.7	0.93	1.05	0.72
17	-"-	At-2	156	Tf-Bc (Gr, Fg, Mg)	24.9	18.1	20.8	21.2	20.4	15.9	0.83	—	681	<M	104	21.8	0.72	1.15	0.77
18	-"-	At-4	158	Ss (Cr, Lt)	64.8	47.3	42.7	43.0	42.6	34.9	2.3	<M	255	—	153	20.2	0.73	0.90	0.82
				av	*19.6*	*19.4*	*18.5*	*18.0*	*17.4*	*22.1*	*0.90*	*3.9*	*477*	*0.3*	*79.9*	*21.6*	*1.60*	*1.01*	*1.0*
				mn	*1.2*	*4.5*	*4.8*	*4.8*	*4.5*	*12.9*	*0.22*	*—*	*22.0*	*0.1*	*9.4*	*20.2*	*0.64*	*0.49*	*0.7*
				mx	*64.8*	*47.3*	*42.7*	*43.0*	*42.6*	*34.9*	*2.3*	*—*	*1263*	*0.6*	*199*	*22.9*	*6.78*	*1.46*	*2.1*

3.1. General characteristics

The activity of the radionuclides varied between the samples by more than one order of magnitude (Table 2). In particular, Th-232 varied between 1.2 and 64.8 Bq/kg (average value of 19.6); U-238 varied between 4.5 and 47.3 Bq/kg (19.4); and U-235 varied between 0.22 and 2.3 Bq/kg (0.9). The activity of K-40 varied by more than one order of magnitude, from 22.0 to 1263 Bq/kg (477). Be-7 was measured in one sample (3.9 Bq/kg), and in trace amounts in others. Cs-137 was measured in several samples in small amounts (0.1 to 0.6 Bq/kg). The activity ratios U-238/U-235 for all samples correspond (within limits of ±10%) to the value of 21.7 (accepted for natural objects), while the ratios of U-238/Th-232 in many samples noticeably deviate (by more than ±10%) from the average value 0.81 (for closed systems); an increase was observed in eleven samples (36, 153, 152, 78, 76, 77, 80, 33, 144, 146, and 155), from 0.93 to 6.78, and a decrease in four samples (34, 31, 159, and 156) from 0.64 to 0.72. The value of the ratio Ra-226/U-238 differs (by more than ±10%) from the equilibrium value for some samples; in five samples (152, 33, 74, 159, and 156) this is greater than the equilibrium value, and in one sample (31) it is lower. The ratio of Pb-210/Ra-226 also differs from the equilibrium value (by more than ±20% [2]) in some samples; in one sample (146), it is greater than the equilibrium value, and in three samples (152, 155, and 156) it is lower (*note:* activity ratios were not determined for all samples, since in eight samples (36, 153, 34, 78, 74, 80, 144, and 159) the activity of Pb-210 was below the MDA). Within the Th-232:Tl-208 chain, equilibrium was observed (except for Th-228, for which the determination error was appreciably greater than for the other radionuclides). The largest groups of samples distinguished by level of radium equivalent activity were those with low (44.4%) and medium (27.8%) radioactivity, while the smallest group (27.8%) was that of the nonradioactive samples (Table 6).

Table 3

Generalized data: average (*av*), minimal (*mn*), and maximal (*mx*) values of concentration of radionuclides of Th-232, U-238, and U-235 families and radionuclide K-40, equivalent activity, activity ratios depending on genesis (G), and sample types (ST)

#	G	ST	Th-232			U-238			Ra-226			U-235			K-40			Ra_{eq}			U-238/Th-232			Ra-226/U-238		
			av	*mn*	*mx*	*av*	*mn*	*mx*	*av*	*mn*	*mx*	*av*	*mn*	*mx*	*av*	*mn*	*mx*	*av*	*mn*	*mx*	*av*	*mn*	*mx*	*av*	*mn*	*mx*
1	Mg	(1 intrusive – 1 sample	58.	-	-	39.	-	-	27.	-	-	1.	-	-	12	-	-	19	-	-	0.6	-	-	0.6	-	-

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[2] The range of limits is expanded, since the determination of the error in Pb-210 was as high as 20%.

	sample)	(31, granite)	8		7			0		8		63			9			8			8		
2	Sd (15 samples)		17.3	1.2	64.8	18.2	4.5	47.3	18.0	4.8	42.7	0.85	0.223	2.31	43	22.0	94.7	72.8	9.4	154	1.65	0.648	6.78	1.003	0.49	1.46
		carbonate (limestone) – 5 samples (33, 144, 146; 74, 80);	5.8	1.2	13.8	10.5	4.5	24.2	13.3	4.8	33.3	0.49	0.222	1.34	21	22.0	551	36.6	9.4	73.9	2.89	0.677	6.78	1.18	0.90	1.46
		sandstone - 6 samples (carbonate sandstone: 158; arkosic sandstone: 34, 159, 153; tuff sandstone: 78, 82);	21.6	5.8	64.8	17.4	5.8	47.3	16.2	4.9	42.7	0.83	0.283	2.50	1	184	947	82.2	151	0.84	0.644	1.14	0.96	0.85	1.12
		clay - 1 sample (155, argillite);	42.7	-	-	39.9	-	-	41.8	-	-	1.8	-	-	732	-	-	154	-	-	0.93	-	-	1.05	-	-
		tuff breccia - 1 sample (156, volcanogenic, sedimentary);	24.9	-	-	18.1	-	-	20.8	-	-	0.83	-	-	681	-	-	104	-	-	0.72	-	-	1.15	-	-
		conglomerate, breccia – 2 samples (carbonate: 36; arkosic breccia and conglomerate: 152)	6.4	5.4	7.4	15.9	6.6	25.2	18.0	7.2	28.8	0.75	0.322	1.33	8	89.3	587	50.8	21.2	80.4	2.32	1.122	3.42	1.11	1.08	1.14
3	Mt (2 samples)	tuff – 2 samples (76, 77).	27.2	23.5	30.8	31.7	27.9	35.5	21.5	17.4	25.6	1.4	1.2	1.6	581	416	746	101	90.1	111	1.17	1.159	1.19	0.70	0.49	0.92

Notes: Mg – Magmatic; Sd – Sedimentary Mt – Metamorphic.

Table 4

Generalized data: average (*av*), minimal (*mn*), and maximal (*mx*) values of concentration of radionuclides of Th-232, U-238, and U-235 families and radionuclide K-40, equivalent activity, and activity ratios depending on the type of tectonic zone (Tct)

#T ct	Th-232			U-238			Ra-226			U-235			K-40			Ra_{eq}			U-238/Th-232			Ra-226/U-238			Pb-210/Ra-226		
	av	mn	mx	av	mn	mx	av	mn	mx	av	mn	mx	av	mn	mx	av	mn	mx	av	mn	mx	av	mn	mx	av	mn	mx
1 II₃¹	9.9	5.4	16.9	17.0	6.6	25.2	17.8	7.2	28.8	0.79	0.32	1.2	416		94 7	61.0	21.2	86.8	1.93	1.14	3.42	1.00	0.91	1.14	0.68	-	-
2 II₂	24.0	3.6	58.8	23.4	6.3	39.7	22.4	6.7	33.3	1.18		0.28	1.8	824	261	1263	114	56.7	1990	2.70	0.64	6.78	1.00	0.68	1.38	0.83	0.83	0.83
3 III₁³	13.0	1.2	30.8	14.2	4.5	35.5	12.0	4.8	25.6	0.64	0.22	1.6	326	22.0	746	53.7	9.4	111	1.48	0.77	4.64	0.96	0.49	1.46	1.29	0.82	2.11
4 III₁²	36.6	14.1	64.8	28.7	9.5	47.3	29.0	10.6	42.7	1.43		0.43	2.3	566	255	732	121	72.7	1546	0.76	0.67	0.93	1.00	0.90	1.15	0.77	0.72	0.82

Table 5

Generalized data: average (*av*), minimal (*mn*), and maximal (*mx*) values of concentration of radionuclides of Th-232, U-238, and U-235 families and radionuclide K-40, equivalent activity, and activity ratios depending on the sample age (T)

#T (SN)	Th-232			U-238			Ra-226			U-235			K-40			Ra_{eq}			U-238/Th-232		
	av	mn	mx	av	mn	mx	av	mn	mx	av	mn	mx	av	mn	mx	av	mn	mx	av	mn	mx
1 Quaternary (36)	5.4	-	-	6.6	-	-	7.2	-	-	0.32	-	-	89.3	-	-	21.2	-	-	1.22	-	-
2 Neogene (152, 153)	12.1	7.4	16.9	22.2	19.2	25.2	23.1	17.4	28.8	1.0	0.89	1.2	579	571	587	81.0	80.4	81.6	2.28	1.14	3.42
3 Paleogene (34, 155, 156,	26.	5.	64	22	5.	47	20.4	4.	42	1.	0.	2.	55	18	94	96	26.	15	0.8	0.61	1.

158, 159; 76,77, 78,82)	1	8	.8	.9	8	.3	6	9	.7	1	28	3	7	4	7	.9	1	4	8	4	19
4 Cretaceous (33, 144, 146; 80,74)	5.8	1.2	13.8	104.5	4.5	24.2	13.3	4.8	33.3	0.49	0.22	1.2	21 4	22.0	55 1	36.6	9.4	73.9	2.89	0.77	6.78
5 Jurassic (31)	58.8	-	-	39.7	-	-	27.0	-	-	1.8	-	-	12 63	-	-	19 9	-	-	0.68	-	-

Table 6

Distribution of average value, Ra_{eq-av}, of equivalent activity, Ra_{eq}, by the activity level group (GA), their quantity (N_s), and percentage (r, %)

#	GA	Ra_{eq}, Bq/kg	Ra_{eq-av}, Bq/kg	N_s	r (%)
1	I	<30	20.4	5	27.8
2	II	30-100	61.7	8	44.4
3	III	100-300	121	5	27.8

3.2. Dependence on the genesis (type)

The activity of the radionuclides of these families and the radionuclide K-40 in magmatic rocks is appreciably greater (Table 3) than in sedimentary rocks (equivalent activity 199 and 72.8 Bq/kg, respectively), although argillite and carbonate sandstone (155 and 158, Table 2) have comparable values (154 and 153 Bq/kg, respectively). Among the sedimentary rocks, a very low level of activity was observed in the group of carbonate limestones (average equivalent activity of 36.6 Bq/kg), a slightly greater activity was observed in the group of conglomerates (50.8 Bq/kg), activity more than twice as great was seen in the group of sandstones (82.2 Bq/kg), and the highest was in tuff breccia (101 Bq/kg) and in the group of clays (154 Bq/kg). The average activity of metamorphic samples (101 Bq/kg) was at an intermediate level between those of magmatic and sedimentary rocks.

The values of the ratio U-238/Th-232 for magmatic rocks were close to the average value, and the ratios of Ra-226/U-238 were much lower than the equilibrium value. For sedimentary rocks, the values of the ratio for various groups differed somewhat, and in particular: a) the ratio U-238/Th-232 for carbonates and conglomerates (2.89 and 2.32, respectively) considerably exceeded the average values, and Ra-226/U-238 corresponded to or slightly exceeded the equilibrium value; b) for sandstones, the values of U-238/Th-232 and Ra-226/U-238 essentially

correspond to the average value; and c) for the groups of clays and tuff breccia, there are one by one sample for which the value of the ratio U-238/Th-232 is close to the average value, and Ra-226/U-238 corresponds to and slightly exceeds the equilibrium value. For metamorphic rocks, the ratio U-238/Th-232 exceeds the average value, and Ra-226/U-238 corresponds to or is less than the equilibrium value.

3.3. Dependence on tectonic zones

The highest activity values (and equivalent activity values) were observed (Table 4) for subzone III_1^2 (with an average equivalent activity of 121 Bq/kg) and for zone II_2 (114 Bq/kg), and were much lower for subzone II_3^1 (with an average equivalent activity of 61.0 Bq/kg) and for subzone III_1^3 (53.7 Bq/kg) (*note:* the sample of granite from subzone II_2 has an abnormally high value of activity in comparison with other samples; if this sample is excluded from the statistics, the values of the activity for subzones II_3^1, II_2, and III_1^3 are comparable to each other). The values for the ratio U-238/Th-232 for subzones II_3^1, II_2 и III_1^3 are generally greater than the average value (0.81), and range from 1.48 to 2.70; small deviations of both less and more than the average value were observed for subzone III_1^2. For the activity ratio Ra-226/U-238 for zone II_2 and subzone III_1^3, there were observed deviations from the equilibrium value of both greater and smaller values (within the range 0.68 to 1.38). The values of the activity ratio Pb-210/Ra-226 generally correspond to the equilibrium value (except for sample 146).

3.4. Dependence on the age of rocks

The lowest activity values for the radionuclides of the three families and K-40 were observed (Table 5) for rocks of the Cretaceous (33, 144, 146, 80, and 74) and Quaternary periods (36); the average equivalent activities were 36.6 and 21.2 Bq/kg, respectively. Almost all values of the ratio U-238/Th-232 were greater than the average value (0.81). A high level of activity of the radionuclides of the three families was observed for rocks of the Jurassic (31) and Paleogene (34, 155, 156, 158, 159, 76, 77, 78, and 82) periods (199 and 96.9 Bq/kg, respectively), while the values of the ratio U-238/Th-232 corresponded to or were smaller than the average value. Mean activity values of 81.0 Bq/kg were observed for rocks of the Neogene period (152, 153); the values of the ratio U-238/Th-232 were noticeably greater than the average value.

4. DISCUSSION

It is known that the concentration of radioactive elements in rocks and soils is formed from the radioactivity of the original structures and the subsequent processes of rock and soil formation. The content and concentration of naturally occurring radionuclides identified in the samples investigated here generally correspond to those usually observed [17] for various rocks and soils. This analysis has been carried out for the first time for the given region (there are also no similar data for other regions in Georgia). In the investigated rock samples, up to 21 natural radionuclides were detected; these are radionuclides of the Th-232, U-238, and U-235 families, the radionuclides Be-7 and K-40, and the technogenic radionuclide Cs-137. All these radionuclides are characteristic of the region of East Georgia, and in particular for soil within the Mtkvari River zone [18].

As discussed above, rock samples were selected from a region that is characterised by a relatively complex geotectonic structure. The selected samples were of sedimentary type, including groups of carbonate (limestones), sandstones, clays, tuff breccia and conglomerates. One sample was taken of a magmatic group (granite), and two samples of a metamorphic group (tuffs). Each of these groups has a specific mineralogical and chemical composition to which the wide range of values of radioactivity concentration is connected; this is the case in practice for all identified radionuclides, and also for the activity ratios of some radionuclides.

The ratio U-238/U-235 observed in all samples corresponds within the limits of error to the natural value that can except methodological aspect testify to an absence of pollution by technogenic uranium.

It should be noted that the activity of radionuclides in the magmatic sample (31) belonging to the acid group is somewhat greater than that of the magmatic samples belonging to the intermediate group, which were taken from the geotectonic system of the main Caucasian ridge [16]. At the same time, the average activity of magmatic rocks is greater than that of sedimentary rocks, which corresponds to the reference data. The results show an insignificant deviation of the ratio U-238/Th-232 from the average value, which may be a consequence of the fact that the given system was essentially closed. A certain disequilibrium within the U-238:Ra-226 system is apparently connected with the leaching of Ra-226 from the surface strata (from which samples were taken).

In sedimentary samples (secondary rocks), a number of features were observed in the activity ratios; in particular, deviations from the average value of the ratio U-238/Th-232 and the equilibrium value of Ra-226/U-238 were noted, indicating that these systems were not closed, and that various geochemical processes took place within these in the past, causing these deviations. As has been noted in previous works [17], [19], the distribution of the chemical properties of a certain group of radionuclides can change within various environmental structures (and particularly in rocks) under conditions of environmental influence. Hence, Th isotopes are only found in natural environments in the tetravalent form; they form compounds that are practically insoluble in water and are transferred mechanically in the form of stable minerals. Meanwhile, U isotopes occur in nature in both tetravalent and hexavalent form; in tetravalent form, their chemical properties are close to those of Th, while in hexavalent form they differ in their high level of chemical activity, and in the form of water-based solutions can migrate large distances. These processes can lead to a decrease in the ratio U-238/Th-232 observed both for magmatic rock and for several sedimentary rocks (34, 159, and 156) in comparison to the average value. It has also been observed that due to profound chemical weathering of parent rocks, Th can migrate in colloid form. These processes can lead to an increase in the ratio U-238/Th-232 in comparison to the average value observed for carbonates and conglomerates (samples 33, 144, 146, and 36, and 152, respectively). It should be noted that these processes can take place simultaneously, causing a reduction in U-238 (and U-235), as well as Th-232. This can decrease their common concentration as well as activity ratios that could take place in a number of samples (for example, 34, 159, 156).

Similar processes can cause a disequilibrium in the radioactive series of the U-238 family, and in particular between U and Ra. Here, in addition to the reasons mentioned above, the influence of the differences of the chemical properties of elements should be considered. Ra isotope is easily leached and washed away by water; in natural formations, Ra-226 often accumulates in quantities exceeding equilibrium with uranium. Combinations of these and other geochemical factors can lead to appreciable variations in the activity ratios of these radionuclides, causing their deviation in a greater or smaller way from the average and equilibrium values. The investigated region is characterised by diverse and complex climatic conditions (in particular, the natural drainage of confined water-bearing horizons) which can cause the processes noted above and lead to the deviations in the activity ratio Ra-226/U-238 away from the equilibrium values (for example, samples 31, 33, and 156).

The observable deviation of ratio Pb-210/Ra-226 from the equilibrium value for one sample (146) can be connected with processes of excess radon exhalation in the bedding area of limestone rocks. The raised porous structure of these rocks can cause the corresponding occurrence of excess concentration of Pb-210 [20]. Observable values of Pb-210/Ra-226 are smaller than the equilibrium value, which is apparently connected with an absence of radon migration from the underlying layers of corresponding rocks. As a result, the radon concentration in the surface layers decreases with respect to the equilibrium value (due to its migration into the atmosphere), and the concentration of Pb-210 decreases accordingly. It should be noted that the recovery time of the Pb-210/Ra-226 equilibrium is not less than 10^2 years, which allows us to estimate a time interval for the corresponding geochemical processes.

The dependence of the sample activities observable in this study according to the tectonic units allows us to note a general tendency towards an increase in rock activity in the western direction; however, the types of rock and their age are likely to have greater importance here. Hence, the group of carbonates (33, 144, and 146) which has the lowest activity values and simultaneously the greatest values for the ratio U-238/Th-232, is of the Cretaceous period. This period was characterised by land domination on the Earth; the climate was hot and dry, and deposits of chalk, carbonates, clay slates and others were formed. Later on (in the Paleogene period and beyond) the climate changed, and the temperature declined. Environmental conditions varied, and this factor promoted changes to the conditions of hypergenesis, leaching, etc. All of these processes, depending on the regional conditions, could have caused appreciable variations in radionuclide concentrations and their activity ratios (as observed for a number of samples of the Paleogene and Neogene periods). In the region investigated here, confined waters developed in Cretaceous sediments, and non-confined waters developed in modern and Quaternary sediments, as well as in the upper parts of pre-Quaternary rocks. Their complex circulation influenced the rock-formation processes, and probably caused observable deviations from the average value of the ratio U-238/Th-232.

In some samples, an insignificant trace concentration of the naturally occurring radionuclide Be-7 (a so-called cosmogeneous radionuclide, formed as a result of nuclear reactions in the upper

atmosphere) apparently appears as a result of precipitation, and in some cases can be identified in gamma-spectra despite a rather low half-life.

The technogenic radionuclide Cs-137 is also observed in the samples as a result of atmospheric precipitation. The presence of Cs-137 in natural objects (for example, in soil) is typically as result of the Chernobyl disaster, as discussed above. Over recent years, its quantity has decreased as a result of both decay and migration. In research carried out here it was observed in several samples at insignificant concentrations (in comparison with soils, where its concentration is considerably higher); this is apparently connected with an intensive process of washing away from the surface of samples.

Reference data from other regions of the world are cited in Table 7. From the results, it appears that the values recorded in this study are on average much lower than those in other regions and world average values.

These results are of doubtless scientific and applied interest for investigated region and confirm the urgency for such research.

Table 7

Activity concentration (Bq/kg) of radionuclides in rocks and other parameters in various regions of the world

#G	GR	ST	SR	Th-232	U-238	Ra-226	U-235	K-40	Ra_{eq}	U-238/Th-232	Ra-226/U-238	*Ref.*
1	Mg	*In*	*Gn*	Ge	58.8	39.7	27.0	1.8	1263	199	0.68	0.68	Present study
				Eg	14.5 9.9-17.7	15.6 12.0-19.3	13.7 9.7-18.9	2.2 1.2-4.8	406 299-956	65.5 49.1-113		0.85 0.63-1.21	[1]
				Gm	70.0		76.1		1465				[4]
				Eg	50.7 47.9-53.4		48.2 39.0-57.4		1036 1031-1041				
				In	11.7 BDL-91.6	7.1 BDL-22.9			224 BDL-505		0.80 0.25-1.49		[5]

2 Sd			Ww	0.8-120	1.2-1107	15-1720		15.5-1270				[21]
	Cl		Ww	45-49	36-41			718-819				-"-
			Ge	42.7	39.9	41.8	1.8	732	154	0.93	1.05	Present study
	Cr		Ww	7 3-22	30 11-148			- 31-372				[21]
	Cr	Ls	In	34.4 22.1-46.8		30.5 13.9-47.2		700 450-951	134 113-154			[6]
			Tk	4.3 1.2-20.9		19 0.7-55.1		55 10.1-258.4				[22]
			Ge	5.8 1.2-64.8	10.5 4.5-24.2	13.3 4.8-33.3	0.49 0.22-1.2	214 22.0-551	36.6 9.4-73.9	2.89 0.77-6.78	1.18 0.90-1.45	Present study
	Ss		Ww	12 26-120	19 3.6-98	26		527 34-930				[21]
			Ge	21.6 5.8-64.8	17.4 5.8-47.3	16.2 4.9-42.7	0.83 0.28-2.3	501 184-947	82.2 26.1-153	0.84 0.64-1.14	0.96 0.85-1.12	Present study
	Tf-Bc		Ge	24.9	18.1	20.8	0.83	681	104	0.72	1.15	-"-
	Cg-Bc		Ge	6.4 5.4-7.4	15.9 6.6-25.2	18.0 7.2-28.8	0.75 0.32-1.2	338 89.3-587	50.8 21.2-80.4	2.32 1.22-3.42	1.11 1.08-1.14	-"-
3 Mt			Ww	0.4-333	0.24-1970			148-1517				[21]

Tf	Ge	27.2 23.5-30.8	31.7 27.9-35.5	21.5 17.4-25.6	1.4 1.2-1.6	581 416-746	104 97.1-111	1.17 1.15-1.19	0.70 0.49-0.92	Present study
	Ct	4.5 1.0-12.9	7.5 1.3-14.6	7.3 2.9-13.0		30.1 5.2-102.6		2.41 0.81-5.30	1.12 0.59-2.22	[23]
	Rm	9.8		10.5		180				[24]

Note. G - Genesis of rock; GR - Group of rock; SR - Studied region; Mg – Magmatic; Sd – Sedimentary; Mt – Metamorphic; In – intrusive; Gn – granite; Cl – clay; Cr – carbonate; Ss – sandstone; Tf-Bc – tuff breccia; Cg-Bc – conglomerate breccia; Tf – tuff; Ls – limestone; Ww – Worldwide; Ge- Georgia, Shida Kartli region; Eg – Egypt; Gm – Germany; In – India; Tk – Turkey; Ct – Croatia; Rm – Romania; BDL – below detection limit.

5. CONCLUSION

1. It was established that up to 22 radionuclides were detected in rock samples; these were radionuclides of the families of Th-232, U-238, U-235, other naturally occurring radionuclides such as Be-7, K-40, and the technogenic radionuclide Cs-137.
2. The main features of the samples' radioactivity were established as follows:
   - The activity of the three radionuclide families and the radionuclide K-40 varied in different samples over a wide range, from 0.22 Bq/kg (U-235) to 64.8 Bq/kg (Th-232) and from 22.0 to 1263 Bq/kg (K-40);
   - The radionuclide Be-7 was measured in only one sample, and occurred in several samples in trace amounts;
   - The technogenic radionuclide Cs-137 was measured in insignificant amounts in several samples, with activity from 0.1 to 0.6 Bq/kg;
   - For the activity ratio U-238/Th-232, there were observed deviations (of more than ±10%) from the average value of 0.81 (for closed systems) of both less than and greater than the average value; a similar picture was observed for the ratios Ra-226/U-238 and Pb-210/Ra-226, for which higher and lower deviations from the equilibrium value (1.0) were also observed.
3. Some features of the activity distribution depended on the genesis, sample type, geotectonic zones, and age of the samples. In particular:
   - The average activity of radionuclides in magmatic rock was noticeably greater than in sedimentary rocks (the values of equivalent activity were 199 and 72.8 Bq/kg, respectively), while a high level of activity change was noted in different groups of sedimentary rocks (9.4 to 154 Bq/kg);

- The highest activity values were observed in subzone III_3^1 (with an average equivalent activity of 121 Bq/kg) and in zone II_2 (114 Bq/kg), and these were appreciably smaller in subzones II_3^1 (61.0 Bq/kg) and III_1^3 (53.7 Bq/kg);
- The lowest activity values were observed for rocks of the Cretaceous and Quaternary periods, with average equivalent activities of 36.6 and 21.2 Bq/kg, respectively. Almost all values of the ratio U-238/Th-232 were greater than the average value (0.81). The highest activity of radionuclides was observed for rocks of the Jurassic and Paleogene periods, with 199 and 96.9 Bq/kg, respectively, while the values of the ratio U-238/Th-232 corresponded to or were smaller than the average value.

4. An analysis of the obtained results and some of their features was carried out and compared with reference data.

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