Preliminary studies on radon concentration in CO_2-rich mineral waters of the Elbrus area (Caucasus, Russia)

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Abstract. The geological and geochemical conditions as well as radon concentrations of ten manifestations of CO_2-rich waters in the Elbrus area are considered in this paper. Also, content of uranium and thorium were measured in waters and in host rocks. The data were compared with chemical and isotopic composition of associated gases. It is established that water bearing rocks are classified into rocks of low and normal radioactivity. The contents of uranium (<1.37 μg/L) and thorium (<0.3 μg/L) in the water are low. Measurements of radon concentrations in water and gas flux of mineral springs in the Elbrus area indicate that most of them are weakly radioactive (6–33 Bq/L, 25-350 Bq/m^3, respectively). The CO_2-rich mineral waters of the Tyrnyauz exhibit the highest level of radioactivity (33 Bq/L) within the Elbrus area. Isotopical gas studies have shown that within the Elbrus region there is a connection with the deep horizons of the Earth's crust, from which various fluids (water and gases) can rise to the surface. Although Rn values are low and cannot be used for medical purposes, natural objects with similar characteristics can be used to observe the state of the geological environment (e.g. earthquakes) and as natural laboratories to establish the mechanisms of deep gas migration to the surface.

1 Introduction

The origins of mineral waters and gasses in the Great Caucasus have been extensively investigated for a long time [1, 2, and 3]. The radon waters of the Caucasian mineral waters are widely known and use [3]. However, no radon studies have been carried out in the Elbrus region. Radon and its parent radionuclide ^{226}Ra are naturally occurring radionuclides that belong to the uranium decay series. Being an inert gas, Rn has the ability to permeate through porous substances like soil or rock [e.g. 4] and can be dissolved in water. In natural springs radon is mostly generated by the leaching process of hexavalent uranium. The inhalation of ^{222}Rn is widely recognized as a major risk factor for lung cancer, whereas the intake of radon through water can increase the risk of stomach and gastrointestinal cancer [e.g. 5].

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The territory of the Elbrus region belongs to the zone of increased risk of earthquakes, avalanches, and mudslides. Research conducted worldwide over the past four decades has provided evidence suggesting that notable fluctuations in radon concentration can be observed in connection with significant geophysical occurrences, such as earthquakes and volcanic eruptions [e.g. 6].

According to its tectonic position, geological conditions, and the spread of natural underground gas outlets, the Elbrus region is an excellent natural laboratory. Our geochemical study is the first step to determining the primary mechanisms involved in the transportation of radon gas (^{222}Rn) to the earth surface.

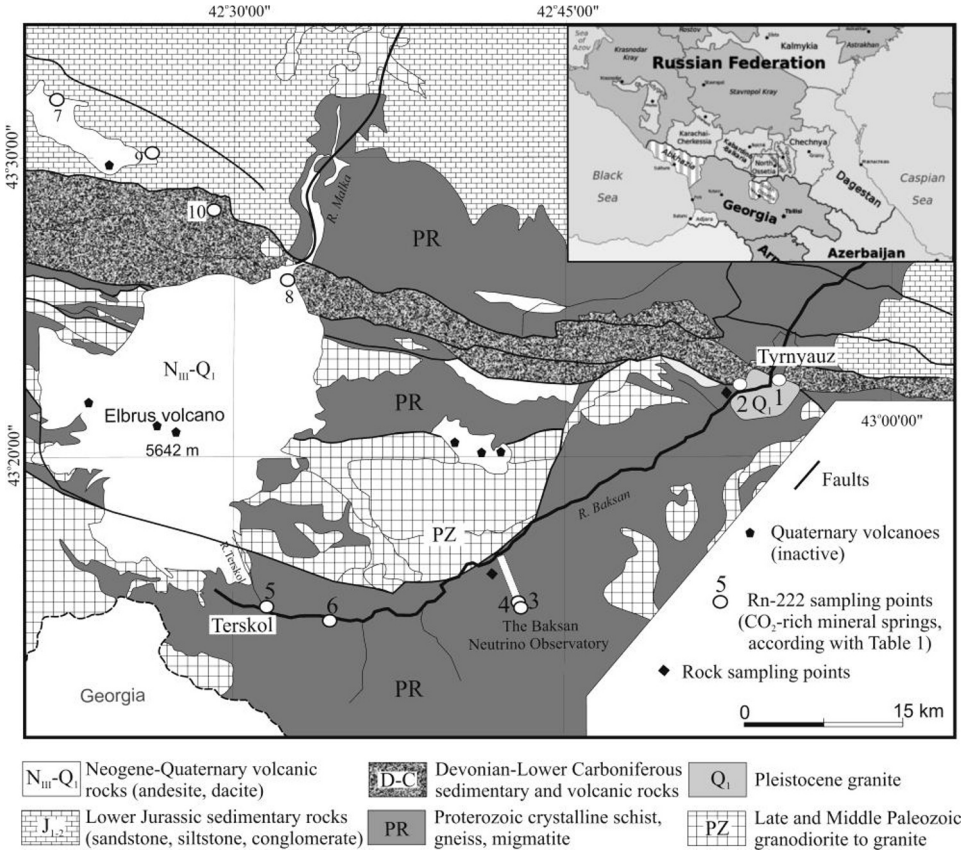

Fig. 1. Main geological structures of the study area (modified after [7]) and sampling sites (numbers according to Table 1).

2 Sampling and analytical procedures

The study is based on the results of the field companies carried out in March 2023 and 2024 in the Elbrus region (Fig. 1). Ten CO_2-rich springs were sampled for gas and hydrochemical analysis. Radon-monitor (Alfarad+, NTM Zashita Co.) has been used to measure ^{222}Rn in gas flow and water samples *in situ*. Verification certificate no. MA 0177828. Equipment measures ^{222}Rn via $^{218}Po^{+}$ (t1/2 = 3.1 min), which is electrically attracted to a silicon alpha detector. The instrument has a measurement range of 1 to $2*10^6$ Bq/m^3 in air and from 6 to 800 Bq/L in water. The instrument has an accuracy of ±30%. The volume activity is an activity per unit of volume of a source (water or air). The maximum allowable quantities of radon in drinking water vary across different countries,

ranging from 11 Bq/L in the United States to 300 Bq/L in Europe. As to the Radiation Safety Standards NRB-99/2009 and SP 2.6.1.1292-2003 [8], the acceptable level of radon in drinking water shall not exceed 60 Bq/L. Mineral waters containing a minimum of 185 Bq/L are categorized as radon waters [8]. The water samples are categorized based on their radon concentrations. There are three categories: low radon concentrations (200–1500 Bq/L), moderate radon concentrations (1500–7500 Bq/L), and high radon concentrations (>7500 Bq/L).

The chemical composition of the gases was analyzed at the Geological Institute, Russian Academy of Sciences, using the Crystal 5000 gas chromatograph. The inaccuracy in identifying the gas composition was no greater than 2–3 vol.%. The $\delta^{13}C$ values in CO_2 and CH_4 gases were determined using DELTA series devices at the Geological Institute, Russian Academy of Sciences. The error in determining the $\delta^{13}C$ value was within a range of ±0.2‰.

3 Results and discussion

The valuable isotope-geochemical characteristics of mineral waters in the Elbrus region and radon concentrations are presented in Table 1.

Mineral spring water and associated gases are characterized by rather low values of radon emanations: 6–33 Bq/L and 25–351 Bq/m^3, respectively. The most elevated concentrations of radon in water are found in borekholes that disclose the youngest granites (Q_1) within Tyrnyauz city. A mineral springs and wells from the Poliana Narzanov area on the south slope of Elbrus volcano have the highest values of ^{222}Rn in free gases (350 Bq/m^3). These waters are linked to proterozoic crystalline schists (Fig. 1) and have highest gas discharge rate. Elevated values were also characteristic of the gases in the Neutrino tunnel and the well in Tyrnyauz (№3, 4).

The observed low levels of radon concentration in water are not typical for granites containing uranium and thorium [e.g. 9]. The CO_2-rich waters lie in rocks of different ages and types, which are represented by granites, gneisess, schists and rare sandstones (Table 1). The age interval of the rocks varies from the Proterozoic to the Quater. Paleozoic intrusions of granitoids are widespread (Fig. 1). The study of youngest Eldjurty granites (Tyrnyauz area, Q_1) showed that based on the U and Th contents, the granites are Th-bearing (Th/U ratio is 5.2) and characterized as moderately radioactive (U=5.1 ppm, Th=26 ppm). CO_2-rich waters circulating in these granites also do not show high concentrations of uranium or thorium (Table 1). The highest values of uranium and thorium are observed in waters occurring in Proterozoic granite gneisses. The concentration of U in the water ranges from 0.01 to 1.51 μg/L, which is well below the Maximum Permissible Concentration of 15 μg/L for drinking water [9]. The values mentioned (U = 0.04 μg/L) [10] are commonly seen in surface waters, but higher amounts (U = 1.5 μg/L) are more characteristic of fluids from the supergene zone [11]. Low contents of uranium and thorium in water are due to the peculiarities of their behavior in the interval of pH from 5.7 to 6.7 and redox conditions from -71 to +100 mV. Within the supergene zone, uranium exhibits significant migration in an oxidizing environment and limited migration in a reducing environment [11]. This is confirmed by the lowest uranium content (0.01 μg/L) in the deepest of the tested parametric well (more than 500 m). Under reducing conditions, the interaction between uranium minerals and water does not result in uranium entering the water from radiogenic minerals. However, water can capture and transport radon to earth surface.

In order to check that the gas emissions have a deep origin, a stable isotope of $\delta^{13}C_{(CO2)}$ was measured (Table 1). The values of $\delta^{13}C$ in CO_2 ranged from -5.7 to -11.0‰ and do not differ from those values observed in other natural CO_2 gases of the Elbrus region [2, 12].The determination of the ($^3He/^4He$) value in a gas sample taken from the lake at the

tunnel end showed (№4 in Table 1) that it contains more than 30% of mantle helium ($^3He/^4He$mant = 1.2 × 10-6) [12]. Isotopical gas studies have shown that within the Elbrus region there is a connection with the deep horizons of the Earth's crust, from which various fluids (water and gases) can rise to the surface. It was found that concentrations of radon dissolved in water have correlations with concentrations of methane (r = 0.7), helium (r = 0.6) and negative correlation with CO_2 gas content (r=-0.8) (Fig. 2a). Radon measured in the gas flows correlates only with the carbon isotope $^{13}C(CO_2)$ (Fig. 2b). To migrate from significant depths to the day surface, radon must have a strong tendency to migrate vertically upwards. However, this process is limited by the large molecular weight of radon (222) and its short half-life of 3.82 days.

Table 1. The isotope-geochemical characteristics of mineral waters of Elbrus region.

№	Host rocks	Age	Type	TDS, g/L	U	Th	CO_2	CH_4	He	$d^{13}C_{(CO2)}$	^{222}Rn	
					ppb		%			‰	Bq/m^3	Bq/L
	Rock		Water				Free gas					d.gas
	CO_2-rich water in the south part of the Elbrus area											
1	Granites (Eldzurty)	Q_1	HCO_3-Cl-Na	5.4	0.07	0.02	76.7	1.22	0.032	-11	159	33
2			HCO_3-Na	5.7	0.01	0.02	90.4	0.45	0.016	-7.3	43	10
3	Granites, gneisses, crystalline schists	PR	Cl-HCO_3-Na	8.5	0.05	0.02	97.1	0.39	0.001	-7.3	76	7
4				7.3	0.05	0.02	97.1	0.39	0.001	-8	137	6
5			HCO_3-Cl-Ca-Mg	0.3	1.37	0.34	97.3	0.38	0.001	-	25	10
6			HCO_3-Cl-Ca-Na	2.3	1.51	0.007	97.8	0.001	0.003	-8.3	351	7
	CO_2-rich water in the north part of the Elbrus area											
7	Granodiorite, andesite, dacite granites	Q_1	HCO_3-Cl-Na	10.6	0.46	0.007	98.8	0.011	0.008	-5.7	9	9
8			HCO_3-Cl-Na-Ca-Mg	3.1	0.41	0.007	98.9	0.005	0.001	-5.8	6	6
9	Sedimentary and volcanic rocks (andesite, dacite)		HCO_3-Na-Ca	3.0	0.04	0.03	98.9	0.012	0.001	-5.8	7	7
10	Sedimentary and volcanic rocks	PZ	HCO_3-Cl-Na	1.9	0.02	0.009	98.7	0.008	0.001	-	6	10

1- Tyrnyauz park well, 2- Parametric well, 3- Neutrino tunnel mineral lake, 4- Neutrino tunnel thermal spring, 5- Terskol mineral spring, 6- Poliana Narzanov mineral spring, 7- Shaushiib mineral spring, 8- Djilusu thermal spring, 9- Toxana low spring,10- Ingushli spring. *d.gas – dissolved in water gas, dash-no data.

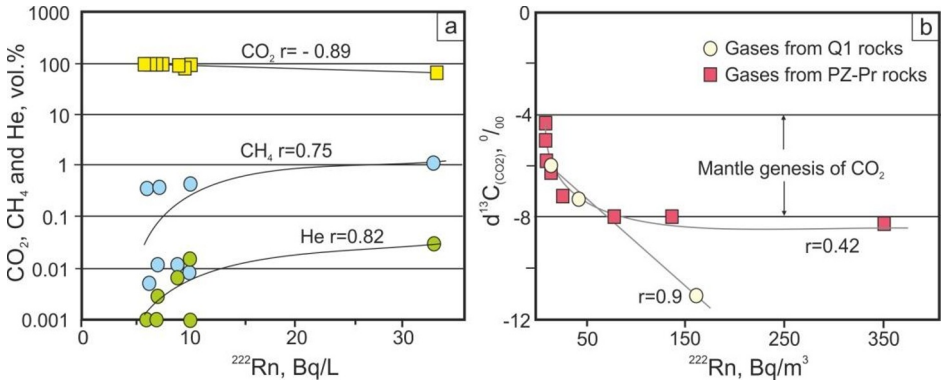

Fig. 2. Variability of the radon gas concentrations with the main gases of the mineral springs (a) and correlations of the Rn concentrations in free-gas flows with $\delta^{13}C$ (CO_2) (b).

4 Conclusion

The primary process how radon accesses the CO_2-rich mineral waters of Elbrus is by the circulation of air water in crystalline massifs (granites, gneiss), which carries radioactive emissions into the subsurface zone. The measured levels of radon are characteristic of the natural condition of host rocks. The low radon levels in this area are mostly attributed to the low rates of water flow (<0.5 L/s) and depend on the amount of freely emitted gas at a particular source. No correlation has been discovered between water temperature, total dissolved solids, or uranium and thorium concentrations and radon emission. Thus, the radon content in water depends on the presence of source radon minerals, the water flow rate, and the half-life of radon (3.8 days). When the stressed state of rocks changes (a seismic event), the speed of gas and water flows will also change, as will the Rn concentrations.

Considering the tectonic conditions, high seismic hazard of the territory, installation of observation points for geochemical precursors is strongly recommended.

Acknowledgements

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References

1. N.S. Pogorelsky, V.N. Bessonova, N.A. Grigoriev et al. *Hydrogeology of the USSR. North Caucasus (*Moscow, Nedra, 1968)
2. V. Lavrushin, *Subsurface fluids of the Greater Caucasus and its surrounding.* (Nauka, Moscow, Russia, 2012)
3. E. Fillimonova, V. Lavrushin, N. Kharitonova, A. Sartykov, E. Maximova, E. Baranovskaya, A. Korzun, A. Maslov, E. Baidariko. *Env. Earth Sci.* **79**, 15-27. (2020)
4. F.Girault, F.Perrier, *J. Geoph. Res.: Solid Earth.* 4056–4086. (2014).
5. P.F. Folger, P. Nyberg, R. Wanty, and E. Poeter. Health Physics, **67**, 244-253. (1994)
6. A. Kumar, S. Singh, S. Mahajan, B.S. Bajwa, R. Kalia, and S. Dhar. Appl. Radiat. and Isotop., **67**, (2009)

7. A.N. Pismenniy, A.N. Pichuzhkov, M.A.Zarubina, S.A. Gorbachev, S.N. Vertiy, I.I. Grekov, Y.N. Gamasa, L.A.Tereschenko *Explanatory Note to the State Geological Map of the Russian Federation.Caucasian Serie*. (St-Petersburg, VSEGEI, Russia, 2004).
8. Radiation Protection Standards (NRB-99/2009): Sanitary-Epidemiological Rules and Standards (Federal. Ts. Gig. Epidemiol. Rospotrebnadzora, 2009).
9. G. A. Chelnokov, V.Lavrushin, I.Bragin, N.Kharitonov, K.Bushkareva, A.Pavlov, and B. Chelnokova. Russ. J. of Pacif. Geol., **17**, 3, 284–296. (2023)
10. S. I. Arbuzov and L. P. Rikhvanov, *Geochemistry of Radioactive Elements: A Textbook* (Tomsk. Politekhn Univ., Tomsk, 2010)
11. S. L. Shvartsev, *Hydrogeochemistry of Supergene Zone*, *2nd ed.* (Nedra, Moscow, 1998)
12. A. Aydarkozhina, V. Lavrushin, A. Ermakov, G. Chelnokov, L. Zhang. *Doklady Earth Sciences* **1**, 34-56 (2024) *in press*