**GEOCHEMISTRY** =

## Pliocene Granitoid Massif in the Kazbek Volcanic Center: First Geochronological and Isotope–Geochemical Data

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Detailed study of Late Cenozoic intrusive magmatism in the Earth remains one of the most pressing and interesting geological problems of both regional and fundamental significance. For example, data on recent plutonic rocks with a short-term modern history can be used to solve important problems, such as the duration of crystallization and cooling of different (in volume and composition) intrusive bodies, recognition of discrete intrusive phases for plutons formed in geologically short intervals, determination of subtle isotope– geochemical differences between rocks of different intrusive phases, and so on.

The present paper is devoted to the geochronological and isotope–geochemical study of one of the reference (but insufficiently studied) terranes of young granitoid magmatism in the Kazbek neovolcanic area of the Greater Caucasus. Data obtained suggests the existence of a single intrusive massif in the area. They make it possible to determine its timing, major petrochemical characteristics of granitoids, and possible sources of magmatic melts.

At the Greater Caucasus and its northern periphery, one can distinguish three stages of Late Cenozoic activity (Late Miocene, Pliocene, and Anthropogene) [1–7 and others]. Pliocene magmatism was mainly expressed in the formation of hypabyssal granite or granodiorite intrusions, as well as usually differentiated (from diorite to granites) intrusive massifs. The Elbrus neovolcanic area incorporates two granitoid massifs (Eldzhurtu and Dzhungusu), for which a great number of isotope, geochronological, isotope–geochemical, and thermochronological data are available [3, 4, and others]. Pliocene intrusive massifs in the Kazbek volcanic area, including the most well-known Tepli and Songuti-Don massifs, have been studied less. In the Kazbek area, plutonic bodies are typically localized in the sublatitudinal zone between Skalistyi Ridge in the north and the Main Caucasus Range in the south. The zone is extended from Mt. Shkhara in the west to Kazbek Volcano in the east. In addition, several small massifs are known on the southern slope of the Main Caucasus Range (Tsurungal, Karobi, and Kalkva). This vast area also includes numerous dikes varying in composition from granite porphyries to subalkaline diabases. Probably, some of them mark the paleovolcanic edifices whose products are present in the Rukhs-Dzuar Formation of the Ossetia depression. The age of this formation was determined on the basis of the faunal assemblage as the end of Pliocene. Geochronological data are scarce for young intrusive rocks of the Kazbek area. There are a few K-Ar datings on granitoids of the Songuti-Don and Tepli massifs (2.5-2.0 Ma), the Karobi and Tsurungal (4.5-4.0 Ma) and Kalkva (1.6 Ma) massifs on the southern slope of the Main Caucasus Range, as well as an andesite porphyrite dike in the upper reaches of the Urukh River (1.3 Ma) and dacite dikes in the Tepli massif (0.9 Ma) [2].

In 1996 and 2000, we carried out fieldwork near the Maili and Suatisi glaciers on the northern and southern slopes of the Khokh Ridge, respectively, in the Kazbek volcanic center. At the upper reaches of the Maili glacier, we could not investigate the "neointrusion" exposures because of difficult ice-cliff situation, but found a great number of boulders and blocks of unaltered granitoids. Cliffs of diorites and granodiorites, which crosscut and alter Jurassic black shales, are exposed sources of the Suatisi-Don River between three tongues of the Suatisi glacier. In this area (west of Kazbek Volcano), Belyankin described the outcrops of young granitoids in the upper reaches of the Suatisi-Don and Tepi-Don rivers as early as in 1914 [8]. He noted that the rocks are mainly represented by granodiorites and granites, while basic rocks ranging up to olivine-bearing gabbrodiorite are less abundant. Later, many geologists found young granitoids in different parts of the Khokh Ridge (upper

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**Fig. 1.** Geological map of the Dzhimara granitoid massif. Compiled by Lebedev based on field observations at the upper reaches of the Suatisi-Don River and large-scale geological maps of the area. (1) Glacier and snow fields; (2) Quaternary sediments; (3) late Quaternary lavas of the Kazbek volcanic center; (4) Pliocene granitoids of the Dzhimara massif; (5) Jurassic gabbroids; (6) Jurassic volcanosedimentary rocks; (7) Late Paleozoic sedimentary and metamorphic rocks

reaches of the Midagrabin, Maili, Kolka, Gol'da, and Suatisi glaciers). In the literature, they are mentioned as Tepi, Genal-Don, Midagrabin, and other massifs [9 and others]. A single K–Ar date  $(2.7 \pm 0.2 \text{ Ma})$  reported in [2] for granodiorites of the Midagrabin glacier indicates its Late Pliocene age. However, petrological and geochronological study of these massifs was not performed later due to their low accessibility.

The mapping of the Kazbek volcanic region (scale 1 : 50 000) in the middle 1980s made it possible to outline the major part of young granitoid exposures on Khokh Ridge and ascribe them to the Neogene neointrusion complex. However, some geologists continue to consider them as Paleogene or Cretaceous rocks [10]. At the same time, gabbroid bodies in the upper reaches of the Tepli-Don River were described as Jurassic rocks during the geological survey [8].

Based on field investigations, as well as published cartographic data, we compiled a refined geological map of young granitoids on Khokh Ridge (Fig. 1). We also took samples for petrological and isotope–geochronological investigations.

Compositionally, the studied rocks correspond to granodiorites with subordinate quartz diorites (tonalites) and occur as fine or medium-grained rocks with massive structure and hypidiomorphic texture. They are mainly composed of plagioclase, amphibole, and quartz with the occasional biotite. Plagioclase has a typically zoned structure with an andesine–labradorite core and andesine–oligoclase rim. Clinopyroxene relicts are found in the core of some amphiboles. Granitoids are often characterized by different degrees of secondary alterations (primarily, chloritization). Based on petrochemical parameters, the rocks belong to calc-alkaline series with high contents of Mg (Mg# 0.56–0.74), Cr (up to 71 ppm), and Ni (up to 47 ppm), as well as very high contents of Zr (up to 172 ppm) and Cl (up to 1864 ppm).

Geochemically, the rocks are comparable with both within-plate A-type granites and postcollisional I-type granites. In particular, their data points are plotted in the field of I-type granites in the K<sub>2</sub>O–Na<sub>2</sub>O, (Na<sub>2</sub>O + K<sub>2</sub>O)–CaO–SiO<sub>2</sub> and FeO<sup>tot\*</sup>(FeO<sup>tot</sup> + MgO)–SiO<sub>2</sub> diagrams [11]. In the Ba–Rb–Sr diagram, data points of studied rocks occupy intermediate position between average compositions of tholeiitic plagiogranites [12] and I-type granites [13]. In the Nb–Y diagram [14], they form a compact field corresponding to volcanic arc and syncollisional granites. By contrast, the propor-

Sample	Mineral	Potassium, $\% \pm \sigma$	$^{40}\text{Ar}_{rad}, \text{ng/g} \pm \sigma$	<sup>40</sup> Ar <sub>air</sub> , % sample	Age, Ma $\pm 2\sigma$
SU-6	Plagioclase	$0.41\pm0.015$	$0.094 \pm 0.005$	91.7	$3.3 \pm 0.3$
SU-8	Biotite	$7.55\pm0.06$	$1.42\pm0.06$	71.2	$2.72\pm0.15$
GZ-70	Biotite	$6.90\pm0.10$	$0.91\pm0.05$	75.1	$1.89\pm0.20$
	Plagioclase (rim)	$3.47\pm0.03$	$0.45\pm0.03$	89.7	$1.88\pm0.20$
	Plagioclase (core)	$0.74\pm0.015$	$0.121\pm0.007$	91.7	$2.35\pm0.25$
GZ-71	Plagioclase	$0.51\pm0.015$	$0.101\pm0.005$	92.8	$2.8 \pm 0.3$
115/66*	Biotite	$6.86\pm0.06$	$1.28\pm0.10$	79.0	$2.7 \pm 0.2$

Table 1. Results of the K-Ar dating of rocks from the Dzhimara massif

Note: (SU-6) Amphibole granodiorite, sources of the Suatisi-Don River; (SU-8) biotite–amphibole tonalite, sources of the Suatisi-Don River; (GZ-70) biotite–amphibole granodiorite, Maili glacier; (GZ-71) amphibole granodiorite, Maili glacier. (\*) K–Ar data obtained at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry for granodiorites of the Midagrabin glacier [2].

 Table 2. Sr and O isotopic compositions of rocks from the Dzhimara massif

Sample	Analyzed material	Rb, ppm	Sr, ppm	$^{87}$ Rb/ $^{86}$ Sr ± 2 $\sigma$	$^{87}$ Sr/ $^{86}$ Sr ± 2 $\sigma$	δ <sup>18</sup> O, ‰
GZ-70	Plagioclase (core)	15	925	$0.0471 \pm 6$	$0.705038 \pm 11$	$4.8 \pm 0.2$
	Plagioclase (rim)	85	760	$0.3235\pm9$	$0.705385 \pm 11$	_
SU-8	Whole-rock	64	554	$0.3370 \pm 9$	$0.705345 \pm 11$	_
	Biotite	398	18	$63.97 \pm 18$	$0.708082 \pm 11$	$3.1 \pm 0.2$
	Plagioclase	39	760	$0.1488 \pm 7$	$0.704889 \pm 10$	$6.3 \pm 0.2$
	Whole-rock	90	554	$0.4771 \pm 12$	$0.704886 \pm 11$	—
	Biotite	554	7.5	$213.2 \pm 6$	$0.714984 \pm 12$	$3.6 \pm 0.2$

Note: Rock name and sampling location are shown in Table 1.

tions of Zr, Ga, and Al (Zr– $10^4$  Ga/Al diagram [14]) in the rocks correspond to those in within-plate A-type granites. In the Y–Nb–Zr/4 and Y–Nb–3Ga diagrams [15], data points are plotted in the A<sub>1</sub> field, indicating their mantle–crustal origin. Thus, the chemical features of the studied granitoids suggests both crustal and significant mantle contribution, which can be explained by their formation under a complex geodynamic environment of continental collision combined with mantle hot field [7].

Four granitoid samples significantly differing in mineral and petrochemical composition were taken from the northern and southern slopes of Khokh Ridge for isotope study. The K-Ar and Rb-Sr isotope dating and determination of  $\delta^{18}$ O were conducted at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (Tables 1, 2). During K-Ar dating, the Ar isotopic composition was determined on a highly sensitive low-noise MI-1201 IG mass-spectrometric complex (SELMI, Ukraine). The main characteristics of the applied technique are scrutinized in [5]. The Rb and Sr isotope ratios were determined on a Micromass Sector 54 multichannel mass spectrometer with an error of 0.5 and 0.002% ( $2\sigma$ ), respectively. The oxygen isotopic composition was determined by E.O. Dubinina on a Delta Plus mass spectrometer. The measurement error of  $\delta^{18}$ O is  $\pm 0.2\%$ . Table 1 also demonstrates the K–Ar biotite date previously obtained at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry for granodiorite from the Midagrabin glacier [2].

As is seen in Table 1, the K-Ar dates point to the Late Pliocene age of the intrusive rocks of Khokh Ridge. This age is close to the formation age of granitoids of other Pliocene neointrusions in the Kazbek area and the entire Greater Caucasus. K-Ar data are subdivided into two discrete groups (~2 and 2.7-2.8 Ma). The first group includes granodiorites of the Maili glacier (sample GZ-70), while the second group includes granodiorites and quartz diorites (tonalites) of the Midagrabin, Suatisi, and Maili glaciers (samples GZ-71, SU-6, SU-8, 115/66). These datings can apparently be interpreted as evidence in favor of the existence of two intrusive phases significantly separated in time. However, the Rb-Sr and oxygen isotope data are inconsistent with this assumption. In the Rb-Sr diagram for biotiteamphibole granodiorite from the Maili glacier (sample GZ-70), data points of biotite, whole rock together with the labradorite-andesine core and oligoclase-sodic andesine rims of zoned plagioclase do not define a single isochron (Fig. 2), indicating a disturbance of the Rb-Sr isotope system of the studied granodiorites



Fig. 2. Rb–Sr isochron diagrams for the studied rocks of the Dzhimara massif.

owing to a superimposed process. The rocks exhibit distinct evidence of hydrothermal alteration, including partial chloritization of biotite. The development of propylitization is also supported by the oxygen isotopic composition of mineral phases in sample GZ-70. The oxygen isotope temperature calculated for granodiorite GZ-70 based on the biotite-plagioclase pair (Table 2) is 1050–1090°C, which is significantly higher than the closure temperature of oxygen isotopic systems of the granite-granodiorite rocks. It should be noted that the plagioclase-biotite pair yielded a reasonable range of closure temperature of the oxygen system (675–700°C) for petrographically similar biotite-amphibole tonalites taken at sources of the Suatisi-Don River (sample SU-8). One can suggest that the superimposed process, which could be related to emplacement of unstudied by us vounger granitoid phases, led to the disturbance of the Rb–Sr isotope system in granodiorite GZ-70 and the simultaneous complete resetting of K-Ar isotope systems in all minerals. This assumption is supported by identical dates obtained for phases having different closure temperatures of the K-Ar system. The positions of data points of minerals from sample GZ-70 in the Rb-Sr diagram (Fig. 2), as well as petrographic and geochemical data, indicate that the disturbance of the Rb-Sr isotope system could be related to the redistribution of Rb, K, and <sup>87</sup>Sr mainly between plagioclase rims and biotite during its chloritization. At the same time, based on the analysis of the plagioclase core-chloritefree biotite pair, the Rb–Sr age of granodiorite GZ-70 from the Maili glacier (with the K-Ar biotite data within 2.4–1.9 Ma) is estimated at 3.35  $\pm$  0.02 Ma  $([^{87}Sr/^{86}Sr]_0 = 0.705036 \pm 11)$ , which coincides, within the error limits, with the Rb-Sr isochron age of unaltered biotite-amphibole tonalite (sample SU-8) from sources of the Suatisi-Don River (Table 2, Fig. 2). In the Rb–Sr diagram, the data points of biotite, whole-rock, and plagioclase from tonalite SU-8 define a regression line corresponding to  $3.34 \pm 0.02$  Ma at  $[^{87}Sr/^{86}Sr]_0 = 0.704873 \pm 19$  (Fig. 2). Let us recall that the K–Ar biotite age of this tonalite is  $2.72 \pm 0.15$  Ma.

The Rb-Sr isochron age of unaltered tonalite from sources of the Suatisi-Don River (sample SU-8) is unambiguously interpreted as the cooling time of this rock below the closure temperature of the Rb-Sr system. In the case of altered granodiorite from the Maili glacier (sample GZ-70), for which the age has been calculated based on the biotite-plagioclase core pair, interpretation of the Rb-Sr isochron age requires some comments. It is known that subvolcanic and hypabyssal bodies are usually subjected to chloritization at lowtemperatures (less than 300°C). As mentioned above, the temperature parameters of this process are comparable with the opening temperature of K-Ar systems in minerals, but they are significantly lower than those of Rb-Sr systems of biotite (300-350°C) and labradorite (500–600°C). Therefore, we can believe that the Rb–Sr isotope systems of biotite and labradorite of the plagioclase core remained undisturbed during the superimposed process. Hence, age based on this mineral pair reflects the time of granodiorite cooling to the closure temperature of Rb-Sr isotope systems of constituent minerals after emplacement of magmatic melt in the framework rocks.

Thus, the Rb–Sr isotope data mentioned above indicate virtually simultaneous formation of the studied plutonic rocks of Khokh Ridge. We believe that the K– Ar mineral data on sample GZ-70 record the timing of propylitization, whereas the data on samples GZ-71, SU-6, SU-8, and 115/66 (2.8–2.7 Ma) indicate the cooling age of Khokh granitoids at temperatures below the closure temperature of K–Ar isotope systems in mineral phases of the studied rocks.

The similarity of the initial Sr isotopic compositions of samples GZ-70 and SU-8 (Fig. 2) and their  ${}^{87}$ Sr/ ${}^{86}$ Sr values (from 0.705036 ± 11 to 0.704873 ± 19) obvi-

ously indicate that granitoids of the Khokh Ridge are products of the evolution of a single parental melt. At the same time, these facts suggest the contribution of both crustal and mantle sources. It should be noted that similar Sr isotope characteristics are typical of recent hybrid rocks from the Kazbek volcanic center [7].

The data presented above indicate that the granitoids are characterized by rather similar chemical compositions, synchronous formation, and possible evolution from a common parental melt. Therefore, we can conclude that intrusions of Khokh Ridge are apical parts of an uneroded (possibly, multiphase) massif, which can be identified as the Dzhimara massif. The distribution of outcrops of young intrusive rocks on Khokh Ridge (Fig. 1) also suggests the presence of a weakly eroded single intrusion, which is similar to the Eldzhurtu or adjacent Tepli massif. All granitoid outcrops are restricted to Mt. Dzhimara (4780 m), the second highest point after Mt. Kazbek along Khokh Ridge. The upper part of the mount is composed of Jurassic shales. The apical part of the massif, which presumably composes the base of the mount, is presently exposed only in the valleys of rivers flowing in different directions (Suatisi-Don, Tepi-Don, Genal-Don, and Midagrabin-Don). A similar situation is observed in the western Tepli massif. For example, Mt. Tepli is composed of Jurassic rocks, while the Tepli massif is only exposed in river valleys as three individual outcrops (Lia-Don, Archon, and Fiag-Don).

Thus, the Dzhimara massif is the easternmost structure in the chain of the youngest massifs extending along the northern slope of the Main Caucasus Range. The observed discrepancy (~0.5 Ma) between the obtained K–Ar (2.8–2.7 Ma) and Rb–Sr (3.35 Ma) dates is explained well by different closure temperatures of the K–Ar and Rb–Sr mineral systems during a slow cooling rate of the massif within the temperature range of 400–200°C. We suggest that the true formation age of the Dzhimara massif is somewhat more than 3.35 Ma. The close location of the late Pliocene Dzhimara intrusion and the Quaternary Kazbek volcanic center suggests the existence of a long-lived magmatic system, which evolved in two (intrusive and volcanic) stages.

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