

# K–Ar Dating of Quaternary Volcanics: Methodology and Interpretation of Results

I. V. Chernyshev, V. A. Lebedev, and M. M. Arakelyants

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

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**Abstract**—The K–Ar method and its modifications play a unique role in the geochronology of young volcanic rocks, which has important fundamental and economic aspects. This method provides an opportunity for dating Quaternary rocks, from the oldest (1–2 Ma) to the most recent ones (<30 ka). This paper discusses physical and geochemical prerequisites for the use of the K–Ar method in the solution of this problem. The key factor providing favorable proportions of radiogenic and nonradiogenic  $^{40}\text{Ar}$  for the K–Ar system in volcanic rocks is the low solubility of argon (0.0n–0.0n ppb) in silicate melts and crystallizing rocks and minerals. The sources and controlling factors of errors in the K–Ar dating of young rocks were evaluated in detail. The main analytical problem in the K–Ar dating of young rocks is concerned with the conditions and methods of measurements of very low (0.0n–0.00n ppb) contents of radiogenic  $^{40}\text{Ar}$  accompanied by much higher (by a factor of 3–10 or even more) contents of nonradiogenic  $^{40}\text{Ar}$ . The main stages in the development of the K–Ar method in Russia and other countries that provided a solution to this problem are described. We describe the analytical mass spectrometer system and method designed in the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, which allowed us to carry out for the first time in Russia systematic studies on the geochronology of Quaternary volcanics up to late Pleistocene–Holocene age. The main characteristics of the method are the absolute sensitivity of measurements ( $5 \times 10^{-3}$  A/Torr) and background signal levels for argon isotopes ( $3 \times 10^{-3}$  ng  $^{40}\text{Ar}$  and  $1 \times 10^{-5}$  ng  $^{36}\text{Ar}$ ). The problems of excess radiogenic argon and variations in the initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in young volcanics are discussed. The results of an investigation of the distribution of K–Ar isotopes among various constituents of young volcanics and the corresponding approach to the choice of material (geochronometer) for analysis are presented. This approach is illustrated by the example of geochronological results for three volcanic centers of the Caucasus differing in the time of occurrence and duration of the active phase: Elbrus, Samsari, and Aragats. A tentative regional time scale was proposed for Neogene–Quaternary magmatic events. This scale generalized the available data for the Greater and Lesser Caucasus and embraces the period from the late Miocene (8.5 Ma) to the late Neopleistocene–Holocene (<35 ka). An interesting feature of the young magmatism of the Caucasus is the synchronous occurrence of distinctive types of volcanic activity in particular volcanic areas. An important prognostic aspect related to the proposed time scale of the young magmatism of the Caucasus is the evidence that the most recent stage of volcanic activity, the youngest occurrences of which were dated at a few thousands to tens of thousands of years, is not yet finished.

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## INTRODUCTION

In the current stage of development of isotopic geochronology, the dating of young volcanic rocks is an important application of the K–Ar method. This is due to two reasons. First, the K–Ar method appeared to be unparalleled for the dating of young, primarily Quaternary complexes among other geochronological methods based on the system long-lived radioactive isotope–radiogenic stable isotope. Other methods are either inapplicable for the dating of rocks younger than 1.0–1.5 Ma or their results are less accurate and reliable. The prospects of other methods for dating young volcanics ( $^{14}\text{C}$ , Rb–Sr, etc.) were evaluated in more detail in our previous paper (Chernyshev *et al.*, 2002b). The second reason is concerned with the theoretical and practi-

cal importance of targets for dating and the universal interest to the investigation of active and dormant volcanoes.

Volcanic rocks are the main source of geological and geochemical information on the chronology of the most recent stage of magmatism in the Earth's history. The results of isotopic and geochronological studies, primarily the data obtained by the K–Ar method, provide a quantitative basis for stratigraphy, geological mapping, and petrological and geodynamic reconstructions. Modern methods and analytical facilities provide an accuracy or resolution of the K–Ar dating of Quaternary volcanic rocks between a few thousands to a few tens of thousands of years. This is sufficient for the comprehensive deciphering of the chronology of erup-

tion of Quaternary volcanoes and volcanic centers, from the most ancient (1–2 Ma) to the most recent (<30 ka) stages of their activity, quantification of the duration of volcanic processes, and determination of activity periods for particular volcanoes.

Another aspect of isotopic geochronological investigations of young, primarily Quaternary volcanoes is related to the prediction of probable volcanic catastrophes. In this context, of special prognostic significance is the timing of magmatic activity of volcanoes and the dates of their most recent eruptions. In the past 7–10 years, this practical aspect has stimulated isotopic geochronological investigations of Quaternary volcanoes in Japan, North America, and the Mediterranean belt, including the Caucasus.

During 1999–2004, we performed more than 250 K–Ar datings for rocks of major volcanic centers of the Caucasus in Russia, Georgia, and Armenia: the Elbrus, Kazbek, Kel', and Dzhava centers in the Greater Caucasus and the Samsari, Aragats, and Geghama centers in the Lesser Caucasus (Chernyshev *et al.*, 1999, 2001, 2002a, 2002b; Lebedev *et al.*, 2003, 2004a, 2004b, 2004c; Arutyunyan *et al.*, 2003; Medvedeva *et al.*, 2003). In addition to K–Ar dating, Rb–Sr and Sm–Nd isotopic characteristics were determined in various mineral components of some samples. These data provided insights into the specific features of isotopic systems of young volcanic rocks and allowed us to develop a methodical approach for obtaining correct K–Ar dates. These investigations are part of a program conducted at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences on the investigation of the geochronology of young and recent volcanism in Eurasia, which involves the volcanism of the Caucasus, southern Siberia, Transbaikalia, Mongolia, and Russia's Far East.

This paper addresses the physical and geochemical prerequisites for the use of the K–Ar method for dating young igneous rocks, sources of errors in age estimates, and fundamental aspects of the technique of measurements of ultralow contents of radiogenic argon, which provided a basis for our investigations cited above. Based on the investigations of K and Ar isotope partitioning among various constituents of young volcanics, an approach to the choice of the analyzed geochronometer material is discussed by the example of geochronological results for three volcanic centers of the Caucasus differing in the time of occurrence and duration of active phases: Elbrus, Samsari, and Aragats. Generalizing the available data, a tentative regional time scale is presented for Neogene–Quaternary magmatic events in the Greater and Lesser Caucasus.

## PREREQUISITES FOR THE USE OF THE K–Ar METHOD FOR DATING YOUNG VOLCANIC ROCKS

### *Physical and Geochemical Prerequisites*

The amount of radiogenic  $^{40}\text{Ar}$  which has formed in volcanic rocks of Late–Middle Quaternary age, i.e., during a time span of tens to a few hundreds of thousands of years, is usually about 0.02–0.002 ppb. Such concentrations of  $^{40}\text{Ar}_{\text{rad}}$  are characteristic of continental intermediate and silicic volcanics of such ages with potassium contents of 1.5–3.5 wt %. Correspondingly, the rocks of Eopleistocene (1.8–0.8 Ma) and Pliocene (5.3–1.8 Ma) age have  $^{40}\text{Ar}_{\text{rad}}$  contents of 0.n ppb and usually no higher than 1 ppb. Of crucial importance for the dating of young, especially Quaternary volcanics by the K–Ar method is that such small contents of  $^{40}\text{Ar}_{\text{rad}}$  are detectable and measurable against the background content of in the rocks. The presence of atmospheric  $^{40}\text{Ar}$  is inferred from the ratio of argon isotope abundances characteristics of the Earth's atmosphere ( $^{40}\text{Ar}/^{36}\text{Ar} = 295.5$ ).

One favorable factor for the possibility of the determination of  $^{40}\text{Ar}_{\text{rad}}$  in Quaternary rocks is the relatively high rate of accumulation of this isotope, which is controlled mainly by the constant of  $^{40}\text{K}$  electron-capture decay. In terms of this parameter, the  $^{40}\text{K}$ – $^{40}\text{Ar}$  system is superior to the  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  system by an order of magnitude and to the  $^{87}\text{Rb}$ – $^{87}\text{Sr}$ ,  $^{187}\text{Re}$ – $^{187}\text{Os}$ , and  $^{176}\text{Lu}$ – $^{176}\text{Hf}$  systems by a factor of 2–3. However, it is inferior to the  $^{235}\text{U}$ – $^{207}\text{Pb}$  and  $^{238}\text{U}$ – $^{206}\text{Pb}$  systems.

The high contents of potassium in the silicate rocks and minerals that are commonly used as geochronometers offer no advantages to the K–Ar method compared with the aforementioned systems, even for dating young rocks. Indeed, the range of most common potassium contents (0.1–10 wt %) corresponds to four orders of magnitude lower concentrations of the radioactive isotope  $^{40}\text{K}$  (0.01–10 ppm). The latter are comparable and even often lower than the abundances of  $^{87}\text{Rb}$ ,  $^{147}\text{Sm}$ ,  $^{238}\text{U}$ ,  $^{232}\text{Th}$ , and other radioactive isotopes in silicate rocks and minerals.

The key factor providing radiogenic to nonradiogenic  $^{40}\text{Ar}$  ratios in volcanic rocks favorable for K–Ar dating is the low solubility of argon in silicate melts and crystallizing rocks and minerals. According to experimental data, the solubility of argon in basalts and andesites at atmospheric pressure in air is 2.0–0.4 ppb (McDougall and Harrison, 1988). The concentration of atmospheric argon in crystallized volcanic rocks is an order of magnitude lower, and numerous isotopic analyses of young volcanic rocks gave about 0.n–0.0n ppb. This is explained by the additional melt degassing during phase transformations accompanying crystallization and vitrification. Thus, the amount of radiogenic  $^{40}\text{Ar}$  that has accumulated in lavas during tens to hundreds of thousands and, especially, millions of years after their crystallization and cooling (0.n–0.00n ppb) is of a similar order of magnitude to the concentration

of atmospheric  $^{40}\text{Ar}$ . The  $^{40}\text{Ar}_{\text{atm}}/(^{40}\text{Ar}_{\text{atm}} + ^{40}\text{Ar}_{\text{rad}})$  ratio characterizing the proportions of these  $^{40}\text{Ar}$  components in young rocks varies from 0.4–0.5 to 1.0. It depends on the age, composition, and formation conditions of particular rocks.

The low solubility of argon in magmas and rocks at atmospheric pressure results in low  $^{40}\text{Ar}_{\text{atm}}$  contents in them and eliminates the effect of entrapment of excess radiogenic  $^{40}\text{Ar}$  by crystallizing solid phases of volcanic rocks from cooling and degassing melt. The presence of excess  $^{40}\text{Ar}_{\text{rad}}$  was detected only in submarine lavas, which were formed under conditions of high hydrostatic pressure, and in minerals from intrusive rocks (Dalrymple and Moore, 1968; Roddick *et al.*, 1980; etc.).

The K–Ar system of young volcanic rocks is in principle rather sensitive to the presence of excess  $^{40}\text{Ar}_{\text{rad}}$  owing to the low content of radiogenic  $^{40}\text{Ar}$  accumulated *in situ* after rock crystallization and cooling. In the last decade, comprehensive studies of Quaternary and Pliocene volcanics have shown that variable amounts of excess  $^{40}\text{Ar}_{\text{rad}}$  occur only in high-pressure phenocrysts that crystallized in magmas before their surface eruption (Matsumoto and Kobayashi, 1995; Singer *et al.*, 1998; etc.). There is no evidence for the presence of excess radiogenic argon in the microlitic or glassy groundmass of young continental lavas crystallizing after magma eruption on the surface.

The nature of excess radiogenic argon in young volcanics is an interesting problem and is discussed below in connection with the choice of material used as a K–Ar geochronometer for the dating of lavas of various compositions.

#### Sources and Controlling Factors of Dating Errors

An important feature of the K–Ar dating of young rocks is related to the conditions and methods of measurement of very low (0.0n–0.00n ppb) contents of radiogenic  $^{40}\text{Ar}$  associating with 3–10 times higher contents of nonradiogenic  $^{40}\text{Ar}$ . This, first, dictates requirements to the parameters of the analytical facilities, which are certainly the highest among other applications and modifications of the K–Ar method. Second, the correct estimation of the errors of obtained age values is an essential part of the dating of young rocks. Age estimates, especially for Late and Middle Quaternary rocks, are crucially dependent on the uncertainties in the isotopic analysis of argon, the total background of the measurement system, and the aforementioned  $^{40}\text{Ar}_{\text{atm}}/(^{40}\text{Ar}_{\text{atm}} + ^{40}\text{Ar}_{\text{rad}})$  ratio in the sample. There are some other factors affecting the dependence of the resulting age error on the uncertainties of the initial values that distinguish the K–Ar dating of Quaternary and Pliocene rocks from the dating of older rocks. Consider these problems in more detail.

The maximum error of K–Ar age, which is a function of several experimentally determined values, is in general expressed as

$$\delta T = \sum_{i=1}^n \left( \frac{\partial T}{\partial x_i} \frac{x_i}{T} \right) \delta x_i = \sum_{i=1}^n A_i \delta x_i \quad (1)$$

or

$$\delta T = A_1 \delta \lambda_{\beta} + A_2 \delta \lambda_{\text{K}} + A_3 \delta R + A_4 \delta \text{K} + A_5 \delta ^{40}\text{Ar}_{\text{rad}}, \quad (2)$$

where  $T$  is the age,  $\delta T$  is its relative error;  $x_i$  are the directly measured values and the parameters (constants) used for the calculation of K–Ar age;  $\delta x_i$  are their relative errors;  $A_i$  are the coefficients depending on  $x_i$  and  $T$ ;  $\lambda_{\beta}$  and  $\lambda_{\text{K}}$  are the constants of  $\beta$ -decay and electron capture of  $^{40}\text{K}$ , respectively;  $\delta \lambda_{\beta}$  and  $\delta \lambda_{\text{K}}$  are their relative errors;  $R$  is the abundance of  $^{40}\text{K}$  in the natural mixture of potassium isotopes;  $\delta R$  is its relative error;  $\text{K}$  and  $^{40}\text{Ar}_{\text{rad}}$  are the contents of potassium and radiogenic argon in the sample;  $\delta \text{K}$  is the relative error of potassium content in the sample; and  $\delta ^{40}\text{Ar}_{\text{rad}}$  is the relative error of radiogenic argon content in the sample.

The coefficients  $A_i$  in Eq. (2) are always positive independent of the sign of the partial derivatives  $\partial T/\partial x_i$  and are expressed as

$$A_1 = \frac{\lambda_{\beta}}{\lambda} \left( 1 - \frac{1 - e^{-\lambda T}}{\lambda T} \right), \quad (3)$$

$$A_2 = \frac{\lambda_{\beta}}{\lambda} \left( \frac{\lambda_{\text{K}}}{\lambda_{\beta}} + \frac{1 - e^{-\lambda T}}{\lambda T} \right), \quad (4)$$

$$A_3 = A_4 = A_5 = \frac{1 - e^{-\lambda T}}{\lambda T}, \quad (5)$$

where  $\lambda = \lambda_{\beta} + \lambda_{\text{K}}$ .

The desired age value,  $T$ , is the only variable in the expressions for  $A_i$ , which characterize the contributions of particular errors into  $\delta T$ . It can be readily shown that, if  $T \rightarrow 0$ , four of the five coefficients, namely,  $A_2$ ,  $A_3$ ,  $A_4$ , and  $A_5$ , approach one and lie between 0.99 and 1.0 within the whole range of Cenozoic ages, from 0 to 60 Ma.  $A_1$  approaches zero when  $T \rightarrow 0$  and varies between 0 and 0.006 in the above age range. Note that  $A_2$ ,  $A_3$ ,  $A_4$ , and  $A_5$  decrease for older ages to about 0.9 at  $T = 400$  Ma and 0.7 at  $T = 1.5$  Ga. In contrast,  $A_1$  increases to 0.09 at  $T = 400$  Ma and 0.28 at  $T = 1.5$  Ga.

Thus, since the values of  $A_i$  are close to one, i.e., almost maximum, the contributions (or weights) of analytical errors and uncertainties of constants (except for  $\lambda_{\beta}$ ) to the errors in the K–Ar age of young rocks are higher compared with pre-Cenozoic and, especially, Precambrian rocks.

As to the numerical estimates, note that the values  $\lambda_{\beta} = 4.962 \times 10^{-10} \text{ y}^{-1}$ ,  $\lambda_{\text{K}} = 0.581 \times 10^{-10} \text{ y}^{-1}$ , and

$R = 0.01167\%$  that are universally accepted in accordance with the recommendation of the Subcommittee on Geochronology of the IUGS (Steiger and Jager, 1977) are associated with the following uncertainties:  $\delta\lambda_{\beta} = 0.2\%$ ,  $\delta\lambda_{\alpha} = 0.9\%$  (Beckinsale and Gale, 1969), and  $\delta R = 0.4\%$  (Garner *et al.*, 1975). Their total effect in accordance with Eqs. (1)–(4) is 1.3%, which is the maximum possible error for the determination of K–Ar age of young rocks related to the uncertainties in the currently accepted values of constants. It can be easily seen that this value is defined by the sum of  $\delta\lambda_{\alpha}$  and  $\delta R$ , whereas the contribution of the uncertainty in the constant of  $\beta$ -decay of  $^{40}\text{K}$  is negligible for young rocks because of the small  $A_1$  value.

In contrast to the errors of constants, random uncertainties are usually associated with the measurement of potassium content, and during the dating of young volcanic rocks they are not fundamentally different from the values obtained from the application of the K–Ar method for the dating of Phanerozoic and Precambrian complexes. Despite the certain difference in the choice of material for the analysis during the K–Ar dating of Late Cenozoic volcanics (microlitic or glassy groundmass separated from phenocrysts) and more ancient igneous rocks (micas, feldspars, and amphiboles), the concentrations of potassium in the majority of samples fall within a rather narrow range (0.5–8.0 wt %). In recent studies such concentrations were commonly measured with uncertainties of 1.0–1.5% relative by flame spectrophotometry using optimized analytical conditions. The uncertainty increases up to 3% relative and more at lower potassium contents (<0.5 wt %), which may occur in volcanic rocks of intermediate and basic compositions. In such cases, and also when it is necessary to analyze microscopic samples of potassium-bearing minerals, for instance, individual phenocrysts, the uncertainty in the measurement of potassium content can be reduced to <1% relative by using isotope dilution mass spectrometry. Thus, variable uncertainty is associated with the measurement of potassium content ( $\delta K$ ) during dating of young volcanic rocks. However, its contribution into the age error,  $\delta T$ , accounting for  $A_4 \approx 1$  is about 1.5% relative in modern studies.

Consider the main source of errors in the K–Ar dating of young rocks, the uncertainty in the measurement of the concentration of radiogenic argon [ $\delta^{40}\text{Ar}_{\text{rad}}$  in Eq. (2)]. The use of isotope dilution mass spectrometry with a pure  $^{38}\text{Ar}$  spike<sup>1</sup> the maximum relative error of  $\delta^{40}\text{Ar}_{\text{rad}}$  is defined by the sum

$$\delta^{40}\text{Ar}_{\text{rad}} = \delta Q + \delta\alpha_{\text{mix}} + \frac{\alpha_{\text{atm}}}{\alpha_{\text{sample}} - \alpha_{\text{atm}}} (\delta\alpha_{\text{atm}} + \delta\alpha_{\text{sample}}), \quad (6)$$

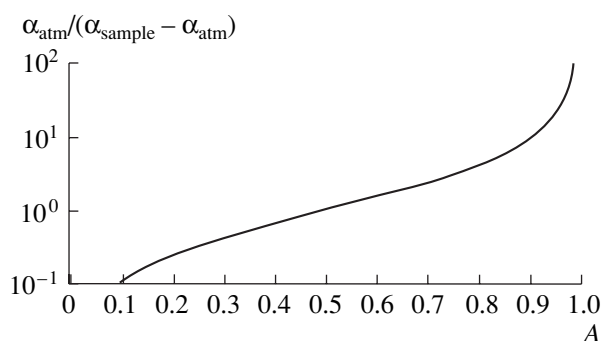
where  $Q$  is the amount of pure  $^{38}\text{Ar}$  spike,  $\delta Q$  is the relative error of dosing the spike;  $\alpha_{\text{mix}}$  is the ratio  $^{40}\text{Ar}/^{38}\text{Ar}$  in the sample–spike mixture;  $\alpha_{\text{sample}}$  and  $\alpha_{\text{atm}}$  are the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios in the sample and atmospheric argon, respectively; and  $\delta\alpha_{\text{mix}}$ ,  $\delta\alpha_{\text{sample}}$ , and  $\delta\alpha_{\text{atm}}$  are the relative errors of the mass spectrometric measurements of the corresponding isotopic ratios. Note that the error of sample weighing is not accounted for by Eq. (6), because the use of modern analytical balances with a precision of  $\pm 0.02$  mg leads to a weighing error of <0.1% even for the smallest charges used in the K–Ar method (20 mg).

The value  $\delta\alpha_{\text{atm}}$  is not an analytical or measurement error *sensu stricto*. It is a possible deviation of the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of nonradiogenic argon, which is involved in the sample analysis, from a standard value of 295.5, which is used to correct the measured total amount of  $^{40}\text{Ar}$  for the admixture of nonradiogenic  $^{40}\text{Ar}$ . Given the low level of the total background of the analytical system,<sup>2</sup> which is no higher than 0.005 ng  $^{40}\text{Ar}$  in most of the recent studies on the K–Ar dating of young volcanics (e.g., Guillou *et al.*, 1997), nonradiogenic argon involved in analyses is mainly represented by air argon from the samples (usually no less than 60% in rocks younger than 0.5 Ma). Taking into account the available data on variations in the initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in the lavas of historic eruptions (Matsumoto and Kobayashi, 1995; Sudo *et al.*, 1998) and the convergence of K–Ar ages obtained from various horizons of Quaternary lava flows (Matsumoto and Kobayashi, 1995; Sudo *et al.*, 1998; Lebedev *et al.*, 2005), it can be inferred that the initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in the majority of young volcanics differed from the reference value (295.5) by no more than 0.1–0.2%. However, in some cases this difference (i.e.,  $\delta\alpha_{\text{atm}}$ ) is rather high (up to 3–5%), which may result in spurious K–Ar age estimates for young rocks (Matsumoto and Kobayashi, 1995).

Each of the three other errors,  $\delta\alpha_{\text{sample}}$ ,  $\delta\alpha_{\text{mix}}$ , and  $\delta Q$ , appearing in Eq. (6) are composed in turn of (1) uncertainties of the mass spectrometric isotopic analysis of argon of the spike, sample, and spike–sample mixture; (2) errors in the calibration of the mass spectrometer using an argon standard or volume calibration of the system of spike dosing (for  $\delta Q$ ). It is known that the numerical values of  $\delta\alpha_{\text{sample}}$ ,  $\delta\alpha_{\text{mix}}$ , and  $\delta Q$  depend on the class and analytical capacity of the instruments and various details in the analytical procedure. However, the uncertainties  $\delta\alpha_{\text{sample}}$  and  $\delta\alpha_{\text{mix}}$  may vary even during routine operations in a single laboratory performed using an optimized method, because  $\delta\alpha_{\text{sample}}$

<sup>1</sup> Other possible variants of the isotope dilution analysis of  $^{40}\text{Ar}_{\text{rad}}$ , namely, the use of argon spikes enriched in  $^{36}\text{Ar}$  or with the atmospheric isotopic composition, are not discussed here. It was previously shown (Gol'tsman *et al.*, 1964; Shanin and Chernyshev, 1967; etc.) that these variants are inferior to the use of pure  $^{38}\text{Ar}$  in terms of the accuracy of results and other analytical characteristics of the method. The advantages of the variant with  $^{38}\text{Ar}$  are especially important for the dating of young rocks.

<sup>2</sup> According to the accepted terminology, this is the value of a hot blank experiment.



**Fig. 1.** Influence of the amount of atmospheric  $^{40}\text{Ar}$  in the sample expressed as  $A$  on the uncertainty of determination of radiogenic  $^{40}\text{Ar}_{\text{rad}}$ .

and, to a lesser extent,  $\delta\alpha_{\text{mix}}$  are inversely dependent on the amount of analyzed argon and, consequently, on such parameters as the age, potassium content, and weight of the sample.

The error of dosing ( $\delta Q$ ) of the amount of spike, which approaches pure  $^{38}\text{Ar}$ , is not very variable and only weakly dependent on mass spectrometric measurements. The main sources are the calibration of  $^{38}\text{Ar}$  concentration in the dosing volume performed using the most reliable geochronological standards and the technique of collection of the desired spike volume. The resulting  $\delta Q$  is 0.5–1.0%.

The improvement of the techniques of the K–Ar method, which opened the possibility of dating young rocks and has promoted the development of this research field, included not only the reduction of mass spectrometric errors (i.e.,  $\delta\alpha_{\text{sample}}$  and  $\delta\alpha_{\text{mix}}$ ) but, to a greater extent, a decrease in the amount of argon necessary for analysis. This was achieved, first, by an improvement in the absolute sensitivity of instruments (or coefficient of the use of gas sample expressed in A/Torr) and, second, the reduction of backgrounds in the mass spectrometer and extraction system for argon and other substances giving isobaric interferences with argon isotopes.

In recent studies on the dating of Quaternary volcanics by very sensitive mass spectrometers (about  $5 \times 10^{-3}$  A/Torr), the accuracy of  $^{40}\text{Ar}/^{36}\text{Ar}$  measurement was nonetheless often limited by the low amounts of argon compared with similar measurements in older rocks, which resulted in low ion currents of  $\text{Ar}^+$ . In principle, this situation can be improved by increasing the amount of argon involved into the analysis, but an increase in the sample weight above 100–200 mg is very undesirable for modern low-background extraction systems.

Our studies and the results of other authors on the dating of young volcanic rocks (Chernyshev *et al.*, 1999, 2001, 2002a; Lebedev *et al.*, 2003, 2004a, 2004b, 2004c; Matsumoto and Kobayashi, 1995; Guillou *et al.*, 1997; etc.) allowed us to quantitatively estimate

the typical errors of argon isotope analyses obtained in recent studies by mass spectrometers with an absolute sensitivity of about  $10^{-3}$  A/Torr in static mode. During the measurement of  $^{40}\text{Ar}/^{36}\text{Ar}$ , which is usually within 295.5–370.0 in the total argon of Quaternary volcanics, the precision of results of parallel analyses of different argon portions extracted from a single sample is 0.2–0.5%. This value is accepted as an estimate of  $\delta\alpha_{\text{sample}}$ . (The standard uncertainty of the internal convergence of measurements of a single gas portion is almost an order of magnitude lower, 0.02–0.1%.) All other analytical conditions being equal, the error of measurement of the  $^{40}\text{Ar}/^{38}\text{Ar}$  ratio in the sample–spike mixture ( $\delta\alpha_{\text{mix}}$ ) is 1.5–2.0 times lower than  $\delta\alpha_{\text{sample}}$ , which is explained for usual values of this ratio of about 0.2–1.0 by considerably higher intensities of the current of  $^{38}\text{Ar}^+$  compared with the intensity of  $^{36}\text{Ar}^+$  during the measurement of the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio.

In contrast to the errors  $\delta Q$  and  $\delta\alpha_{\text{mix}}$ , which are summed in accordance with Eq. (6) with constant coefficients of one, the contributions of  $\delta\alpha_{\text{sample}}$  and  $\delta\alpha_{\text{atm}}$  into the  $\delta^{40}\text{Ar}_{\text{rad}}$  value are controlled by the variable coefficient  $\alpha_{\text{atm}}/(\alpha_{\text{sample}} - \alpha_{\text{atm}})$ , which depends on the content of atmospheric  $^{40}\text{Ar}$  in the bulk argon of the sample ( $A$ ):

$$\frac{\alpha_{\text{atm}}}{\alpha_{\text{sample}} - \alpha_{\text{atm}}} = \frac{A}{1 - A}, \quad (7)$$

where  $A = ^{40}\text{Ar}_{\text{atm}}/(^{40}\text{Ar}_{\text{atm}} + ^{40}\text{Ar}_{\text{rad}})$ .<sup>3</sup> The parameter  $A$  was mentioned above in connection with the discussion of argon solubility in silicate magmas and rocks and is usually reported together with analytical data and the results of K–Ar dating, which allows one to qualitatively estimate the reliability of calculated age values. Equation (7) provides a means for quantifying the influence of  $A$  through the coefficient  $\alpha_{\text{atm}}/(\alpha_{\text{sample}} - \alpha_{\text{atm}})$  on the error of measurement of the content of radiogenic argon,  $\delta^{40}\text{Ar}_{\text{rad}}$  (Fig. 1).

The numerous available K–Ar datings obtained up to now by modern low-background analytical instruments and methods have shown that  $A = 0.5$  is practically the lowest possible value for Quaternary volcanic rocks. This case is the most favorable, because the coefficient  $\alpha_{\text{atm}}/(\alpha_{\text{sample}} - \alpha_{\text{atm}})$  or the weight of  $\delta\alpha_{\text{sample}}$  and  $\delta\alpha_{\text{atm}}$  is equal to one. Within the range  $A = 0.5$ – $0.9$ , which is the most common in Quaternary volcanics,  $\alpha_{\text{atm}}/(\alpha_{\text{sample}} - \alpha_{\text{atm}})$  increases rapidly from 1 to 9. A dramatic increase in this coefficient is observed at  $A > 0.9$ , when the weight of  $\delta\alpha_{\text{sample}}$  and  $\delta\alpha_{\text{atm}}$  increases by a factor of 10 or more. The situation when  $A$  is much higher than 0.9 and approaches 1 corresponds to  $^{40}\text{Ar}_{\text{atm}} \gg ^{40}\text{Ar}_{\text{rad}}$ . It may occur either (1) during the analysis of very young samples of late Neopleistocene–Holocene age, when a very low  $^{40}\text{Ar}_{\text{rad}}$  content is accompanied by

<sup>3</sup> Coefficient  $A$  is expressed here for the convenience of error evaluation in fractions of one. However, in Tables 3–7 presenting K–Ar geochronological data,  $A$  is expressed in percent.

ordinary  $^{40}\text{Ar}_{\text{atm}}$ , or (2) at anomalously high contents of atmospheric argon ( $^{40}\text{Ar}_{\text{rad}}$ ), which are often observed in ignimbrites, altered lavas, and glasses. The latter case concerns the dating of both Late Quaternary and older rocks, for instance, Pliocene volcanics, because the contribution of radiogenic  $^{40}\text{Ar}$  has no significant effect on the value of  $A$  at high  $^{40}\text{Ar}_{\text{atm}}$  contents.

The lower left segment of the curve in Fig. 1 characterizes the relationships between  $A$  and  $\alpha_{\text{atm}}/(\alpha_{\text{sample}} - \alpha_{\text{atm}})$  for a common case of the K–Ar dating of various Mesozoic and older rocks. There is extensive analytical data showing that  $A$  lies in such a case within 0.05–0.5, and usually within 0.1–0.3. Correspondingly,  $\alpha_{\text{atm}}/(\alpha_{\text{sample}} - \alpha_{\text{atm}})$  is practically always below 1 and usually 0.1–0.4.

Thus, compared with the dating of ancient rocks, the K–Ar dating of young, especially Late Quaternary volcanic rocks is characterized by significantly different dependence of the error of measurement of radiogenic argon content and, accordingly, the error of age determination on the raw analytical errors. In the case of ancient rocks,  $\delta^{40}\text{Ar}_{\text{rad}}$  is mainly controlled by the sum of  $\delta Q$  and  $\delta\alpha_{\text{mix}}$ , i.e., the errors related to the method of isotope dilution, whereas the contributions of  $\delta\alpha_{\text{sample}}$  and  $\delta\alpha_{\text{atm}}$  are from 0.5 to 0.1 of their values. During the analysis of young rocks,  $\delta^{40}\text{Ar}_{\text{rad}}$  also includes the sum of  $\delta Q$  and  $\delta\alpha_{\text{mix}}$ , but the major contribution is that of the error of measurement of the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio ( $\delta\alpha_{\text{sample}}$ ) and the uncertainty in the initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in the sample ( $\delta\alpha_{\text{atm}}$ ).

As was mentioned above, there is a problem of  $\delta\alpha_{\text{atm}}$  estimation, which is related to the possible, sometimes demonstrated, departure of the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in the nonradiogenic Ar component from an accepted standard (atmospheric) value of 295.5. It should be emphasized that this problem is especially important for the dating of young volcanic rocks, because the content of atmospheric argon in the sample exerts a dramatic influence on the contribution of  $\delta\alpha_{\text{atm}}$  into the total error, which was noted above (Fig. 1). It is obvious that this problem cannot be solved by metrological approaches within the traditional K–Ar method. However, its importance and the interest to the determination of the real initial  $^{40}\text{Ar}/^{36}\text{Ar}$  value stimulated the development of a special technique known as the unspiked K–Ar method for the dating of young volcanics. The analysis of this method, its advantages and limitations, is beyond the scope of this paper, and we only mention some key publications on the unspiked method (Cassignol *et al.*, 1978; Gillot and Cornette, 1986; Takaoka, 1989; Matsumoto *et al.*, 1989; Matsumoto and Kobayashi, 1995; Guillou *et al.*, 1997; Sudo *et al.*, 1998).

Using the above numerical estimates of analytical uncertainties<sup>4</sup>, we calculated total errors,  $\delta^{40}\text{Ar}_{\text{rad}}$ , corresponding to some average or characteristic values of

**Table 1.** Dependence of the total errors of measurement of radiogenic argon content,  $\delta^{40}\text{Ar}_{\text{rad}}$ , and age estimation,  $\delta T$ , on the concentration of atmospheric argon in samples

$A = ^{40}\text{Ar}_{\text{atm}}/(^{40}\text{Ar}_{\text{atm}} + ^{40}\text{Ar}_{\text{rad}})$	$\delta^{40}\text{Ar}_{\text{rad}}$ , %	$\delta T$ , %
0.2 (ancient rocks)	1.5	3
0.5 (Neogene volcanics)	3	4.5
0.9 (Early Quaternary volcanics)	8	9.5
0.97 (Late Quaternary volcanics)	25	26.5

atmospheric argon content in samples, i.e.,  $A$  values (Table 1).

The resulting analytical uncertainty in the determination of K–Ar age,  $\delta T$ , which includes both  $\delta^{40}\text{Ar}_{\text{rad}}$  and the error of potassium measurement,  $\delta K$  [Eqs. (2) and (5)], is significantly higher (by 1.5%) than a  $\delta^{40}\text{Ar}_{\text{rad}}$  value of 3–5% associating with the dating of relatively old (pre-Quaternary) rocks. However, in the case of Quaternary and, especially, Neopleistocene rocks, this difference is insignificant, and the resulting uncertainty of dating,  $\delta T$ , is controlled almost entirely by the error of measurement of low and ultralow contents of radiogenic argon.

#### *Development of the K–Ar Method and Previous Work on the Geochronology of Cenozoic Volcanism*

The development of various aspects of the K–Ar method (determination of the decay constant of  $^{40}\text{K}$ , improvement of analytical methods, investigation of argon behavior under various conditions, etc.) began immediately after Aldrich and Nier (1948) and Gerling and Titov (1949) had experimentally confirmed the hypothesis of the radiogenic origin of  $^{40}\text{Ar}$  through electron capture by the  $^{40}\text{K}$  nucleus. These studies and the early applications of the K–Ar method utilized rather old, mainly Archean rocks and minerals with very high radiogenic argon contents, up to 1–2 nmm<sup>3</sup>/g (about 2000–4000 ppb). In early studies, the volume method (Gerling, 1961) was used for the measurement of argon content.

The advent of isotope dilution (ID) mass spectrometry in 1950 (Inghram *et al.*, 1950) was of crucial importance for the following progress of K–Ar geochronometry and its application. Its use for the determination of argon content was the main prerequisite for the first successful attempts of the K–Ar dating of Late Cenozoic magmatic complexes (Everenden *et al.*, 1957, 1964; Everenden and Curtis, 1965), where the concentration of radiogenic argon was 3–4 orders of magnitude lower than in Precambrian rocks. The following practical application of the possibilities of the ID method in terms of analytical sensitivity and accuracy, which are not yet exhausted, was associated with the work of researchers from various countries, including the USSR and, then, Russia, on the construction of

<sup>4</sup> The maximum values were used.

special mass spectrometers and low-background apparatuses for argon extraction and purification from rocks and minerals and development of methods and procedures for argon analysis.

In 1962 L.L. Shanin with colleagues developed in detail and applied at the IGEM a variant of the ID method optimized in terms of sensitivity and accuracy with the  $^{38}\text{Ar}$  monoisotope as a spike.  $^{38}\text{Ar}$  was specially produced for this purpose in a nuclear reactor by irradiation of ampoules with aluminum chloride via the reaction  $^{37}\text{Cl}(n) \rightarrow ^{38}\text{Cl} \xrightarrow{\beta^-} ^{38}\text{Ar}$ .

This variant of the ID method was described in detail by Gol'tsman *et al.* (1964) and provided a basis for the subsequent development of the K–Ar method, which resulted in a series of methodical and analytical studies on the mass spectrometric isotopic analysis of argon concerned with the evaluation of the sources of errors, metrology of measurement of radiogenic argon, and means for the improvement of the techniques of vacuum extraction of argon, loading of small gas samples, and other experimental aspects of the K–Ar method (Shanin and Chernyshev, 1967; Shanin *et al.*, 1967; *etc.*).

The achieved sensitivity of isotopic analysis and the total background level of the whole measurement system with respect to air argon provided an opportunity to measure radiogenic  $^{40}\text{Ar}$  contents of about 0.5–2.0 ppb in potassium-bearing mineral samples weighing about 2 g and launch the dating of Late Cenozoic igneous rocks in Russia (Afanas'ev *et al.*, 1964; Arakelyants *et al.*, 1968; *etc.*). The main facilities used in this work were a fundamentally modernized MI-1301 mass spectrometer and a special glass argon apparatus with induction heating for sample melting. Pliocene age and the sequence (from 9 to 1.8 Ma) of formation were determined for a number of hypabyssal granitoid intrusions of the Greater Caucasus (Elbrus, Tyrnyauz, Chegem, Mineral'nye Vody, and Kazbek regions), which had been assigned on the basis of geological data to the Cenozoic magmatic suite. The analysis of the dacite lavas of Elbrus Volcano constrained their age as <0.5 Ma.

The following stage of geochronological studies of young igneous rocks at the IGEM relied on two approaches, which provided a considerable improvement in the sensitivity of argon isotope analysis and allowed dating intermediate and basic volcanics with low potassium contents (usually <2 wt %). These were, first, the static mode of mass spectrometer measurements and, second, the system of gas extraction from samples with a high-temperature (up to 1700°C) heater isolated in vacuum from the zone of sample melting. Such a system for gas extraction was designed by German researchers (Staudacher *et al.*, 1978) and was implemented in the IGEM in two construction modifications. Using these devices and other stainless steel systems for argon preparation for mass spectrometric analysis, the level of the total working background for  $^{40}\text{Ar}$  was reduced to about  $5 \times 10^{-9}$  ncm<sup>3</sup> (or 0.008 ng)

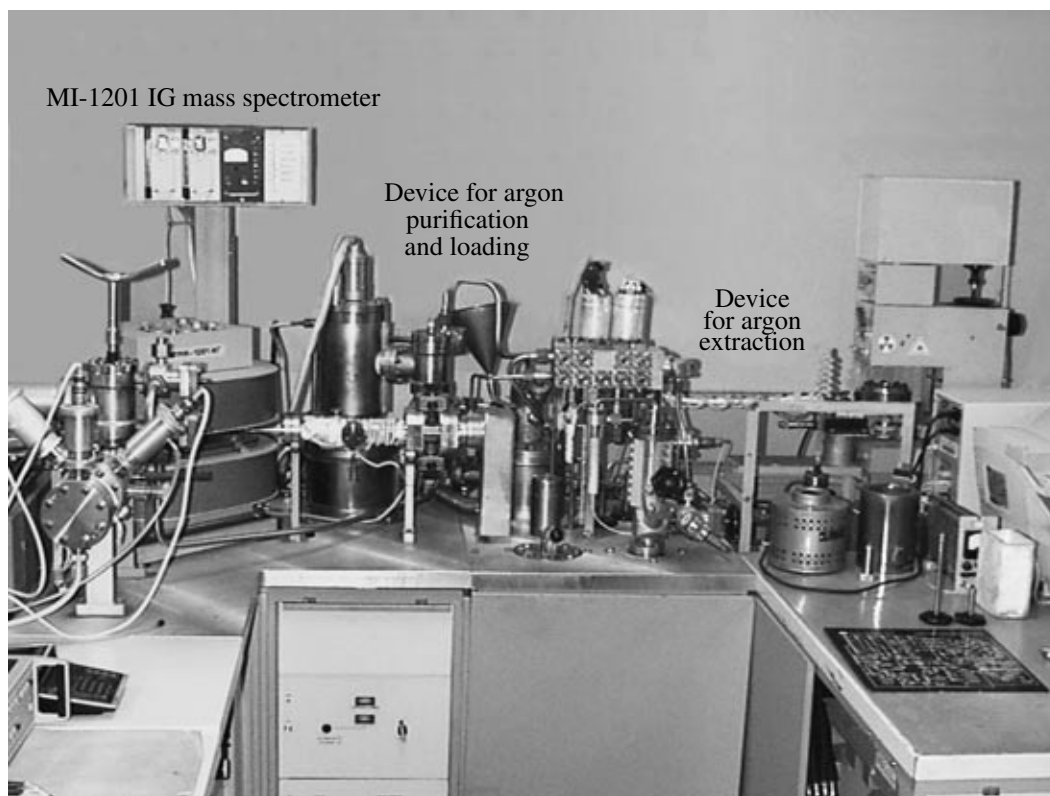
(Ivanenko and Karpenko, 1987; Karpenko and Ivanenko, 1993). The static mode of argon isotope analysis was performed on a MI-1330 mass spectrometer with a 180° analyzer and a small-volume chamber (Rafal'son *et al.*, 1979). Its argon sensitivity in the static mode was  $1 \times 10^{-2}$  A/Torr. The use of these methods and devices allowed dating of rocks containing up to 0.05–0.1 ppb of radiogenic  $^{40}\text{Ar}$  (Ivanenko and Karpenko, 1987; Karpenko and Ivanenko, 1993). This method served as a basis for a series of studies on the geochronology of Cenozoic (Miocene and Pliocene) basaltic volcanism in the Baikal rift zone (Kononova *et al.*, 1988), Khubsugul rift in Mongolia (Ivanenko *et al.*, 1989), southern Vietnam (Novikov *et al.*, 1989), Russia's Far East (Lower Amur region) (Novikov *et al.*, 1991), and Syria (Novikov *et al.*, 1993; Sharkov *et al.*, 1994).

There were several attempts at dating Late Cenozoic volcanic rocks by the K–Ar method in other Russian laboratories. However, they were not accompanied by the implementation of methods accounting for the peculiarity and complexity of the problem and allowing control of the quality of the obtained age estimates. A few datings that were published have approximate character, and the reliability of some of them is questionable.

During the past four decades, studies of the geochronology of young and recent volcanism, including the necessary improvement of the K–Ar method, have been carried out in several research centers of Japan, USA, Russia, France, Italy, and some other countries. In the past decade, these studies have resulted in fundamental achievements: a decrease in the measured amount of radiogenic argon to 0.00n ppb, interphase investigations of the K–Ar system in volcanics and revealing of primary heterogeneity in the initial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in them, and obtaining new comprehensive data on the chronology of Quaternary volcanism and, which is especially important, its most recent stage, late Neopleistocene–Holocene. The results of both methodical and geological investigations obtained by the authors during this last period are discussed in the following sections.

#### METHODS OF MEASUREMENT OF ULTRALOW CONTENTS OF RADIOGENIC ARGON

The measurement of ultralow (0.0n–0.00n ppb) concentrations of radiogenic  $^{40}\text{Ar}$  for the estimation of the age of young volcanic rocks is a major challenge in the application of mass spectrometry in isotopic geology. It requires the maximum use of the possibilities of mass spectrometer facilities with respect to the absolute sensitivity of measurements and the level of background signals on the masses of argon isotopes. The extreme values of these parameters (sensitivity of  $5 \times 10^{-3}$  A/Torr and background levels for  $^{40}\text{Ar}$  and  $^{36}\text{Ar}$  of  $3 \times 10^{-3}$  ng and  $1 \times 10^{-5}$  ng, respectively) were obtained by the authors at the laboratory of isotopic geochemistry and geochronol-



**Fig. 2.** High-sensitivity low-background mass-spectrometer system of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences.

ogy of the IGEM on a modernized MI-1201 IG mass spectrometer complex (Chernyshev *et al.*, 1999, 2002b).

The MI-1201 IG mass spectrometer (Fig. 2) was manufactured by the SELMY Company (Sumy, Ukraine) and has a 90° magnetic sector analyzer with a radius of 200 mm. In addition to these characteristics, of special importance for the isotopic analysis of radiogenic argon are the following: the threshold of isotopic sensitivity is  $2 \times 10^{-6}$ , and the maximum resolution at a 10% level of peak height is 2300.

The most important modifications of the apparatuses and methods of measurement of very low concentrations of radiogenic argon in young volcanics are the following: the use of novel special means for the ultrahigh vacuum pumping off and purification of argon from foreign gases, the static mode of measurement of argon isotope compositions, the elimination of the effect of isobaric interference on a mass of 36 at the expense of measurements in the high resolution regime (~1800), and systematic control and correct accounting for the effect of mass discrimination of argon isotopes and background signals on masses of 36, 38, and 40.

Consider these elements of the method in more detail. The analyzer chamber and the ion source are pumped off by a Varian Star Cell VakIon Plus 75 ion triode ultrahigh vacuum pump, which is a special modification of this pump type providing a high (up to 50 l/s)

pumping rate of noble gases. In the measurement cycles of mass spectrometer operations, vacuum of about  $5 \times 10^{-10}$  Torr was maintained in the chamber. An additional or operation device for pumping is a Turbo-V 70LP turbomolecular pump of Varian Company with a performance of 70 l/s. The system of initial evacuation of the mass spectrometer and the argon set-up is also completely oil-free: it utilizes three sorption pumps using a sorbent cooled with liquid nitrogen.

The high resolution mass spectra (Fig. 3) recorded during the isotopic analysis of argon allow control of the fine structure of the peak at a mass of 36, which in addition to  $(^{36}\text{Ar})^+$  may contain the isobaric ions  $(^1\text{H}^{35}\text{Cl})^+$  and  $(^{12}\text{C}_3)^+$  having slightly different masses:  $(^{36}\text{Ar})^+$ , 35.98;  $(^1\text{H}^{35}\text{Cl})^+$ , 35.99; and  $(^{12}\text{C}_3)^+$ , 36.01. As was noted above, the most important parameter for dating young rocks is the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio, the accuracy of which is mainly controlled by the correctness of measurement of the low-intensity peak of  $(^{36}\text{Ar})^+$ , i.e., the separation of the  $(^{36}\text{Ar})^+$  peak from those of isobaric ions. The analysis in the high-resolution regime (although not complete) helps to resolve this problem.

The system of gas extraction includes a high-temperature (up to 1700°C) heater, which is isolated in vacuum from the sample volume (tantalum or molybdenum crucible). The two-stage purification of argon is performed using titanium and zirconium getters. The

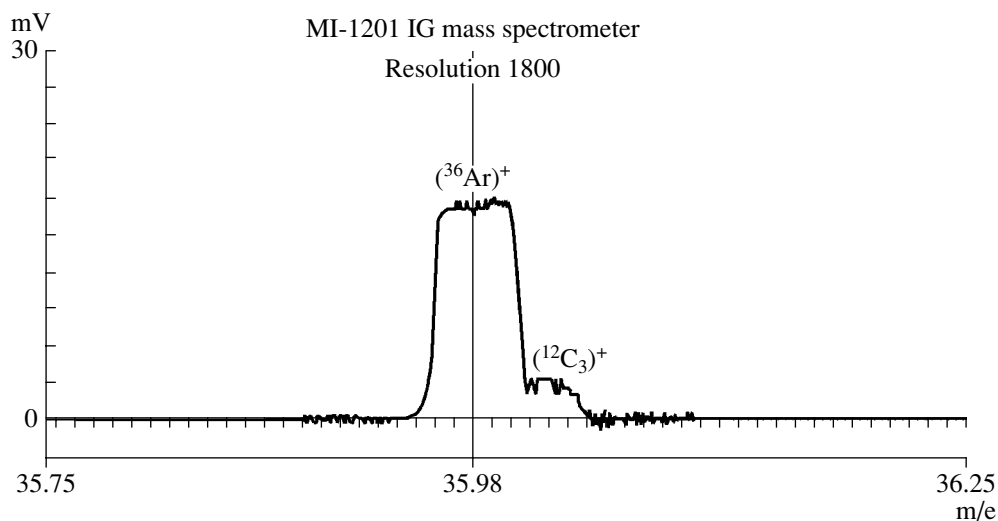


Fig. 3. Fine structure of the 36 m/e mass line at a resolution of mass spectrometer of ~1800.

minimum working level of backgrounds for argon isotopes in the measurement complex extraction system—mass spectrometer was achieved by the use of the aforementioned specialized ion pump and Zr–V–Fe getters (Table 2).

The measurement of ion currents on the MI-1201 IG mass spectrometer is carried out in a single-beam regime using an electrometric amplifier (input resistance of  $10^{11} \Omega$ ) with low noise levels ( $<40 \mu\text{V}$ ) and time drift of the zero point ( $<50 \mu\text{V}$ ). The intensity of the  $^{40}\text{Ar}$  signal during the measurement of samples of Quaternary volcanics usually varies within 1–3 V and that of  $^{36}\text{Ar}$ , from 3 to 10 mV. The mass spectrometer is calibrated by measuring argon with the atmospheric isotopic composition.

The concentration of  $^{40}\text{Ar}$  is determined by isotope dilution using pure  $^{38}\text{Ar}$  isotope. The mentioned parameters and methods allow us to date young volcanics using separated samples no more than 100 mg in weight. The potassium content is determined by the method of flame spectrophotometry. The results are checked by the systematic analyses of small charges

(usually, no more than 2 mg) of homogeneous standard geochronological samples of Bern-4 muscovite, 1/76 basalt, and P-207 muscovite. The real analytical errors are given in Tables 3–7. They are individual, i.e., dependent on the characteristics of the sample and particular analytical conditions.

#### INTERPHASE HETEROGENEITY OF THE INITIAL ARGON ISOTOPE COMPOSITION IN YOUNG VOLCANICS AND THE CHOICE OF K–Ar GEOCHRONOMETER

The problem of the choice of a geochronometer, i.e., the mineral material that is directly used for analysis, is often discussed and solved in some way in geochronology, especially in pilot or methodical studies. Most frequently, this is concerned with the choice among varieties of mica, pitchblende, zircon, and other accessory minerals differing in morphology, structure, and other properties. Owing to the extremely low absolute content of radiogenic  $^{40}\text{Ar}$  in young volcanic rocks, a number of geochemical factors may exercise a significant

Table 2. Hot blank levels obtained on the MI-1201 IG measurement system (mass spectrometer + device for argon extraction) at the IGEM

Date	$^{40}\text{Ar}$ , ng	$^{36}\text{Ar}$ , ng	Conditions	
			Pumping of MS chamber	Argon purification
1997–2001	0.012	0.000037	NMD-016 diode pump Ti getters	Stage 1: Ti getters Stage 2: Ti getters
February 2002	0.010	0.000029	Varian Star Cell 75 pump	Stage 1: Ti getters
December 2002	0.0056	0.000016	Zr–V–Fe getters	Stage 2: Zr–V–Fe getters
March 2003	0.0041	0.000012		
June 2003	0.0030	0.000009		

**Table 3.** K–Ar isotopic ages of the young volcanic rocks of the Geghama Range (Armenia) obtained for groundmass and phenocrysts

Sample no.	Rock	Material	K, wt %	$^{40}\text{Ar}_{\text{rad}}$ , ppb	$^{40}\text{Ar}_{\text{atm}}$ , % in sample	Age, Ma $\pm 1.6\sigma$
10G/01	andesite	groundmass	1.42	0.460	43.0	4.70 $\pm$ 0.30
		plagioclase	0.44	0.294	49.0	9.70 $\pm$ 0.80
11G/01	andesite	groundmass	1.95	0.710	72.5	5.25 $\pm$ 0.35
		plagioclase	0.46	0.198	60.2	6.20 $\pm$ 0.50
12G/01	andesite	groundmass	1.85	0.730	57.4	5.65 $\pm$ 0.35
		plagioclase	0.29	0.122	66.7	6.10 $\pm$ 0.80
19G/01	rhyolite	glass	3.25	0.079	97.2	0.35 $\pm$ 0.06
		plagioclase	0.58	0.085	75.0	2.10 $\pm$ 0.20
		biotite	4.46	0.300	90.3	0.97 $\pm$ 0.10
20aG/01	rhyodacite	glass	3.44	1.090	2.4	4.55 $\pm$ 0.30
		plagioclase	0.38	0.140	44.4	5.25 $\pm$ 0.55
20bG/01	rhyodacite	groundmass	3.45	1.160	24.2	4.85 $\pm$ 0.30
		plagioclase	0.43	0.170	47.5	5.80 $\pm$ 0.55
27G/01	rhyolite	groundmass	3.33	1.160	24.4	5.00 $\pm$ 0.25
		plagioclase	0.53	0.258	49.8	7.00 $\pm$ 0.60
		biotite	6.98	2.410	55.2	5.00 $\pm$ 0.25
32G/01	trachyandesite	groundmass	2.47	0.027	91.3	0.160 $\pm$ 0.045
		plagioclase	0.83	0.046	74.1	0.79 $\pm$ 0.09

influence on the K–Ar age estimates for such rocks. Our experience suggests that most detailed investigations of individual mineral components of young volcanics are of crucial importance for the assessment of the contributions of these factors and the choice of geochronometer materials. Our isotopic investigations of minerals from various rocks of several volcanic centers of the Caucasus revealed a considerable discrepancy between the K–Ar ages (from 30 ka to several million years) obtained for rock groundmass and phenocrysts of biotite, plagioclase, and pyroxene (Chernyshev *et al.*, 1999, 2002b). This effect can be exemplified by the results obtained for components of lavas from the Geghama volcanic center (Arutyunyan *et al.*, 2003) and ignimbrites from the Elbrus center (Chernyshev *et al.*, 2001) (Tables 3, 4).

This effect was also documented in young volcanic rocks from other regions: in the lavas of Younger Ontake Volcano, central Japan (Matsumoto and Kobayashi, 1995), and the rocks of the Tatara–San-Pedro volcanic complex, Chile (Singer *et al.*, 1998). The distribution of the  $^{40}\text{Ar}/^{40}\text{K}$  ratio defining the value of K–Ar age suggests that biotite, plagioclase, and other phenocryst minerals from young volcanic rocks contain excess radiogenic  $^{40}\text{Ar}$ . As a result, the respective apparent K–Ar ages are strongly variable and significantly older (especially in the case of plagioclase) than the real age of rock crystallization.

The following natural mechanisms may be responsible for this phenomenon, which is related to the earlier crystallization of plagioclase and biotite with respect to the microlitic groundmass.

(1) Argon from the gas component of the melt was trapped (diffused) into the lattices of crystallizing phenocrysts. Argon with the isotopic ratio  $^{40}\text{Ar}/^{36}\text{Ar} \gg 295.5$  (i.e., higher than the atmospheric value) could be released from basaltic or basaltic andesite magmas derived from the oceanic crust or the mantle. High  $^{40}\text{Ar}/^{36}\text{Ar}$  values were detected, for instance, in ocean island rocks (Dalrymple and Moore, 1968). Another possible source of radiogenic  $^{40}\text{Ar}$  dissolved in magma is the assimilation of older sialic crustal material by the melt.

(2) The excess radiogenic  $^{40}\text{Ar}$  in plagioclase and biotite phenocrysts is inherited by these minerals. Such

**Table 4.** Results of K–Ar dating for ignimbrite sample Bt-12 from the Elbrus volcanic center

Material	K, wt %	$^{40}\text{Ar}_{\text{rad}}$ , ppb	$^{40}\text{Ar}_{\text{atm}}$ , % in sample	Age, Ma $\pm 1.6\sigma$
Biotite	7.06	0.363	81.6	0.74 $\pm$ 0.06
Glass	4.30	0.263	88.1	0.88 $\pm$ 0.07
Plagioclase	0.84	0.913	82.3	15.7 $\pm$ 1.0
Pyroxene	0.18	0.033	90.1	2.7 $\pm$ 0.5

**Table 5.** Results of K–Ar dating for the groundmass of lavas from the Elbrus volcanic center

Sample no.	K, wt % $\pm \sigma$	$^{40}\text{Ar}_{\text{rad}}$ , ppb $\pm \sigma$	$^{40}\text{Ar}_{\text{atm}}$ , % in sample	Age, ka $\pm 2\sigma$
Lavas of the southern slope of Elbrus Volcano (Baksan valley)				
1993Ea	2.97 $\pm$ 0.03	0.0193 $\pm$ 0.0013	93.1	95 $\pm$ 15
Az-21	2.56 $\pm$ 0.03	0.0025 $\pm$ 0.0016	99.6	15 $\pm$ 15
Az-22	2.50 $\pm$ 0.03	0.0062 $\pm$ 0.0019	99.0	35 $\pm$ 20
Az-23	2.38 $\pm$ 0.03	0.0033 $\pm$ 0.0012	99.2	20 $\pm$ 10
Az-25	3.54 $\pm$ 0.04	0.041 $\pm$ 0.002	84.4	170 $\pm$ 15
Az-26	2.83 $\pm$ 0.03	0.0052 $\pm$ 0.0020	96.8	25 $\pm$ 15
Az-28	2.88 $\pm$ 0.03	0.0059 $\pm$ 0.0024	98.4	30 $\pm$ 20
Az-29	2.78 $\pm$ 0.03	not detected	$\geq$ 99.9	$\leq$ 30
Az-30	2.86 $\pm$ 0.03	0.021 $\pm$ 0.002	93.7	105 $\pm$ 20
Az-31	3.07 $\pm$ 0.03	0.024 $\pm$ 0.002	90.3	110 $\pm$ 20
Lavas of the western slope of Elbrus Volcano (Biitik-Tebe valley)				
Bt-6	3.05 $\pm$ 0.04	0.046 $\pm$ 0.003	64.9	220 $\pm$ 30
Bt-17	2.86 $\pm$ 0.04	0.045 $\pm$ 0.003	75.2	225 $\pm$ 30
Lavas of the northern slope of Elbrus Volcano (Malka valley)				
MI-41	3.14 $\pm$ 0.04	0.047 $\pm$ 0.003	93.4	215 $\pm$ 30
MI-36	3.23 $\pm$ 0.03	0.015 $\pm$ 0.002	85.3	70 $\pm$ 20
MI-43	3.30 $\pm$ 0.03	0.016 $\pm$ 0.002	83.8	70 $\pm$ 20
MI-37	3.04 $\pm$ 0.03	0.007 $\pm$ 0.003	94.9	30 $\pm$ 25
Ignimbrites and tuffs (Biitik-Tebe valley)				
Bt-12	4.30 $\pm$ 0.04	0.263 $\pm$ 0.015	88.1	880 $\pm$ 70
Bt-13	3.67 $\pm$ 0.04	0.206 $\pm$ 0.015	97.2	810 $\pm$ 90

a mechanism could operate in those cases when the silic material contaminating the initial magma was not completely assimilated and retained in part as a solid phase, which subsequently served as nuclei for phenocryst growth.

The latter possible reason for the presence in magma of argon with elevated  $^{40}\text{Ar}/^{36}\text{Ar}$  ( $\geq 295.5$ ) explaining the observed heterogeneity of the initial  $^{40}\text{Ar}/^{36}\text{Ar}$  in various constituents of volcanic rocks is consistent with the results of an investigation on the Sr and Nd isotopic systematics of the lavas of the Kazbek and Elbrus volcanic centers (Chernyshev *et al.*, 1998, 2000). These results suggested a contribution from the material of the crystalline basement of the Greater Caucasus into the genesis of recent lavas. The partial retention of radiogenic argon in plagioclase and biotite phenocrysts under conditions when the temperature of magma before its eruption and cooling was  $\geq 700^\circ\text{C}$ , which is

much higher than the closure temperature of the K–Ar systems of these minerals, can be explained by the brevity of processes from the crystallization of phenocrysts to the eruption of melts onto the surface and cooling.

Owing to the aforementioned low solubility of argon in silicate melts and rocks under atmospheric pressure, the microlitic groundmass of lavas formed from an erupted and already degassed melt probably does not contain excess argon, and the  $^{40}\text{Ar}_{\text{rad}}/^{40}\text{K}$  ratio of rock groundmass must therefore reflect the time of lava eruption.

The data presented above served as a basis for the choice of groundmass separated from phenocrysts as a geochronometer for the K–Ar dating of Neogene–Quaternary volcanics. With such an approach, which is also accepted by other researchers, a detailed inspection of volcanics remains to be important. In addition to the analysis of rock groundmass varieties, for instance

**Table 6.** Results of K–Ar dating for the groundmass of lavas from the Samsari volcanic center

Sample no.	K, wt % $\pm \sigma$	$^{40}\text{Ar}_{\text{rad}}$ , ppb $\pm \sigma$	$^{40}\text{Ar}_{\text{atm}}$ , % in sample	Age, ka $\pm 1.6\sigma$
Didi-Abuli Volcano				
YuG-62	2.06 $\pm$ 0.02	0.041 $\pm$ 0.003	92.4	290 $\pm$ 30
YuG-64	1.92 $\pm$ 0.02	0.054 $\pm$ 0.002	79.1	410 $\pm$ 30
YuG-65	2.15 $\pm$ 0.02	0.048 $\pm$ 0.002	83.0	320 $\pm$ 30
YuG-66	1.90 $\pm$ 0.02	0.037 $\pm$ 0.004	97.5	280 $\pm$ 60
YuG-67	1.71 $\pm$ 0.02	0.029 $\pm$ 0.004	98.4	240 $\pm$ 60
Samsari caldera				
YuG-68	1.68 $\pm$ 0.02	0.021 $\pm$ 0.004	99.0	180 $\pm$ 70
YuG-69	1.74 $\pm$ 0.02	0.029 $\pm$ 0.005	99.0	240 $\pm$ 70
YuG-70	1.71 $\pm$ 0.02	0.024 $\pm$ 0.002	89.7	200 $\pm$ 40
YuG-71	1.70 $\pm$ 0.02	0.025 $\pm$ 0.001	83.7	210 $\pm$ 20
YuG-72	1.70 $\pm$ 0.02	0.023 $\pm$ 0.005	95.8	200 $\pm$ 40
Shav nabada Volcano				
YuG-74	1.76 $\pm$ 0.02	0.021 $\pm$ 0.003	97.2	170 $\pm$ 50
YuG-75	1.92 $\pm$ 0.02	0.039 $\pm$ 0.001	97.1	290 $\pm$ 60
YuG-76	1.66 $\pm$ 0.02	0.037 $\pm$ 0.004	98.1	320 $\pm$ 70
Godorebi Volcano				
YuG-63	1.89 $\pm$ 0.02	0.003 $\pm$ 0.003	99.7	30 $\pm$ 30
Tavkvetili Volcano				
YuG-77	1.63 $\pm$ 0.02	not detected	>99.9	<30
Babakhngo Volcano				
YuG-73	1.68 $\pm$ 0.02	0.089 $\pm$ 0.009	91.4	760 $\pm$ 80

glass and microlitic matrix, phenocryst minerals must also be investigated. Such data, even for a limited number of representative samples, provide valuable information for the interpretation of the state of the K–Ar system of rocks.

The systematic use of this approach, i.e., the K–Ar geochronometry of rock groundmass, provided a basis for the geochronological investigation of three large Quaternary volcanic centers in the Caucasus region: Elbrus, Samsari, and Aragats, the results of which are described below.

#### GEOCHRONOLGY OF ERUPTIONS IN SOME LARGE QUATERNARY VOLCANIC CENTERS OF THE CAUCASUS

##### *Neogene–Quaternary Magmatism of the Caucasus*

The Caucasus mountain system is part of the Alpine Mediterranean orogenic belt. Its structure consists of genetically and compositionally diverse complexes of deformed and folded rocks of Paleozoic, Mesozoic, and Paleogene age. The folded block structure of the Greater Caucasus extends linearly over 1300 km in the NW–SE direction between the Black and Caspian seas. In contrast to the Greater Caucasus, there is no axial anticlinorium in the structure of the Lesser Caucasus.

However, Neogene–Quaternary volcanic rocks are much more widespread in the Lesser Caucasus and occupy about one fourth of its area.

It is universally accepted (Philip *et al.*, 1989) that the extensive Neogene–Quaternary magmatism of the Caucasus was related to late collisional events (Fig. 4). It began in the middle Miocene, when the Caucasus segment of the Alpine Mediterranean orogenic belt was entrained into the process of strong collision between the Arabian and Eurasian continental plates, and had continued up to the Holocene.

Milanovskii and Koronovskii (1973) and other researchers distinguished three stages of Neogene–Quaternary magmatism in the Caucasus: (1) late Miocene–early Pliocene, (2) late Pliocene, and (3) late Pliocene–Anthropogene. The first stage was most extensive in the Lesser Caucasus, whereas the rocks of the second stage occur in various zones of the Caucasus. The magmatism (mainly volcanism) of the third stage was also manifested in both the Greater and Lesser Caucasus and resulted in the formation of large stratovolcanoes, including Elbrus, Kazbek, Aragats, and others.

**Table 7.** Results of K–Ar dating for the groundmass of extrusive rocks from the Aragats volcanic center

Sample no.	Sample, sampling site	K, wt % $\pm \sigma$	$^{40}\text{Ar}_{\text{rad}}$ , ppb $\pm \sigma$	$^{40}\text{Ar}_{\text{atm}}$ , % in sample	Age, Ma $\pm 1.6\sigma$	Stage of volcanism
Plateau basalts of the basement of the Aragats region						
1/A	olivine basalt	1.45 $\pm$ 0.02	0.254 $\pm$ 0.012	77.1	2.5 $\pm$ 0.2	
Arteni volcanic center						
2a/81	obsidian	3.73 $\pm$ 0.04	0.38 $\pm$ 0.03	70.0	1.45 $\pm$ 0.15	
2b/81	rhyolite	3.53 $\pm$ 0.04	0.39 $\pm$ 0.03	66.1	1.60 $\pm$ 0.15	
Aragats volcanic center						
2/A	basaltic andesite, Ambert R. canyon	2.39 $\pm$ 0.03	0.152 $\pm$ 0.012	55.5	0.92 $\pm$ 0.08	I–II ( $Q_{\text{El}}$ )
3/A	"	1.89 $\pm$ 0.02	0.117 $\pm$ 0.007	67.8	0.89 $\pm$ 0.08	
8/A	basaltic andesite, Shamiram Plateau	2.13 $\pm$ 0.03	0.135 $\pm$ 0.012	91.2	0.91 $\pm$ 0.10	
6/A	andesite–dacite, southern slope of Aragats Mt.	3.10 $\pm$ 0.04	0.209 $\pm$ 0.013	47.3	0.97 $\pm$ 0.09	
10/A	basaltic andesite, southwestern slope of Aragats Mt.	2.41 $\pm$ 0.03	0.092 $\pm$ 0.006	89.0	0.92 $\pm$ 0.10	
5/A	basalt, Paros Volcano	1.74 $\pm$ 0.02	0.108 $\pm$ 0.010	80.8	0.90 $\pm$ 0.09	
14/A	basalt, northern slope of Aragats Mt.	1.63 $\pm$ 0.02	0.084 $\pm$ 0.005	87.8	0.74 $\pm$ 0.08	III ( $Q_1^1$ )
7/A	dacite, summit of Aragats Mt.	3.47 $\pm$ 0.04	0.164 $\pm$ 0.012	71.5	0.68 $\pm$ 0.07	
11/A	"	2.64 $\pm$ 0.03	0.131 $\pm$ 0.011	50.4	0.72 $\pm$ 0.07	
13/A	dacite, western summit of Aragats Mt.	4.58 $\pm$ 0.03	0.172 $\pm$ 0.012	79.5	0.54 $\pm$ 0.06	IV ( $Q_1^2$ )
9/A	basaltic andesite, Ashtarak Volcano	1.76 $\pm$ 0.02	0.064 $\pm$ 0.005	85.5	0.53 $\pm$ 0.07	
4/A	basaltic andesite, Tirin-Katar Volcano	2.65 $\pm$ 0.03	0.084 $\pm$ 0.005	90.8	0.45 $\pm$ 0.07	
12/A	"	1.24 $\pm$ 0.02	0.048 $\pm$ 0.003	91.2	0.56 $\pm$ 0.07	

#### *Elbrus Volcanic Center, Great Caucasus*

Elbrus is widely known as a geographic site and a tourist center, which explains the increasing interest to this large Quaternary, presumably dormant volcano. In the European part of Russia, it is one of the most hazardous in terms of the probability of resumption of volcanic activity. The highest summit of the Caucasus, Elbrus Volcano (5643 m a.s.l.) is situated in a densely populated region of the northern Caucasus near large residential settlements, well-known tourist centers, and mining enterprises.

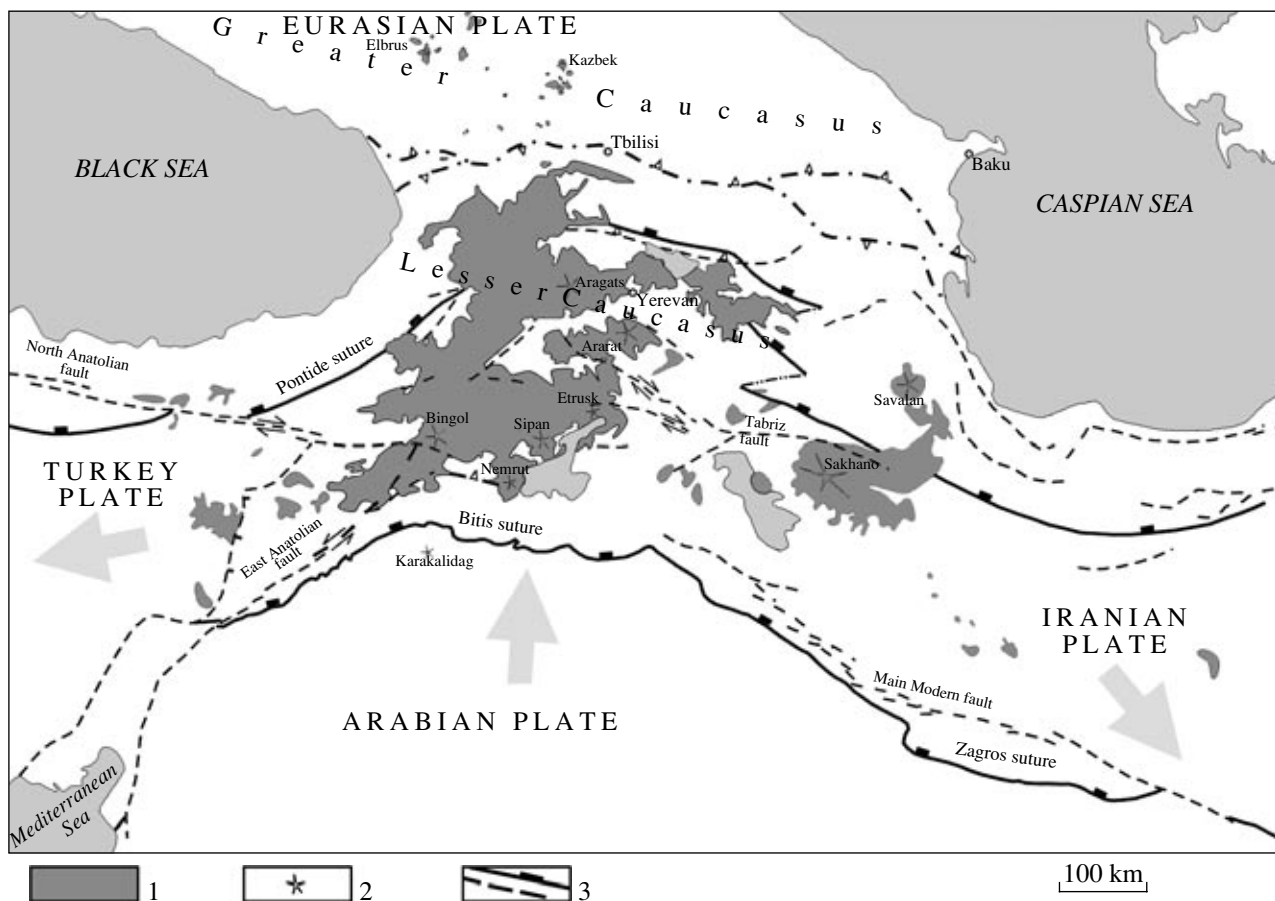
The Elbrus volcanic center is located on the northern slope of the Main Caucasus Range and includes Elbrus Volcano proper (water divide between the Malka, Baksan, and Kuban' rivers), a number of small volcanic edifices on its slopes, and several isolated exposures of lavas and pyroclastic rocks in the eastern and northern margins of the volcano in the basins of the Khudes, Kyrtk, and Tyzyl rivers. The volcanic edifice of Elbrus has two conical summits with distinct volca-

nic craters. The base of the volcano is built up of Paleozoic metamorphic rocks, which crop out up to heights of 3.0–3.9 km a.s.l.

The most common extrusive rocks of the Elbrus volcanic center (including pyroclastic rocks) are dacites.

Most authors agree that the oldest volcanic rocks of the Elbrus center are tuffs and ignimbrites. The potassium-rich phases of ignimbrite sample Bt-12 (biotite and glass) yielded similar age values of 740 and 880 ka, respectively. A similar K–Ar age estimate (810 ka) was obtained from the groundmass of another ignimbrite sample (Bt-13, Table 5) (Chernyshev *et al.*, 2001, 2002b).

The presented K–Ar data and previously published Rb–Sr results (Chernyshev *et al.*, 2001) suggest that explosive activity occurred within the Elbrus volcanic center about 900 ka ago. A sample of trachyandesite collected at the periphery of the Elbrus center in the basin of the Khudes River, where Quaternary volcanism also occurred, was previously dated by the K–Ar



**Fig. 4.** Neotectonic scheme of the Caucasus segment of the Alpine Mediterranean orogenic belt. (1) Areas of occurrence of Neogene–Quaternary volcanics; (2) large Quaternary volcanoes; and (3) major tectonic dislocations.

method at  $800 \pm 150$  ka (Borsuk *et al.*, 1989b). It is worth noting that these authors also reported a K–Ar age of  $850 \pm 250$  ka for an andesite–dacite dike cutting the granodiorites of the Tepli neointrusion. These data suggest that the ancient (about 900 ka) stage of the development of Quaternary magmatism occurred not only in the Elbrus region but probably also over the whole Greater Caucasus.

Based on the results of K–Ar dating for the lavas of Elbrus Volcano (Table 5), three main phases were distinguished in its magmatic activity and their age boundaries were determined: 225–170 ka, middle Neopleistocene; 110–70 ka, late Neopleistocene; and <35 ka, late Neopleistocene–Holocene (Chernyshev *et al.*, 2001, 2002b; Medvedeva *et al.*, 2003; Lebedev *et al.*, 2005).

A considerable time gap (more than 0.5 Ma) between the formation of pyroclastic rocks and lava flows of Elbrus Volcano allows us to suggest that the explosive activity was not directly related to the activity of the volcano. Moreover, the conjecture on the existence of Elbrus Volcano over such a long period of time (more than 800 ka) seems to be improbable, because the life span of even a very large polyphase volcano is usually no longer than a few hundreds of thousands of

years (Melekestsev, 1980). Most likely, an active explosive center (Paleo-Elbrus) or several mainly explosive centers existed in the late Eopleistocene–early Neopleistocene (about 800 ka ago) in this region.

The distinguished phases of activity of the Elbrus center were synchronous with the main stages of magmatic activity in a number of other recent volcanic centers of the Greater Caucasus (Kazbek, Kel', etc.) (Chernyshev *et al.*, 1999; Lebedev *et al.*, 2004c). The K–Ar data with estimated errors obtained in this study and previously published radiocarbon results (Bogatikov *et al.*, 1998) are indicative of the possible occurrence of Holocene volcanism in this region, which supports the classification of Elbrus as hazardous in terms of resumption of volcanic activity.

#### *Samsari Volcanic Center, Lesser Caucasus*

The volcanic chain of the Samsari Range is situated in southern Georgia, in the central part of the large Dzhavakhet upland. It extends in an approximately N–S direction from the southern slopes of the Trialet Range in the north to the valley of the Paravani R. encircling it in the south. The bases of volcanic edifices are

amalgamated forming an almost continuous mountain chain 35–40 km long. The total number of volcanoes in the Samsari Range is more than 20; the largest among them are (from north to south) Tavkvetili, Beberiklde (Egoisar), Shavnabada, Samsari caldera (about 10 km in diameter), Kerogly, Godorebi, Didi-Abuli, Patara-Abuli, and Eshtia. Many of these volcanoes are complicated by lateral fissure eruptions.

Almost all the samples of Samsari Range volcanic are dacites in composition.

Inspection of the K–Ar data obtained for the Samsari volcanic center (Table 6) leads us to several conclusions concerning the history of its development in Quaternary time (Lebedev *et al.*, 2003, 2004b). The obtained age estimates suggest the existence of four phases of volcanic activity separated by long time gaps: (I) early Neopleistocene (about 800–700 ka ago); (II) early and middle Neopleistocene (about 400 ka); (III) middle Neopleistocene (320–170 ka); and (IV) late Neopleistocene–Holocene (less than 50 ka). The volcanoes of the western segment of the Samsari Range were formed during stage I. Phase II produced ancient flows of Didi-Abuli Volcano. The beginning of phase III (320–250 ka) was associated with the activity of Didi-Abuli Volcano and its lateral centers, ancient Shavnabada Volcano, probably former Samsari Volcano, and a number of other edifices in the Samsari Range. The development of the Samsari caldera, eruptions of postcaldera lavas, and formation of the young volcano of Shavnabada occurred about 200 ka ago. Phase IV of volcanic activity in the Samsari center was less extensive and resulted in the formation of Tavkvetili and Godorebi volcanoes and probably some other volcanic edifices. However, it is very probable that the last pulse of volcanic activity is not yet accomplished, and the resumption of volcanic activity is possible in this region. Note that we did not reveal any correlation between the chemical composition and age of the rocks, i.e., there has been no evolution of magmatic melts in their deep source over the past several hundreds of thousand years.

A comparison of the obtained geochronological data with our previous datings for a number of volcanic areas of the Caucasus shows that phases II, III, and IV of magmatic activity in the Samsari center were almost synchronous with phases I, II, and III of the development of the Kazbek neovolcanic center and the Elbrus center (Chernyshev *et al.*, 1999, 2001).

Thus, using the obtained isotopic and geochronological data, the Samsari volcanic area can be characterized as a large center of Late Quaternary volcanism in southern Georgia. Age boundaries were determined for the main phases of its development, which appeared to be synchronous with the previously distinguished phases of magmatic activity in other neovolcanic areas of the Caucasus region. According to the obtained results, the last volcanic events occurred in this region in the end of the Neopleistocene and Holocene, which

allows us to regard this region as potentially hazardous in terms of the resumption of volcanic activity.

#### *Aragats Volcanic Center, Lesser Caucasus*

One of the largest centers of Quaternary volcanism in the Caucasus, the Aragats volcanic center, is confined to the Aragats neovolcanic region in the western part of Armenia. This area comprises the highest summit of the Lesser Caucasus, the polygenic stratovolcano of Aragats (4090 m a.s.l.). It has a specific place in the neovolcanic history of Armenia with respect to the diversity of igneous rocks, extent and duration of activity, diversity of eruptive phenomena, and complexity of geologic and tectonic structures. The volcano has a shape of an asymmetric flattened convex shield (40–42 km in diameter) with the main crater in its northeastern part.

The rocks of the basement of the Aragats center are distinctly transgressively overlain by a complex volcanic pile with olivine plateau basalts and basaltic andesites at the base. Plateau basalts are widespread in the adjoining areas of Georgia and Turkey and are assigned to the Pliocene stage of the late collisional magmatism of the Lesser Caucasus. This stage is separated by a considerable time gap from the subsequent Quaternary volcanism of the Aragats center. The small volcanic center of Arteni, which erupted rhyolite-obsidian lavas, was formed during the Eopleistocene at the southwestern margin of the Aragats region. The development of the Aragats center proper took place in Late Quaternary time.

Olivine plateau basalts exposed in the valley of the Akhuryan R. represent the basement of the complex Aragats upland. They were dated by the K–Ar method at  $2.5 \pm 0.2$  Ma, which corresponds to the late Pliocene (Table 7) (Chernyshev *et al.*, 2002a). According to geological data, the rhyolite and obsidian lavas of the Arteni volcanic center predated the formation of the Aragats center. The K–Ar age of these lavas is about 1.5 Ma (Table 7). This age estimate is, on the one hand, much younger than the age obtained for the plateau basalts and, on the other hand, significantly older than the isotopic age of the products of eruption of the Aragats volcanic center proper (see below). Thus, the felsic volcanism of Arteni can be regarded as an individual Eopleistocene stage in the development of the Aragats region (Chernyshev *et al.*, 2002a).

The K–Ar ages of Aragats lavas are distinctly separated into three compact groups: 0.97–0.89, 0.74–0.68, and 0.56–0.45 Ma (Table 7) (Chernyshev *et al.*, 2002a). Based on the obtained isotopic datings, three stages can be distinguished in the development of the Quaternary volcanism of the Aragats center. During the most productive stage, which is referred to as stage I–II, the formation of the Aragats volcanic edifice began about 900 ka ago. It was accompanied by eruptions from the main crater and a number of lateral volcanic centers. Stages III (about 700 ka ago) and IV (about 500 ka ago) were less extensive and associated with the activity of

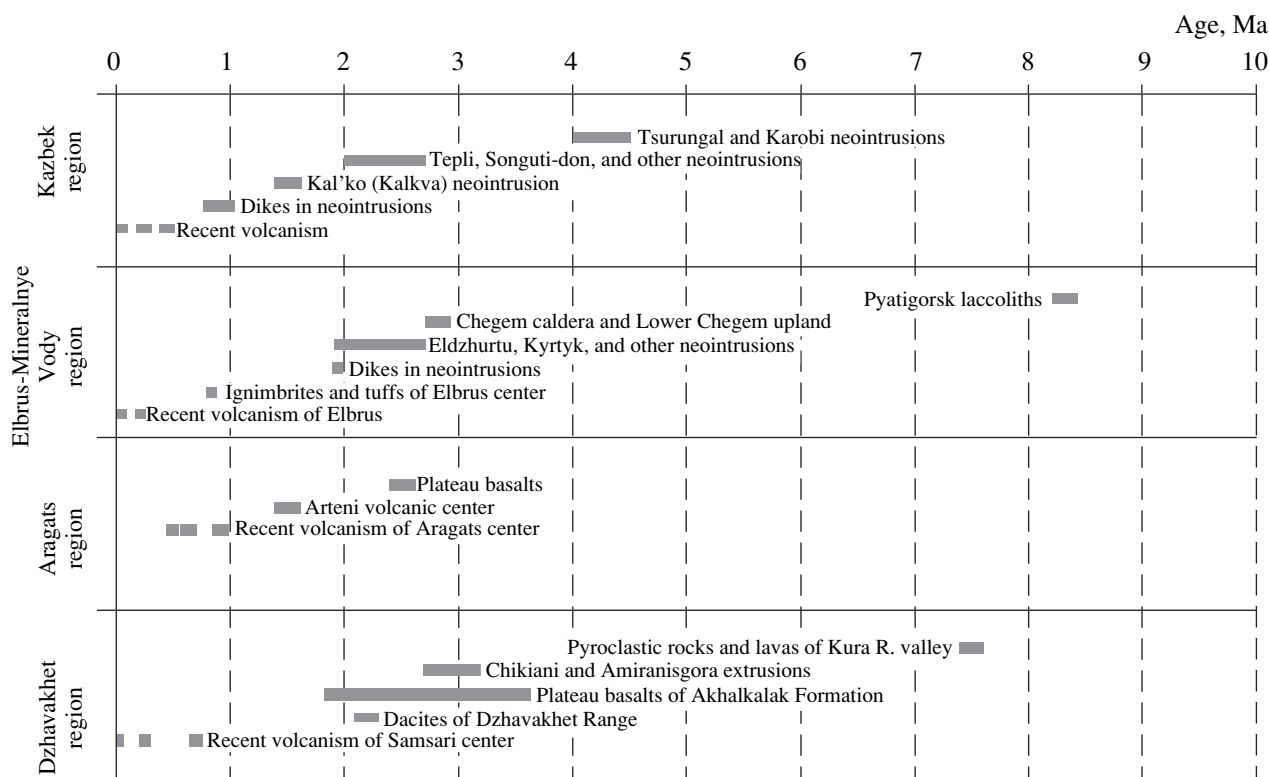


Fig. 5. Tentative geological time scale for the Neogene–Quaternary magmatism of the Caucasus.

the main volcanic edifice and a number of lateral eruptive centers on the slopes of the massif. According to the isotopic data, an important feature of Aragats is the brevity of volcanic activity within particular stages (tens of thousand years) with two practically equal periods of volcanic quiescence (about 200 ka) separating these stages.

The time period of the activity of the Aragats center was estimated on the basis of isotopic evidence as about 400 ka. It is interesting that similar values were obtained for the duration of volcanic activity in the Kazbek and Elbrus centers of the Greater Caucasus, 450 and 250 ka, respectively (Chernyshev *et al.*, 1999, 2001). Taking into account that the life span of even a very large polyphase volcano is usually no longer than a few hundreds of thousands of years (Melekestsev, 1980) and that the last eruptions in the Aragats center happened about 0.5 Ma ago, Aragats Volcano can probably be classified as extinct.

#### TENTATIVE GEOLOGICAL TIME SCALE FOR THE NEOGENE–QUATERNARY MAGMATISM OF THE CAUCASUS

The main result of the isotopic and geochemical investigations of young magmatic rocks of the Lesser and Greater Caucasus was the construction of a quantitative time scale for the development of Late Cenozoic magmatism in this region (Fig. 5). This scale was based

on the isotopic data obtained at the IGEM during many years (Arakelyants *et al.*, 1968; Borsuk *et al.*, 1989a, 1989b; Chernyshev *et al.*, 1999, 2001, 2002a, 2002b; Lebedev *et al.*, 2003, 2004a, 2004b, 2004c) and reported by other Russian and foreign authors (Kostitsyn and Kremenetskii, 1995; Hess *et al.*, 1993; Gazis *et al.*, 1995; etc.). The proposed time scale is tentative, because the available datings do not characterize all the regions of young magmatism in the Caucasus, and, moreover, in many cases the available isotopic age estimates that were used for the construction of the scale should be confirmed for various reasons.

The proposed time scale allows us to draw several important conclusions leading to a better understanding of the history of young magmatism in the Caucasus. First, it supports the existing concepts on the duration of Late Cenozoic magmatism in the Caucasus (Milanovskii and Koronovskii, 1973): from 9–8 Ma to the Holocene inclusively. Second, age boundaries are determined for the three previously distinguished stages of young magmatism: (I) 9.5–7.5 Ma (late Miocene); (II) 3.7–1.9 Ma (Pliocene); and younger than 1.5 Ma (Anthropogene). These stages are discontinuously distributed in time and separated by long periods without volcanic activity. Not all of the three stages may occur in a particular region.

During the initial stage of Late Cenozoic magmatism (late Miocene), hypabyssal intrusive bodies were emplaced in the Greater Caucasus in the Mineralnye

Vody region (9.5–8.3 Ma), and thick pyroclastic and extrusive sequences of andesite–dacite composition were formed in the Lesser Caucasus (7.5 Ma). The following Pliocene stage produced mainly intrusive granitoid massifs in the Greater Caucasus (2.8–1.9 Ma) and widespread subalkaline basaltic volcanism of the areal type in the Lesser Caucasus (3.7–1.9 Ma). The most recent (Anthropogene) stage of volcanism took place during the past 1.5 Ma and was associated with the formation of many large andesite–dacite stratovolcanoes in the Greater and Lesser Caucasus (Elbrus, Kazbek, Aragats, etc.).

An interesting feature of the young magmatism of the Caucasus is the synchronous occurrence of various types of volcanic activity in particular volcanic areas. For instance, eruptions of basaltic lavas were practically synchronous with the formation of felsic and moderately silicic extrusions during the Pliocene magmatic stage in the Dzhavakhet region.

The most important prognostic aspect of the proposed time scale for the young magmatism of the Caucasus is the evidence that the most recent stage of volcanic activity, the last products of which were dated at a few thousands–few tens of thousands of years, is probably not yet finished.

#### ACKNOWLEDGMENTS

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