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The Elbrus Volcanic Center: New Features of EPR Dating of Rocks

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Abstract—The restoration of the evolution of the Elbrus Volcanic Center (EVC) is of great importance for predicting possible eruptions. Some stages of its development occur in a time interval that is difficult to measure by conventional radioisotope techniques. In this regard, in this work, we studied the possibility of using the dating method by radiation centers in quartz for which the concentration was measured with electron paramagnetic resonance (EPR) spectroscopy. When dating lava flows with an age of less than 50 ka, there is a good convergence of the results obtained by the EPR dating, radiocarbon, and comparative geomorphological methods. Due to the low thermal stability of radiation centers in quartz, in some cases, the measured values of age reflect a later thermal impact of overlying lava flows or intrusive bodies. The improved technique of EPR dating with intermediate annealing led to results that have better convergence with the data obtained by the ^{40}Ar/^{39}Ar and K–Ar methods for rocks older than 50 ka.

Keywords: Elbrus, dating, radiation centers, quartz, electron paramagnetic resonance

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INTRODUCTION

Studies of Elbrus, including evolutionary reconstructons, have been carried out since the middle of the 19th century. The geomorphological method of dating applied to the volcanic formations of the Elbrus region was used by Muratov and Gzovskii (1948), Paffengol'ts (1959), Masurenkov (1961), Milanovskii and Koronovskii (1961). The first and most comprehensive scheme of evolution of the Elbrus volcano was created by Koronovskii (1968). The development of radioisotope dating methods made it possible to make a significant contribution to clarification of the evolution of the Elbrus volcanic center (EVC) (Chernyshev et al., 2011, 2014; Gurbanov et al., 2021a, b).

The K–Ar, ^{40}Ar/^{39}Ar, and radiocarbon (^{14}C) methods were used to date the volcanic rocks of Elbrus of different ages (from the Neopleistocene to the Holocene). Until recently, the limits of applicability of these methods did not cover time intervals from 100–150 to 50 ka. As well, volcanic rocks are located at high altitudes where the materials necessary for the radiocarbon method are not available. One possible method to determine the age in the interval of interest is the method of dating by radiation centers in minerals recorded by electron paramagnetic resonance spectroscopy (EPR dating) (Ikeya, 1993), in particular in rock-forming quartz (Bogatikov et al., 2001; *Prirodnye*..., 2004; Shabalin et al., 2004; Koshchug et al., 2005; *Noveishii*..., 2005; Vyatkin, 2007). We note that this method was first used in Russia systematically since 2000 to determine the age of volcanic rocks of the EVC. It turned out that a number of methodological aspects require refinement, in particular, consideration of the true grain size of the mineral being dated, the superimposed heating of rocks, and differences between the conditions of laboratory and natural irradiation. It is therefore obvious that the obtained EPR dates require verification and calibration using other reliable isotope methods, which would allow EPR dating of events in the time interval from 500 years to 3 million years (Ikeya, 1993). This publication covers the results of one such attempt.

The EPR dating method is evaluated here on the basis of comparison of the data obtained with the geological and geomorphological data and with radiocarbon (^{14}C), potassium–argon (K–Ar) and argon–argon (^{40}Ar/^{39}Ar) dates (Chernyshev et al., 2011, 2014; Gurbanov et al., 2021a, 2021b). The work is based on the study of a large collection of samples and the data of field, mineralogical, and petrological studies performed by the IGEM RAS research team and published earlier (Bogatikov et al., 2001; Novov..., 2005); we used the scheme of EVC evolution proposed in these works to estimate the age of the rocks. Clarification of the chronology of the EVC evolution was beyond the frame of this contribution.

MATERIALS AND METHODS

Methods of collecting and preparation of quartz samples and EPR dating. Samples of rock-forming quartz for EPR dating were extracted from the Elbrus volcanic rocks by two methods. The first method involved selection of areas (up to 100 m^2) of lava flows, ignimbrite, or tuff horizons unaltered by post-magmatic processes, where these volcanics were not directly overlain by younger lavas, which could have heated it to 100°C. Samples of ~20 kg were taken from these sections by chipping. The samples were then crushed, sieved to yield –0.5 + 0.25 and –0.25 + 0.10 mm fractions, washed on a concentration table, and then monomineral quartz samples with purity up to 90–95% were separated by flotation, heavy fluids and electromagnetic method. The purity of quartz sample was then brought to 99–100% using a binocular microscope; 300–400 mg of the 0.15–0.25 mm fraction were then taken for EPR dating.

The second method was manual sampling of isolated quartz grains not less than 2–3 mm from the middle of the section of lava flow or pyroclastic horizons. The quartz samples were crushed to a size of 0.5–1.0 mm and their purity was refined to 99–100% under a binocular microscope.

The EPR dating method is based on the accumulation of radiation centers in solids under the influence of natural ionizing radiation. The natural radiation background is caused by the radioactive isotopes ^{238}U, ^{232}Th and ^{40}K, whose decay is accompanied by α-, β-, and γ-radiation, as well as by cosmic rays. Exposure of minerals to ionizing radiation leads to a redistribution of electrons between ions, resulting in the formation of electron and hole centers. If radiation centers are stable under natural conditions they accumulate over time. The number of formed centers (C) is proportional to the paleodose (D_n), i.e., the product of the radiation background power (D_y) by the duration of exposure to ionizing radiation (t). Under these conditions, the age of a mineral (the interval of time elapsed since the last cooling of the mineral to the closure temperature) is determined by the relation:

$$t\,(\text{years}) = \frac{\text{paleodose}}{\text{annual dose}} = \frac{D_n\,(\text{Gy})}{D_y\,(\text{Gy/y})}.$$

The paleodose can be estimated by two methods: the additive dose method and the regeneration method. In the first case the sample (quartz) extracted from the rock is irradiated with an additional dose of γ-radiation, which is superimposed on the paleodose. The value of the paleodose (D_n) is obtained by extrapolating the dependence of the concentration of paramagnetic centers on the laboratory irradiation dose to zero concentration (Fig. 1). The dependence $C = f(D_n)$ is required for the correct extrapolation. For aluminum centers in quartz, this dependence has a form of a saturation curve.

The regeneration method is annealing paramagnetic centers in the sample after measuring their natural concentration. The annealed sample is then irradiated with a series of γ-doses until the natural center concentration is reached. This laboratory irradiation dose is assumed to be equal to the paleodose (Fig. 2).

Many researchers have shown that the scatter of data points obtained using the regeneration method is significantly smaller than those obtained with the additive dose method; therefore, the accuracy of determining the paleodose value (D_n) is higher. The major fault of the regeneration method is that annealing may affect radiation sensitivity of the mineral (Prescott, 1993).

Lava flows were dated by accumulation of Al centers in quartz. Entry of impurity aluminum in quartz is accompanied by capture of univalent charge-compensating ions and formation of diamagnetic centers $[\text{AlO}_4^-/\text{M}^+]^\circ$ ($\text{M}^+ = \text{H}^+, \text{Li}^+, \text{Na}^+$). Under the influence of natural ionizing radiation, this center captures a hole, after which it loses the M^+ ion and transforms into a paramagnetic radiation center $[\text{AlO}_4^-/\text{h}^+]^\circ$. At the same time, the M^+ ion diffuses to the electron radiation center.

The concentration of radiation Al centers was determined in accordance with the instructions (Kolichestvennoe..., 1986) by comparing the intensity of characteristic lines in the EPR spectrum of the studied and the reference (with a known concentration of centers) samples. The high-field line of the superfine structure with $g_{\text{ef}} = 1.993$ was chosen as a characteristic line for the Al center. The concentration of Al centers was measured after γ-irradiation of samples with an analytical dose equal to 1×10^5 J/kg.

Spectra were recorded using a Varian E-115 EPR spectrometer in the X-band (~9.4 GHz) with a modulation amplitude of 0.1 mT, modulation frequency of 100 kHz and UHF radiation power of 10 mW. Al-center spectra were recorded at liquid nitrogen temperature using a quartz cryostat.

Radiation background. The dose rate of α-, β-, and γ-radiation was calculated from the U, Th, and K contents in rock and quartz. The U and Th concentrations were determined by instrumental neutron activation and K concentrations were determined by X-ray fluo-

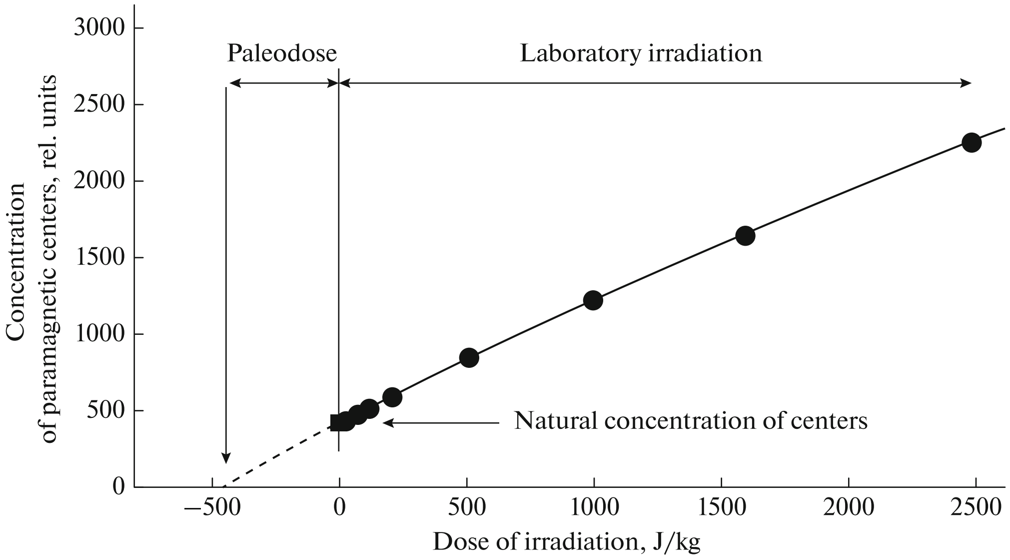

Fig. 1. Estimation of the paleodose by the method of additive doses.

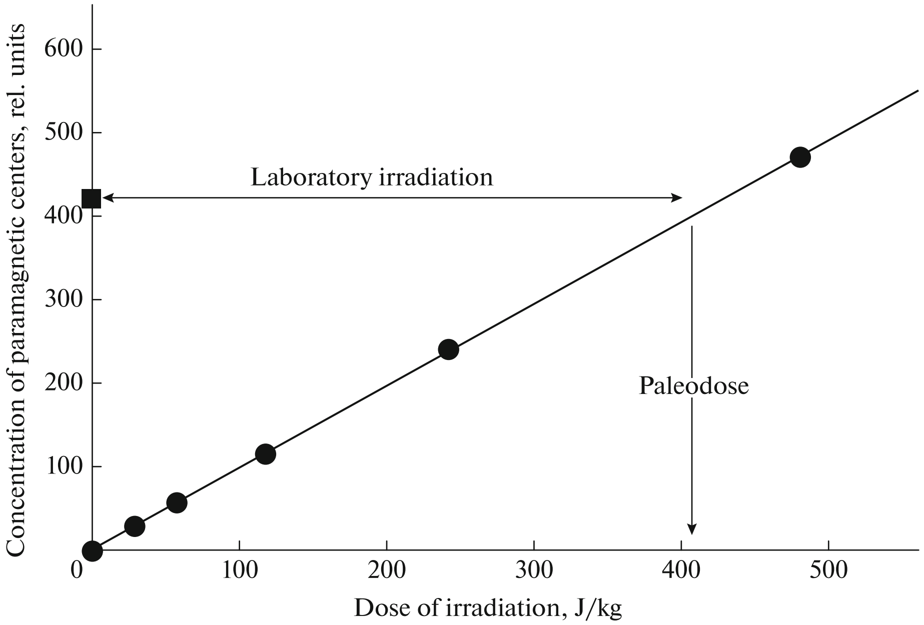

Fig. 2. Evaluation of the paleodose by the regeneration method.

rescence analysis or flame photometry. Due to the different penetration abilities of the α-, β-, and γ-components, the linear size of grains of the mineral being dated should be taken into account when calculating the irradiation dose. The α-track in the substance with the density of 2.7 g/cm^3 is about 20 μm (Grun, 1989). The average β-track is 2 mm. Consequently, the effective radiation background depends on the size of quartz grains in the lavas. We calculated the age of the samples using the software kindly provided by R. Grun, but only for quartz grains less than 1 mm in size, which allowed one, as noted above, to estimate only the upper age limit for rocks containing quartz grains of larger size.

Due to the fact that the radiation Al centers in quartz are stable at less than 100°C (Grun, 1989), while the temperature of the outpouring lavas and subvolcanic bodies according to data on homogenization of melt inclusions in minerals reached 1100–1170°C (Naumov et al., 2001), special requirements on sampling had to be applied. To obtain reliable EPR dating of quartz and to exclude the influence of superimposed thermal effects in cases of direct overlapping of several lava flows, samples were taken from the central part of the section of underlying lava flow of 20 m or more or at a considerable distance (up to 50–100 m) from exocontacts of subvolcanic bodies and in areas of volcanic rocks unaffected by fumarole activity recorded by formation of geyserrite veins. In spite of these measures, in some cases it was not possible to take samples that were unaffected by the later events.

At the same time, the low temperature stability of the radiation Al-centers in quartz and very high temperature of the outpouring lavas offered an opportunity to evaluate the possibility of using the EPR method for dating lava flows for the first time by rock-forming quartz from xenoliths of ancient igneous or metamorphic rocks in direct contact with volcanic rocks. This is especially important for the lava flow with no quartz phenocrysts or ignimbrite horizons in.

The age of two lava flows was determined by quartz from a xenolith of Late Paleozoic granite located in the lava-breccia (Ullukam River headstream) and from burnt Proterozoic mica schists occurring in direct contact with the base of the lava flow (Baksan River headstream, Polyana Azau). The ancient rocks containing quartz were in both cases heated to a temperature well above 100°C, which should have provided reliable EPR dating of the volcanic rocks. Thus, to date the lowest lava flow (early stage of postcaldera stage) in the Baksan River headstream (Polyana Azau), sample No. 5/98 was collected from the underlying Proterozoic burnt mica schists. The age of this sample is 23 ± 2 ka (Bogatikov et al., 2001). We note that the age of the moraine remnants found at the base of this lava flow was estimated as Late Pleistocene (22–24 ka, Scherbakova, 1973)), which agrees well with the dating obtained by EPR.

To date the lava breccia horizon in the upper part of the section of late caldera stage rocks at the Ullukam River headstream, a sample (No. 48g/98) was taken from a Late Paleozoic leucocratic granite xenolith (size of 20 × 30 cm); its age was determined as 72 ± 8 ka. It cannot be excluded, however, that the obtained value is rejuvenated, as the sample was located in the zone of possible thermal influence of a younger large subvolcanic body of dacite composition, embedded in the lavobreccia.

The results and discussion of the EPR dating. At this stage of the study, 74 quartz samples from ignimbrites, lava flows of different age, tuff horizons, and subvolcanic bodies were collected and dated. The petrological, geochemical, and mineralogical characteristics of the samples, as well as the stages of EVC development, were given in previously published works (Bogatikov et al., 2001). These samples characterized volcanic formations of the caldera: early stage (ignimbrites, tuffs with characteristic pink quartz, lavas of rhyolite composition), late stage (lavas, lava breccias, tuffs and subvolcanic bodies of dacite composition), and post-caldera stages (dacite lava flows, and tuffs of early Late Pleistocene and Late Holocene stages) of EVC evolution (Ibid). The results of the EPR dating are given in Table 1.

The data presented in the table shows that the formation of the section of the early caldera stage (ignimbrites and tuffs of rhyolite composition) occurred in the interval 337–254 ka BP (we note that this is only the upper age limit of rock formation), which is much younger than the dating obtained by U–Pb SHRIMP-RG zirconometry (Gurbanov et al., 2004) and the K–Ar method (Chernyshev et al., 2011, 2014). The most ancient EPR age values were obtained for the remnants of ignimbrite horizons located outside of the caldera at the sites where their base is located at a relative height of 350–400 m above the modern bed of the Malka River (Tuzluk mountain, 283 ka), Chemartkol River (287 ka) and for caldera ignimbrites of Aerodrom tract (lower strata, 314 ka), and the headstream of Bitiik-Tebe River (337 ka). However, the EPR dates are significantly lower than those obtained by isotope methods.

The results of EPR dating are affected by the presence of aluminum centers with different temperature stabilities in quartz (Vyatkin et al., 2007). To compensate for this, the technique of dating with preliminary low-temperature heating was applied to several samples. The essence of the technique is that after each laboratory irradiation the sample was briefly annealed at a certain temperature in order to destroy Al centers with low thermal stability and leave the most thermally stable centers, which are less affected by secondary heating. As a result, the age of the Tuzluk and the Chemartkol River ignimbrites increased to 727 ka and to 772 ka, respectively (Table 1). Even these values are significantly lower than the values obtained by ioisotope methods.

Such a discrepancy can be related, first, to the imperfections of the EPR dating method and, second, to the actual evolution of the geological object. The first reason should be attributed to the fact that the closure temperature of the quartz EPR dating method is significantly lower than the closure temperature of the K–Ar method. Since the recombination rate of the radiation centers exponentially depends on the temperature, the results obtained by these methods should differ significantly. In addition, it is possible that the radiation sensitivity of quartz may be altered by annealing or as a result of more powerful laboratory irradiation compared to the natural background; accurate accounting for the quartz grain size is necessary.

The EPR data may also indicate reflect later processes whose geological signs are either not yet detected or have been destroyed. Additional studies, including field studies, are needed to solve these problems.

Table 1. The results of EPR dating of rock-forming quartz from volcanics of the Elbrus volcanic center

Sample	Code	Paleodose, J/kg	Quartz		Rock			Age, ka
			U, ppm	Th, ppm	U, ppm	Th, ppm	K, %	
Ignimbrite, Chemartkol R.								
80k/97	CE	1042 ± 197	0.27	0.76	5.4	23	3.05	287.6 ± 46.2
79k/97	CE	998 ± 88	0.43	2.73	5.4	22.3	3.05	273.3 ± 42.2
Ignimbrite, Aerodrome tract								
70/99	CE	1095 ± 203	0.19	1.21	5.4	26.5	3.24	297.5 ± 21.9
								772 ± ***183***
352	CE	1127 ± 18	0.46	0.19	4.1	23.2	3.23	314.5 ± 60.3
351	CE	1024 ± 20	0.66	0.79	4.1	23.4	3.58	253.7 ± 53.4
39/97	CE	1196 ± 112	0.4	1.7	6.0	25.9	3.51	276.6 ± 43.7
Ignimbrite, Birjaly su R.								
353	CE	1210 ± 17	0.26	1.47	4.4	24.2	3.46	288.8 ± 51
354	CE	1234 ± 21	0.12	0.48	4.1	23.0	3.48	337.5 ± 60.1
Ignimbrite, Biytik-Tebe R.								
76	CE	308 ± 4	0.25	0.59	4.0	22.6	3.04	82.5 ± 9.1
30/99	CE	243 ± 3	0.23	0.93	7.0	24.5	3.34	62.0 ± 2.6
50/98	CE	443 ± 37	0.1	0.2	4.2	29.5	2.90	84.3 ± 5.7
Ignimbrite, Kyukyurtlyu R.								
82	CE	409 ± 5	0.17	0.25	4.0	22.4	3.02	116.0 ± 8.5
82-1	CE	377 ± 5	0.97	10.14	4.0	23.8	2.99	76.5 ± 7.8
82-2	CE	314 ± 5	0.09	0.26	4.5	32.4	3.94	73.9 ± 3.5
83	CE	373 ± 3	0.09	0.31	2.7	20.5	3.07	83.7 ± 5.4
Rhyolite, Ullukam R.								
25/99	CER	313 ± 12	0.4	1.6	5.9	26.2	3.24	79.6 ± 3.5
25-1/99	CER	287 ± 10	0.24	0.85	5.3	23.5	2.58	85.1 ± 4.1
26-1	CER	467 ± 52	0.44	0.68	5.9	17.9	3.24	129.2 ± 7.0
								529 ± ***210***
Rhyolite, Kyukyurtlyu R.								
86	CER	442 ± 6	0.24	0.26	4.2	22.8	3.17	122.1 ± 13.9
85-1 neck	CER	1204 ± 14	0.49	7.42	3.6	23.7	3.21	304.0 ± 55.3
1086	CE (section, top)		2.2	6.1	6	25.6	2.82	***331*** ± ***83***
Rhyolite tuff with rose quartz, Birjaly su R.								
47/97	CER	1002 ± 656	0.3	0.9	5.6	23.0	3.19	184.0 ± 41.1
30-1/99	CER, Biytik-Tebe	226 ± 21	0.63	1.53	3.8	20.4	2.61	70.6 ± 4.0
								313 ± ***37***
Dacite, Biytik-Tebe R.								
36/99	CL (section, top)	233 ± 10	0.24	0.78	4.3	22.1	2.80	67.3 ± 3.8
48/99	CL (section, top)	242 ± 0	0.61	2.07	4.6	25.0	2.75	46.2 ± 2.7
79/99	CL (section, top)	163 ± 3	0.15	0.09	3.0	21.1	2.09	59.2 ± 7.0
78/99	CL (section, middle)	237 ± 1	0.08	0.09	2.4	18.1	3.07	89.9 ± 16.2
80/99	CL (section, bottom)	306 ± 1	0.01	0.14	2.8	21.8	2.43	114.1 ± 12.3
405-2	CL (section, bottom)	319 ± 6	0.29	0.65	3.0	16.4	3.16	102.8 ± 13.7
19/97	CL (section, bottom)		1.85	90.6	5.4	23.7	2.80	110.5 ± 6.1
40/99	CL (section, bottom)	356 ± 6	0.28	1.04	3.5	23.5	2.63	109.7 ± 5.2
41/99	CL (section, bottom)	386 ± 16	0.19	0.93	3.7	22.6	2.63	121.3 ± 67.5
Dacite, Ullukam R.								
22	CL (section, top)	133 ± 6	0.27	0.71	4.8	19.3	2.76	37.6 ± 2.2
22m	CL (section, top)	231 ± 6	0.49	0.85	4.8	19.3	2.76	48.7 ± 3.1
22-1m	CL (section, top)	206 ± 0	0.28	0.92	4.2	19.4	2.80	44.9 ± 2.7
22-3m	CL (section, middle)	288 ± 0	0.92	2.52	5.5	19.8	2.80	55.0 ± 3.2
22-2m	CL (section, bottom)	386 ± 17	0.28	0.89	4.5	19.8	2.80	82.5 ± 6.1
98-2	CL (section, bottom)	382 ± 7	0.09	0.14	4.1	25.7	2.88	122.9 ± 10.4

Sample	Code	Paleodose, J/kg	Quartz		Rock			Age, ka
			U, ppm	Th, ppm	U, ppm	Th, ppm	K, %	
Dacite, Malka R.								
374	CL	393 ± 7	0.09	0.28	3.6	21.0	2.82	123.1 ± 13.2
Dacite, Kizilkol R.								
386	CL	343 ± 1	0.17	0.35	3.9	23.8	2.85	94.5 ± 11.9
Dacite, Kyukyurtlyu R.								
144-1	CL (section, middle)	335 ± 4	0.14	0.26	4.3	30.6	3.31	77.6 ± 10.2
Dacite, Siltransu R.								
53	CL	728 ± 128	1.15	4.58	3.2	22.3	2.99	171.9 ± 9.5
62-1	CL	728 ± 4	0.81	4.67	4.1	20.6	2.99	174.5 ± 10.0
Dacite tuff with gray quartz, Biytik-Tebe R.								
50/98	CL (lower horizon)	443 ± 37	0.1	0.2	4.2	29.5	2.90	84.3 ± 5.7
32m	CL (lower horizon)	359 ± 1	0.3	1.56	3.6	21.2	2.81	77.0 ± 4.6
131	CL (upper horizon)	322 ± 0.3	0.05	0.24	5.9	28.3	3.08	78.7 ± 8.3
32	CL (upper horizon)	269 ± 3	0.37	0.87	3.6	21.2	2.81	76.3 ± 3.7
Subvolcanic body, Kyukyurtlyu R.								
93	CLS	226 ± 4	0.31	1.97	3.5	23.1	2.92	72.6 ± 10.8
93M1	CLS	279 ± 18	0.4	2.1	3.5	23.1	2.92	77.0 ± 4.5
93M2	CLS	271 ± 198	0.3	1.3	3.5	23.1	2.92	85.7 ± 33.6
88-3	CLS	278 ± 6	0.12	0.34	3.7	24.3	3.01	90.7 ± 5.7
Subvolcanic body, Ullukam R.								
23/99	CLS	241 ± 3	0.42	0.66	4.0	19.8	2.71	76.0 ± 3.5
96-3	CLS	203 ± 4	0.42	0.66	4.0	19.8	2.71	68.9 ± 17.6
Subvolcanic body, Biytik-Tebe R.								
36-2/99	CLS	216 ± 7	0.4	9.29	3.6	21.6	2.48	53.9 ± 3.1
Dacite, Ullukam R.								
95	PCP	228 ± 0.5	0.05	0.36	3.7	24.2	2.68	68.7 ± 17.1
Dacite, Azau R. (Baksan)								
5/98	PCP	150 ± 5	0.1	0.2	4.8	19/2	2.8	23 ± 2
78-1	PCP	270 ± 5	0.5	2.1	4.7	16.7	2.57	36.7 ± 2.3
1124-28	PCP	299 ± 9	0.4	1.5	5.3	23.3	2.91	47.8 ± 3.2
1123-25	PCP	269 ± 5	0.4	1.8	5.5	24.0	3.15	37.6 ± 2.4
4618	PCP	280 ± 5	0.4	0.8	5.4	25.2	2.34	48.1 ± 2.9
601	PCP (section, upperbottom)	329 ± 10	1.5	5.1	9.4	26.3	3.26	78.9 ± 2.6
Dacite, Malka R.								
2356m	PCP	231 ± 2	0.2	1.2	3.0	22.4	3.01	49.0 ± 3.1
388	PCP	160 ± 43	0.08	0.17	4.2	23.5	3.05	46.4 ± 12.7
395	PCP	214 ± 0.2	0	0.21	4.1	21.7	2.99	63.8 ± 10.6
394	PCP	107 ± 39	0.2	0.66	3.3	23.0	3.33	15.1 ± 5.5
396	PCP	207 ± 28	0.13	0.61	3.9	23.6	3.16	57.7 ± 8.2
44-1	PCP		2.25	9.5	7.3	24.1	3.0	43.4 ± 9.3
Andesidacite, Mount of Tash-Tebe								
97/98	PCP	230 ± 4	0.1	0.5	6.1	21.4	2.9	39.0 ± 5.0
Dacite, Malka R.								
399	PCH	57 ± 4	0.24	0.9	3.8	24.6	3.24	6.7 ± 0.7
Ignimbrite altered by fumaroles, Irik R.								
13	CKP	87 ± 10	0.43	0.83	4.4	22.2	3.45	16.2 ± 2.1
Dacite, altered by fumaroles, Biytik R.								
44/99	CLS	94 ± 7	0.13	1.57	4.3	23.8	1.99	20.4 ± 1.3

Plain font, samples measured by regeneration method, bold italics show samples measured by new technique of EPR dating by additive doses with intermediate annealing. CE, early caldera stage, ignimbrites; CER, early caldera stage, rhyolites and tuffs with pink quartz; CL, late caldera stage, lavas, dacite lava breccias and tuffs with gray quartz; CLS, late caldera stage, subvolcanic dacites (rods and dikes); PCP, postcaldera stage, early stage, lavas, lava breccias of dacite composition of Late Pleistocene; PCH, postcaldera stage, late (Holocene) stage, lavas, lava breccias of dacite composition.

At the same time, for quartz from ignimbrites, tuffs, and lavas of rhyolite composition, which are close in their time of formation and which lie at the base of volcanic sections at the sources of the Ullukam, Biytik-Tebe, and Kyukyurtlyu rivers, which experienced thermal impacts due to lava streams directly overlapping them or breaking through subvolcanic bodies, three groups of age values ranging from 129–116, 85–79, and 76–62 ka were obtained. These dates are clearly rejuvenated due to the thermal impact on the mentioned rocks by series of different-age subvolcanic bodies of dacite composition, dated to the range from 620 to 50 ka by $^{40}Ar/^{39}Ar$ method (Gurbanov et al., 2021b).

We note that part of the EPR dating of lava flows and tuff horizons of the early and late stages of the caldera and post-caldera stages could also be rejuvenated due to thermal influence (~100°C) during direct outpouring of younger melt portions with temperatures up to 1100–1170°C onto the underlying flows (Naumov et al., 2001). This assumption is confirmed by the EPR dating of a neck of rhyolite composition (304 ka, sample No. 85-1), cutting through the Late Paleozoic granites (not subjected to the superimposed thermal influence) and possibly serving as a supply channel for a lava flow of the same composition that is fully eroded.

According to EPR dating, the Syltran volcanic edifice, which is located outside the caldera structure and is correlated by the set and composition of its rocks with typical sections of the late caldera stage, was formed 175–172 ka BP. These dates most likely reflect the upper age limit of the outpouring of dacite lavas, while the age of the typical late caldera stage sections observed at the headstream of the Ullukam, Kyukyurtlyu, and Biytik-Tebe rivers was rejuvenated to an unknown extent due to the two aforementioned thermal scenarios. Thus, for the lower parts of these sections we obtained dates (ka) varying between 122.9–102.8; for the middle parts of the section, 89.9–76.3 and for the upper parts, 67.3–43.1. We note that the EPR age of the two latter parts correlates well with the EPR age of subvolcanic dacite bodies.

During the early post-caldera stage (Late Pleistocene), according to EPR dating, lava outpourings occurred: 68.7 ka BP (Sample no. 95, Ullukam River headstream), 63.8, 49, 43.4, and 15.1 ka BP (Samples No. 395, 356m, 44-1, and 394, respectively from Malka River headstream); a 39 ka BP eruption of the small Tash-Tebe volcano (sample No. 97/98) located on the Bechasynskoe plateau outside the caldera structure, and 23 ka BP the lowest lava flow (sample no. 5/98), located above the Polyana Azau in the upper Baksan River valley. Evidence of another explosive eruption in the form of an ash horizon with a ^{14}C age of 22 ka was found near Temirzhebekskaya Station in the high terrace of the Kuban River (Bogatikov et al., 2001).

Only sample (No. 399) corresponding to the late (Holocene) post-caldera stage from a lava flow in the upper reaches of the Malka River was dated by EPR to 6.7 ± 0.7 ka BP. In addition, the rejuvenating effect of different-age fumarole activity (with temperatures up to 250–300°C according to the study of gas-liquid inclusions) on older volcanics was proved quite convincingly in the process of the research. Traces of fumaroles and thermal spring deposits are recorded by geyserite fields, e.g., dacite lava flow from a typical section for late caldera stage (sample No.44/99, Bityik-Tebe River headstream) is dated to 20.4 ka BP; and ignimbrites from the early caldera stage (sample No. 13, Irikchat Pass) were dated at 16.2 ka BP. Most likely, these dates reflect the age of fumarole activity.

CONCLUSIONS

The age values obtained by EPR dating for nonisothermal and multistage geological systems reflect only the upper age limit of rock formation and the most correct data refer to the age of rocks of the last stages of the system. To obtain reliable dates for the rocks of earlier stages, it is necessary to apply the technique of additive doses with intermediate annealing, but the obtained data must be verified and calibrated using other isotope methods.

A good convergence of the dates obtained by EPR, radiocarbon and comparative geomorphological methods was observed for EVC lava flows with age values less than 50 ka. This is confirmed by the data obtained for the lowest dacite lava flow over the Polyana Azau and for the trachyandesidacite lava flow of Tash-Tebe volcano.

The development and application of EPR quartz dating using the additive-dose technique with intermediate annealing led to results that have a better agreement with those obtained by U–Pb SHRIMP-RG zirconometry, $^{40}Ar/^{39}Ar$, and K–Ar methods. The results we obtained are characterized by a lower rejuvenation value compared to previous EPR dates and validate the additive dose technique with intermediate annealing as a more correct dating method.

The low temperature stability of the radiation Al centers in quartz and the very high temperature of the outflowing lavas allowed us to evaluate the possibility of using the EPR method for dating lava flows in rock-forming quartz from xenoliths of ancient igneous or metamorphic rocks and in quartz from xenoliths in direct contact with volcanic ancient metamorphic or igneous rocks. This is especially important for those cases when there are no phenocrysts of rock-forming quartz in the rocks of lava flows or in ignimbrite horizons.

The application of EPR dating to determining the age of EVC rocks is of great importance for the dating of recent and modern volcanism in various regions of Russia and the world.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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