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GEOCHEMISTRY

Heterogeneity of Ar and Sr Initial Isotopic Composition in the Coexisting Minerals from Miocene Hypabyssal Granitoids in the Caucasian Mineral Waters Region

V. A. Lebedev, Corresponding Member of the RAS I. V. Chernyshev, A. S. Avdeenko, A. A. Nosova, A. Ya. Dokuchaev, T. I. Oleinikova, and Yu. V. Gol'tsman

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Late Miocene subalkaline granite magmatism in the Caucasian Mineral Waters (CMW) region is related to the first stage of Late Cenozoic magmatic activity in the Caucasian segment of the Alpine foldbelt. The young age and presence of uranium mineralization, as well as other factors including easy availability, promoted detailed study of these intrusions in geological [1, 2], mineralogical, petrographical, geochemical, and physicochemical aspects [3–7]. The CMW region known as Mineral'nye Vody (Fig. 1) is confined to the ring structure in the northern termination of Transcaucasus Transverse Uplift. The intrusions typically form stocks with deep subvertical contacts, and their exposures are no more than 5 km^2 in area. The presence of granite pebbles at the base of Late Miocene sedimentary sequence unambiguously indicates the Post Paleogene age of the subalkaline magmatism in the region.

The massifs are made up of leucogranite–granite and alkaline granite–granosyenite–syenite series [1, 7]. The granitoids typically exhibit porphyritic texture and consist of phenocrysts and fine-grained groundmass. Syenites and granosyenites contain phenocrysts of sanidine, plagioclase, phlogopite, and clinopyroxene. In granites which also contain quartz, clinopyroxene is replaced by hornblende. Phenocrysts in leucogranites occur as quartz and feldspars. In terms of geochemical characteristics, subalkaline rocks of the CMW region are classified as latite (shoshonite) granites typical of late collisional and postcollisional stages of the evolution of foldbelts [7]. The geology, composition, and crystallization conditions of granitoids of the CMW region are considered in detail in [1, 7].

Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Staromonetnyi per. 35, Moscow, 119017 Russia
e-mail: leb@igem.ru

The problem of age and chronology of CMW granitoid massifs remains debatable. Available K–Ar and ^{39}Ar–^{40}Ar datings do not always coincide and span only part of the known massifs. Of special interest is their formation history, especially in view of the recognition of two or even three phases for some massifs in petrological works [1, 7].

The first K–Ar determinations were performed 30 years ago and ranged within 10.5–8 Ma [3, 8] which unambiguously confirmed their Late Miocene age previously inferred from geological data. In later studies, the granites were dated by analytically improved K–Ar method at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (Moscow) [9] and for the first time by the ^{39}Ar–^{40}Ar method at Heidelberg University [5, 6].

K–Ar datings on five phlogopite samples from the Kinzhal, Sheludivaya, Ostraya, Zmeika, and Verblyud massifs are reported in [9]. Three datings are within 8.40–8.25 Ma, while two others fall around 9.3 Ma. No correlation was found between the age and composition of the rocks, while K–Ar data were interpreted as the uplift time, i.e., exhumation of the host crustal blocks above the 300°C isograd. These authors believed that the intrusions are slightly older than 9 Ma. Based on our more detailed K–Ar data, we shall show that the apparent different ages of the CMW massifs noted in [9] can be interpreted in a different way.

An incremental step heating ^{39}Ar–^{40}Ar method was applied by Hess, Paul, and others to date these massifs [5, 6]. They studied three sanidine–phlogopite mineral pairs from rocks of the Razvalka, Kinzhal, and Zmeika massifs and two sanidine samples from rocks of the Ostraya and Zolotoi Kurgan massifs. All dated samples define plateau age spectra, indicating rapid cooling and subsequent closure of the K–Ar isotope mineral system. The obtained data are plotted in a narrow range of 8.4–8.1 Ma, which allowed the authors to conclude that the age of CMW massifs is ~8.25 Ma. It should be

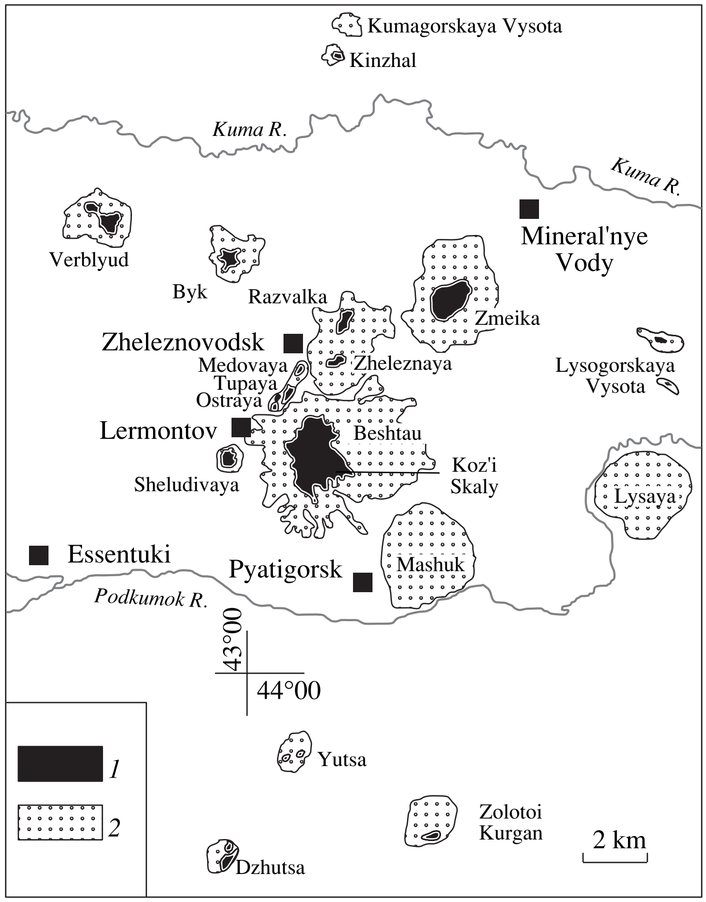

Fig. 1. Location scheme of Late Miocene granitoid massifs in the CMW region (modified after [1, 7]). (*1, 2*) Exposed and unexposed massifs, respectively.

noted that ^{39}Ar–^{40}Ar and K–Ar datings on phlogopites from the Zmeika Massif [9] coincide within error limits, whereas the dates obtained by these methods for the Kinzhal and Sheludivaya massifs differ by ~1 Ma. Thus, datings within the range 8.4–8.1 Ma and significantly older values were obtained on different samples from the same intrusive bodies.

To refine the age of hypabyssal massifs of the CMW region and explain the discordance of K–Ar mineral dates, the coexisting minerals from samples representing ten intrusions were dated by K–Ar and Rb–Sr methods. The applied procedure of K–Ar dating of young magmatic rocks was reported in detail in [10]. The Rb and Sr isotope analysis was performed on a Micromass Sector 54 multichannel thermoionization mass spectrometer.

Eight of ten studied massifs were dated by the K–Ar isotope method on the sanidine–phlogopite pair. In addition, this mineral pair was also used to date aplites crosscutting the main intrusive phase of the Razvalka Massif. Due to the absence of phlogopite, the studied samples of subalkaline granites of the Beshtau Massif were dated on the sanidine–amphibole pair. Fine-grained quartz–feldspar groundmass was dated in the rocks of the Byk Massif. It was used as an additional geochronometer for granitoids of the Sheludivaya and Ostraya massifs.

The K–Ar method yielded 8.70–8.15 Ma for 16 (among 23) samples, while data points of 13 samples plot within an even narrower interval of 8.50–8.15 Ma (Table 1). At the same time, seven samples including both phlogopite and sanidine yielded appreciably older ages (12.8–8.8 Ma). In all cases of an older age for one of the minerals in the dated pair, the data point of the second mineral always plotted in the interval of 8.50–8.15 Ma. Since granitoid massifs of the CMW region are hypabyssal bodies, which crystallized at shallow depths (1–2 km [1]) and, as a result, cooled rather rapidly, such long intervals (4 Ma) between the closure of K–Ar isotope system in sanidine phenocrysts (closure temperature 700–800°C [11]) and phlogopite (closure temperature ~400°C [13]) hardly seem possible.[1] In addition, only two "old" dates were obtained on

[1] According to [12], the Quaternary Takidani granodiorite massif, Japan (area 21 km^2, formation depth 2–5 km), had a cooling rate of 550–810°C/Ma in temperature range 800–400°C. In our case, the shallower formation depths and smaller size of the massifs suggest at least the same or even higher cooling rate.

Table 1. K–Ar isotope data on mineral phases of granitoids from the CMW region

Sample no.	Mineral	Potassium, % ± σ	$^{40}Ar_{rad}$, ng/g ± σ	$^{40}Ar_{air}$, %	Age, Ma ± 2σ
		Lysogorskaya Vysota			
TKh-02-1	Sanidine	7.94 ± 0.08	4.624 ± 0.015	22.5	8.38 ± 0.18
	Phlogopite	7.47 ± 0.08	6.461 ± 0.025	49.9	12.4 ± 0.3
		Sheludivaya			
Sh-02	Sanidine	6.51 ± 0.07	3.687 ± 0.016	41.0	8.15 ± 0.2
	Phlogopite	7.14 ± 0.07	5.076 ± 0.020	57.4	10.2 ± 0.2
	Groundmass	3.45 ± 0.04	2.088 ± 0.009	34.6	8.7 ± 0.2
		Zmeika			
Z-02	Sanidine	7.98 ± 0.08	5.964 ± 0.019	23.3	10.75 ± 0.25
	Phlogopite	6.06 ± 0.06	3.486 ± 0.011	19.9	8.27 ± 0.17
		Razvalka			
R-02	Sanidine	8.98 ± 0.09	5.202 ± 0.016	9.9	8.33 ± 0.17
	Phlogopite	7.78 ± 0.08	4.501 ± 0.016	39.4	8.32 ± 0.18
		Razvalka (aplites)			
R-02-A	Phlogopite	6.90 ± 0.07	4.024 ± 0.013	26.8	8.39 ± 0.18
	Sanidine	7.16 ± 0.07	6.401 ± 0.019	9.7	12.8 ± 0.3
		Zolotoi Kurgan			
ZK-03	Phlogopite	6.97 ± 0.07	5.079 ± 0.016	29.5	10.5 ± 0.2
	Sanidine	7.64 ± 0.08	4.432 ± 0.015	21.4	8.34 ± 0.18
		Medovaya			
M-03	Phlogopite	7.55 ± 0.08	4.667 ± 0.017	40.0	8.9 ± 0.2
	Sanidine	8.23 ± 0.09	4.649 ± 0.016	13.6	8.18 ± 0.19
		Beshtau			
MB-03	Amphibole	1.25 ± 0.02	0.755 ± 0.006	32.9	8.7 ± 0.3
	Sanidine	8.35 ± 0.09	5.020 ± 0.018	23.4	8.65 ± 0.2
		Zheleznaya			
Zh-03	Phlogopite	7.56 ± 0.08	4.619 ± 0.016	35.7	8.8 ± 0.2
	Sanidine	8.32 ± 0.09	4.790 ± 0.016	22.8	8.28 ± 0.19
		Ostraya			
O-03	Phlogopite	7.54 ± 0.08	4.463 ± 0.016	40.6	8.51 ± 0.19
	Sanidine	8.19 ± 0.09	4.664 ± 0.023	23.0	8.2 ± 0.2
	Groundmass	4.85 ± 0.06	2.829 ± 0.012	19.9	8.4 ± 0.2
		Byk			
B-03	Groundmass	4.65 ± 0.05	2.707 ± 0.011	48.8	8.37 ± 0.19

sanidine, whereas five dates were obtained for phlogopite, which had the lower closure temperature of the K–Ar system. This indicates that all age values within 12.8–8.8 Ma obtained in this study and in [9] can be explained by the presence of excess ^{40}Ar in some dated phases. It is interesting that dates of ~8.3 and >9 Ma were obtained by different researchers on different rocks and minerals of rocks from several massifs. Excess ^{40}Ar, presumably incorporated from a deep-seated source or host rocks and unevenly distributed over granite magma, was apparently concentrated in the relatively low-temperature melt in some zones of the apical part of the crystallizing magma chambers.

It is evident that degassing at the final crystallization stage presumably resulted in the higher partial Ar pressure in the volcanic gases in the upper parts of the magma chambers. At present, only the upper, near-roof parts of the intrusions are exposed and accessible. Therefore, the above explanation of anomalously old datings seems to be probable. The fact that excess ^{40}Ar

Table 2. Rb–Sr isotope data on granitoids from the CMW region

Sample no.	Analyzed material	Rb (g/t)	Sr (g/t)	$^{87}Rb/^{86}Sr \pm 2\sigma$	$^{87}Sr/^{86}Sr \pm 2\sigma$
Zh-03 (Zheleznaya)	Rock	336	1106	0.8785 ± 22	0.708653 ± 23
	Phlogopite	860	58	42.72 ± 12	0.713288 ± 9
Sh-02 (Sheludivaya)	Rock	518	274	5.478 ± 14	0.709147 ± 13
	Phlogopite	980	86	33.19 ± 9	0.712150 ± 10
M-03 (Medovaya)	Rock	340	1060	0.9267 ± 50	0.708546 ± 90
	Phlogopite	860	116	21.50 ± 6	0.710838 ± 10
ZK-03 (Zolotoi Kurgan)	Rock	339	1190	0.8235 ± 20	0.708354 ± 14
	Phlogopite	773	205	10.90 ± 3	0.709562 ± 10
TKh-02-1 (Lysogorskaya Vysota)	Rock	328	1044	0.9094 ± 22	0.708492 ± 14
	Phlogopite	840	207	11.73 ± 5	0.710320 ± 9

is recorded for sanidine in some datings and for phlogopites in the majority of datings can be explained by crystallization of different phenocrysts at different stages of fractionation in a wide range of partial Ar pressure.

Thus, K–Ar mineral datings older than 9 Ma presumably have no geological sense, and they are related to the presence of excess radiogenic argon in some phenocrysts. Taking into consideration the oldest K–Ar dates (12.4–12.8 Ma), the initial $^{40}Ar/^{36}Ar$ ratio in mineral phases of granitoids varied from 295.5 (atmospheric value) to 1300.

Five granitoid samples, which contain phlogopite with excess ^{40}Ar, were dated by the Rb–Sr method based on the phlogopite–whole rock pair (Table 2). The analyzed phlogopites are characterized by an elevated Sr content (60–200 ppm) and, correspondingly, low $^{87}Rb/^{86}Sr$ values (10–40). The Rb–Sr age calculated for the studied phlogopite–whole rock pairs display a significant scatter from 7.6 to 11.9 Ma. The age coincides with the K–Ar date (8.44 ± 0.12 Ma) only in sample ZK-03. At the same time, isochron constructed on four (among five) dated phlogopites showed an age of 8.21 ± 0.16 Ma (Fig. 2). The observed discrepancies in the age estimates of phlogopite–whole rock pairs and separate phlogopite samples may be explained by disequilibration of initial Sr isotopic composition between individual mineral phases of the granitoids. This disequilibration is presumably related to the existence of compositionally heterogeneous microdomains in the melt and their preservation during crystallization. The microheterogeneity of the granitoid melts is indicated by the wide development of rhythmic layering in granitoids of the CMW region, which is well expressed in minor fluctuations of chemical and mineral compositions [7]. We suggest that the layering of the melt was driven by spinodal decomposition, which provides a rapid continuous unmixing of starting matrix over the entire volume, thus causing a transition from the thermodynamically unstable to the metastable state. This results in the periodic (oscillatory) distribution of concentrations.

The melt probably contained not only Sr related to the melting of source but also Sr enriched in the radiogenic isotope. The latter was presumably obtained during the contamination of magmatic melts by upper crustal ancient rocks. Crystallizing minerals, phlogopite inclusive, entrained Sr from ambient microheterogenous melt into crystal lattice. This is supported by the high Sr contents in the analyzed micas. In some cases (sample ZK-03), the Sr isotopic composition of phlogopite and feldspars, the major minerals of the rock, had time to become equilibrated, while the equilibrium was

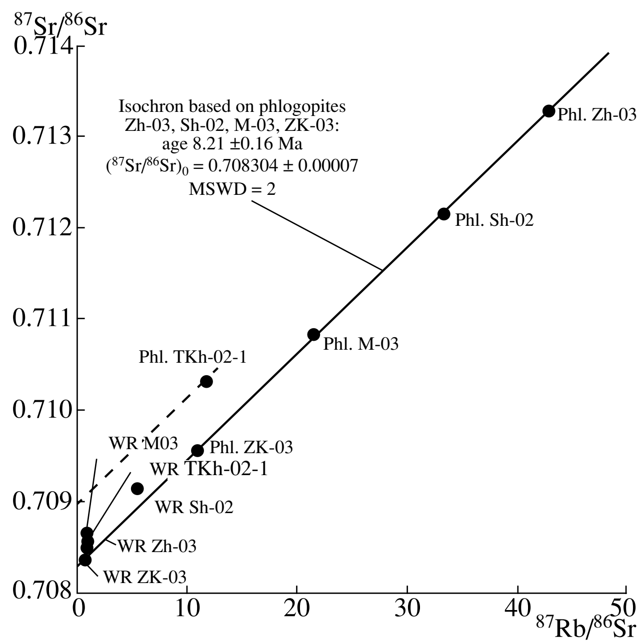

Fig. 2. Rb–Sr isotope diagram for the studied granitoid samples from the CMW region.

not attained up to solidification of the rocks and closure of the Rb–Sr mineral systems in other cases. In the analyzed samples Zh-03, Sh-02, and M-03, the initial Sr isotopic composition in the whole rock (or its feldspathic part) seemed to be more radiogenic than that in phlogopite. The situation was the opposite in sample TKh-02-1. The dashed line in the Rb–Sr isotope diagram (Fig. 2) shows the initial $^{87}Sr/^{86}Sr$ ratio corresponding to the phlogopite age of 8.3 Ma. This value is presumably the upper limit of variations of this ratio (~0.709) in the granitoid mineral phases. The data point of sample ZK-03 is plotted in the isochron based on four other phlogopites, which defines the lower limit (0.7083) of this range. Let us note that close data were obtained for several apatite samples from the CMW granitoids ($^{87}Sr/^{86}Sr$ from 0.7083 to 0.7086) [6].

All presently available K–Ar, $^{40}Ar/^{39}Ar$, and Rb–Sr data on minerals from 12 (among 16) exposed intrusions point to nearly simultaneous formation of all intrusive bodies of the CMW region. According to isotope–geochronological data, their age is 8.3 ± 0.2 Ma (2σ). The fact that K–Ar data on aplites from the Razvalka Massif coincided within measurement error with the age of granosyenites of the main intrusive phase also supports the short-term (tens to a few hundred of thousand years) formation history of crystallization and subsequent cooling of the studied intrusions, although the multiple character of melt injection has been established for some massifs.

Our data and those of previous studies [14] show that the timing of CMW massifs was significantly (by ~2 Ma) separated from the subsequent impulse of young magmatism (6.3–6.1 Ma) in the Greater Caucasus represented by mafic volcanism of Central Georgian region. Petrogeochemical data [7] together with Sr isotope data published in [6] and reported in the present paper constrain the role of mantle material in the genesis of subalkaline CMV granitoids. Approximately 2 Ma after the formation of the CMW massifs, the mantle material began to play a significant (in some cases, leading) role in the genesis of magmatic melts as a result of the continuing ascent of asthenosphere beneath the Greater Caucasus [13–15].

The presence of excess ^{40}Ar and disequilibration of the initial Sr isotopic composition in coexisting minerals of Late Miocene hypabyssal granite intrusions of the CMW region are probably typical of such massifs. The experience of their investigation shows that the phenomena described above can only be discovered by detailed investigations, and they must be taken into account for correct isotope dating of young subvolcanic rocks.

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