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SYSTEMATIC STUDY OF ARID TERRITORIES

Variations in $^{87}Sr/^{86}Sr$ Ratios in Contemporary Snail Samples Obtained from the Eastern Caucasus

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Abstract—Variations of $^{87}Sr/^{86}Sr$ ratios in different natural objects make it possible to obtain new data having great importance for the identification of the possible place of origin and migration routes of ancient humans. The discussed data were obtained from contemporary snail samples inhabiting the landscapes of the eastern Caucasus, which is characterized by different parent rocks. It has been found that the $^{87}Sr/^{86}Sr$ ratios in samples originating from landscapes with rocks of the same type are generally the same, while those in samples originating from landscapes distinguished by the character of underlying rocks vary to a significant degree.

Keywords: variations of $^{87}Sr/^{86}Sr$ ratios, rocks, Caucasus

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INTRODUCTION

Recent studies on the interpretation of archeological data lay great importance on the "isotopic signature" preserved in various material objects, the bones of buried humans, animals, and plants. One of the main indicators of human mobility are variations in the $^{87}Sr/^{86}Sr$ ratios of bone tissue.

Calcium-containing minerals account for about 50% of all biominerals; phosphates comprise 25% of the biogenic mineral types. This is natural, because calcium performs numerous functions in the cellular metabolism. Nonstoichiometric carbonated hydroxyapatite is the most common phosphatic biomineral, which turns out to be the main mineral component of bones and teeth in vertebrates.

Dental tissues contain many microelements. Some of them (such as chrome and zinc) determine the normal functioning of the body. On the contrary, a whole number of elements (aluminum, strontium, etc.) are not that relevant for the activity of the body and particular elements (lead, cadmium, and mercury) are dangerous even at low concentrations. The composition of calcined tissues is currently widely used as an indicator of environmental contamination, in particular with heavy metals, since they are accumulated by the mineral phase of the tissue in the course of its development and excreted for several years. Comparison of the contamination levels is often performed on archeological samples: the dental tissues of humans who lived on the studied territory in different preindustrial epochs.

Human tooth enamel is a crystalline mass composed of several types of apatite and is contaminated with protein components that are present in large amounts in the mature and nonliving structure. Enamel crystals have a microscopic size. They can be restored only by the introduction of the needed ions in the mouth cavity and careful maintenance of the physico-chemical conditions for the equilibrium of products in the solution.

During the life of a human, the cells responsible for mineral phase formation respond to numerous biochemical factors of the environment, such as nutrient intake, growth hormones, mechanical loads, etc. Dentine is a living tissue that reacts to these factors and, thus, it changes to perform its functions. The mineral composition of enamel is quantitatively and structurally fixed after its formation. This has become the basis for a method that is actively developed and widely used in archeology for the identification of the place of origin and first years of human living by the isotopic composition of strontium in tooth enamel (Bentley and Knipper, 2005; Montgomery et al., 2005; Evans et al., 2006; Price et al., 2012).

As a geochemical substitute of calcium, strontium is able to incorporate into the matrix of hydroxyapatite, thereby replacing it and accumulating in dental and bone tissues. Strontium (Sr) is a chemical element of the second (IIa) group in Mendeleev's periodic table. Natural strontium consists of four stable isotopes: ^{88}Sr (82.56%), ^{86}Sr (9.86%), ^{87}Sr (7.02%), and ^{84}Sr (0.56%). The abundance of ^{87}Sr varies depending on its formations as a result of the dissociation of natural rubidium (^{87}Rb). The $^{87}Sr/^{86}Sr$ ratios in rock or mineral containing Rb depend on the age and Rb/Sr ratio in the source or parent rock and vary significantly.

Sr appears in the trophic food chain from plants which, in turn, absorb it from soil and surface and ground waters. The most significant variations in $^{87}Sr/^{86}Sr$ ratios are observed in the upper 20-cm humic soil layer, where atmospheric precipitations have a considerable impact on the composition and concentrations of chemical elements. However, the isotope composition of Sr becomes more similar with a soil depth equal to that of underlying rocks. The $^{87}Sr/^{86}Sr$ ratios of water also depend on the composition and age of eroded rocks. The geological and geochemical situation typical for a particular region determines the composition of Sr, which occurs in plants and other living organisms inhabiting the studied territory (Shishlina et al., 2012).

Sr accumulates in the tooth enamel of humans from their birth until they reach the age of about 12 and have permanent teeth; its isotopic composition reflects the nutritional system, the components of which originate from a particular geological and geochemical region or several regions (Bentley et al., 2004; Eckardt et al., 2009). The $^{87}Sr/^{86}Sr$ ratio in tooth enamel does not change with time (premolars and M1 and M2 molars are the most informative). Identification of the $^{87}Sr/^{86}Sr$ ratio in tooth enamel samples and knowledge of the regional geological and isotopic-geochemical characteristics of possible living areas of ancient humans make it possible to reveal the place of origin and childhood of a human.

The objective of this study is to present new data of the Atlas of Variations in $^{87}Sr/^{86}Sr$ Ratios based on materials from the eastern Caucasus.

The Caucasus is characterized by a long and intricate history of development. Thus, there are several structural levels composed of various rocks of different ages (*Geologiya* ..., 1968). The characteristic tectonic structure of the Caucasus (*Tektonika* ..., 2009) on the background of significant neotectonic activization and rocks of various ages at the soil surface is a characteristic feature of these vast highlands.

The specifics of the formation of the Caucasus led to its division into large natural regions. The northern part (Ciscaucasia) is the territory of the Sarmatian Craton, which has been activated to varying degrees by neotectonics. It stretches to the north up to the Kuma–Manych Depression in the geographical sense of zoning and the folded structure of Donbass (the Karpinskii Mountain Ridge) in the tectonic sense. The southern part (Caucasus) is the highlands with a sharply asymmetric structure having smooth northern and steep southern slopes. Furthermore, transversal differentiation of the region is observed, i.e., the western, central, and eastern parts are singled out. Such division is typical for both Ciscaucasia and mountainous territory.

In the formation of the Caucasus, it is possible to differentiate the contemporary (Alpine) stage of development and the previous pre-Jurassic stages (*Tektonika* ..., 2009), the sediments of which, on the whole, comprise the foundation, which used to be extremely dislocated and eroded. In the central part of the Caucasus, it is elevated to a high altitude, where it comes to the surface. Roks of this time are distinguished by their great variety. They are also more transformed by metamorphic processes. Pre-Jurassic rocks from the rest of the territory (including the high-mountain part of the western and eastern Caucasus) lay at depths of several kilometers.

The Jurassic period was the onset of the contemporary Alpine stage of development of the Caucasus. The current territory of the Caucasus at the beginning of this stage went along the northern margin of the Tethys Ocean and started moving with the vast territories of the Alpine-Himalayan orogenic belt due to active processes initiated by the movement of continents and their blocks. During this time, there was a considerable rearrangement of the previously developed structures, which resulted in the formation of the contemporary structure of the Caucasus.

The eastern Caucasus is characterized by the following large groups of rocks (from bottom to top): argillaceous slates and sandstones of the Lower and Middle Jura; hard armoring limestones of the Upper Jura–Lower Cretaceous; clays of the Lower Cretaceous; fractured limestones and marls of the Upper Cretaceous and Palaeogene; a thick layer of Maikop clays (Palaeogene–Neogene) that is widely developed along the Caucasian foothills and adjacent mountain structures; standstones with interlayers of Chokrak-Karagan clays (Miocene) that form the external front range of the Caucasus, which stretches continuously along the northern slope forming, in turn, the larger part of Central Ciscaucasia (Stavropol Upland); a thick layer of clay with a subordinate interlayer of limestones of the Sarmatian age, the rocks of which are strongly eroded but form a number of cameo mountains along the northeast of the Caucasus. Occurring higher are theterrigenous rocks of the Late Pliocene-Quaternary, which are particularly well-developed along the south-eastern edge of the Caucasus.

The progressively intensifying collision led to the rapid growth of the Caucasus during the Neogene and Pleistocene. Synchronously, various downfolds were formed (Indola-Kuban, Tersk-Caspian, North Absheron, Rioni, Lower and Middle Kura). The east of the Tersk-Caspian downfold was not compensated by sedimentation and has turned into the deep-water trench of the Middle Caspian. In other areas, the thickness of sediments accumulated in the Neogene–Quaternary period reaches 3–5 km; it exceeds 10 km in the southeastern and northwestern downfolds of the Caucasus (Absheron and Taman). The Quaternary volcanism developed intensively in the central part of the Caucasus when the tops of volcanoes (Elbrus and Kazbek) became higher than 5 km.

The rapid growth of the Caucasus resulted in an increased proportion of rudaceous rocks in the sediments of the surrounding lowlands. This is related to the acceleration of erosion processes as the size and height of adjacent mountain ridges grows. Another characteristic feature of the Pleistocene sediments of the region is seen in the sharp fluctuations in the level of the Caspian Sea, with an amplitude of more than 1000 m for 3 million years and about 180 m over the last 20000 years.

During the Neopleistocene, the vast areas to the north of the Caucasus (including some low-hill terrains) developed a trail of loess rocks. On the whole, such sediments are characterized by similar geochemical features.

MATERIALS AND METHODS

In order to create a geochemical map of variations in $^{87}Sr/^{86}Sr$ ratios for the eastern Caucasus, snail samples, an excellent source of data on the local $^{87}Sr/^{86}Sr$ signal, were collected. The collection and subsequent gridding were performed with a GPS navigator (Fig. 1). If possible, the snail samples were identified to species level (Table 1).

Snails use lime from soil and plants to build their shells. When there is lack of calcium material, they extract it directly from hard rocks and minerals. As a geochemical substitute of calcium, strontium is concentrated in mollusk shells and its isotopic composition reflects the geochemical signal of the environment from which it was taken by a living organism. In recent decades, data have been obtained on the functioning of strontium stable isotopes in living organisms ($^{88}Sr/^{86}Sr$ in corals) due to enhancement of the accuracy of analytical equipment. $^{87}Sr/^{86}Sr$ fractionation is still not understood: it either does not take place or its effect is so insignificant that one can not detect it.

The isotopic composition was investigated in the Laboratory of Isotopic Geology and Geochronology of Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences.

RESULTS AND DISCUSSION

Snail samples were collected from sites in the eastern Caucasus that differ by their parent rocks and altitude belts (Russia, Azerbaijan, and Georgia). They are, in their general features, characteristic of the geological diversity of the region under study. We analyzed data from nine sites (in two cases, two samples per site were taken to verify the accuracy of measurements). The mean statistical correction was ±0.000010 (Table 1).

Although the Sr content in the samples (determined by the specifics of the geochemical situation) differs, the ratios of the studied isotopes are relatively similar. The $^{87}Sr/^{86}Sr$ ratio in the eastern Caucasus varies from 0.70727 to 0.70859.

The highest values are typical in recent marine sediments (New Caspian and Khvalynsk), which have preserved the chemical features of marine water and their source of accumulation. The map of sampling sites with a geological map superimposed is provided below (Fig. 2).

In other Caucasian regions, the $^{87}Sr/^{86}Sr$ ratio varies from 0.7074 (Abrau-Dyurso) and 0.7075 on the coast of the Black Sea in Abkhazia (Gagry) to 0.7089 (Temryuk) (Shishlina et al., 2012; Trifonov et al., 2012). In the lowland-piedmont belt of the Northwestern Caucasus, the $^{87}Sr/^{86}Sr$ changes from 0.7075–0.7076 (Otkhara, Lykhny, Psybe, Shepsi) to 0.7087 (village of Starokorsunskaya), thereby varying within the range of 0.7093–0.7099 in the mountain regions (Lower Afon, etc.). The relatively high variations in the values are associated with the contrasting lithologic features of alluvium, of which the piedmont territories in this part of Caucasus are composed (determined by the diversity of rocks eroded in the upper reaches of rivers).

The ratio on the lowlands of the Central Ciscaucasia is 0.7089–0.7092 (Shishlina et al., 2012) with the minimum spread in values, which is probably due to the wide distribution of loess rocks.

The studied samples from the eastern Caucasus can be organized into several groups. The first group includes samples collected in the midmountain and piedmont landscapes of the eastern Caucasus, at altitudes from +480 to 1515 m. The ratios vary here within the range of 0.70786–0.70810, confined to the areas with the Jura and Cretaceous limestones. Such rocks are dominant in this part of the Caucasus.

For the lowland (Cis-Caspian) regions, the ratios were within the range of 0.70832–0.70859 (samples 5–6). Data were obtained based on contrasting samples: the clays of the Late Neopleistocene (Khvalyn') and shell detritus of the Middle Holocene. This $^{87}Sr/^{86}Sr$ ratio may reflect the specifics of the compositions of the Caspian Sea waters, which is preserved in these marine sediments. Accordingly, such values can be expected for all Khvalynsk and New Caspian sediments along the entire coast of the Caspian Sea (from Volgograd to Western Turkmenia).

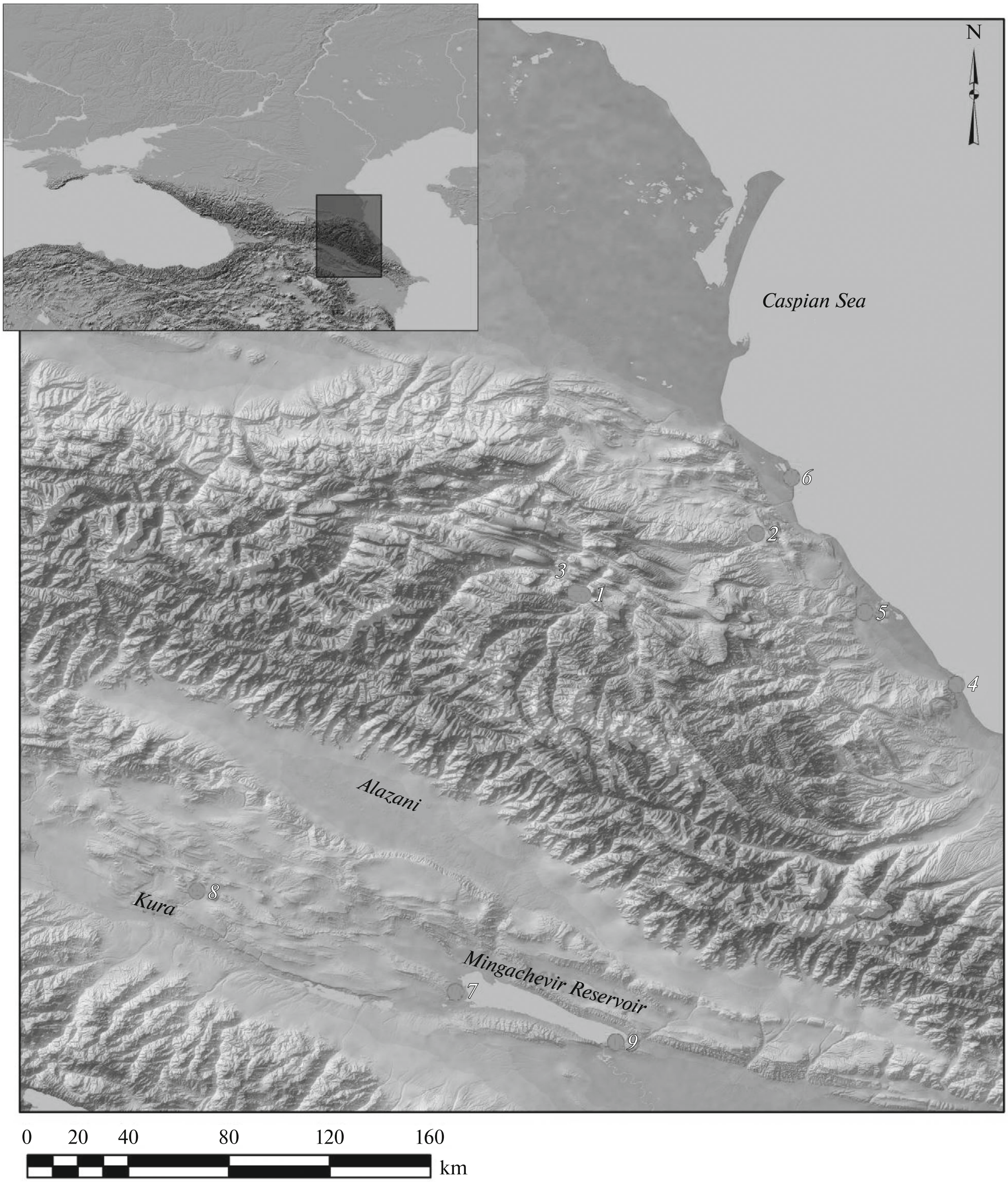

Fig. 1. General map of the eastern Caucasus with sampling sites.

One sample was obtained for the belt of foothills (low-mountain areas) of the northeastern Caucasus—0.70854 (sample 4) for the area with Sarmatian limestones of the Neogene that are widely distributed along the south of the East European Plain (from the Carpathians to the Ustyurt Plateau). Sarmatian limestones lying directly along the northeast of the Caucasus are preserved in the form of several small remnants having a total area of less than 500 km^2 (Tarki-Tau, Dzhalgan, Izberbash, Sheryabash, etc.). Moreover, Variations in $^{87}Sr/^{86}Sr$ ratios of contemporary snail samples from the eastern Caucasus

No.	Sample	Sr, μg/g	$^{87}Sr/^{86}Sr$	±2σ
1	Dagestan, Gunibskii district, Gunib village. Altitude 1235 m. Limestones—Lower Cretaceous. N 42°23′20″ E 46°57′47″	1031	0.708044	0.000011
2	Dagestan, Karabudakhkentskii district, Gurbuki village. Alluvium-deluvium. Altitude 480 m. Limestones—Upper Cretaceous. N 42°36′25″ E 47°34′55″	739	0.708099	0.000009
3	Dagestan, Gunibskii district, Gunibskoe Plateau. Altitude 1515 m. Limestones—Lower Cretaceous. *Helicopsis* N 42°23′44″ E 46°56′14.7″	851	0.707859	0.000012
4	Dagestan, Derbent; Naryn-Kala Citadel. Altitude 110 m. Limestones—Sarmatian stage—Neogene. *Helicopsis* N 42°04′09″ E 048°17′45″	1488	0.708542	0.000010
5	Dagestan, Kayakentskii district, Gerga village. Altitude 30 m. Oak forest. Clay. Early Khvalynsk terrace—Late Neopleistocene. N 42°19′35″ E 047°58′09″	2700	0.70859	0.000009
6	Dagestan, Karabudakhkentskii district, Turali Training Station. Altitude 21 m. Sands, shell detritus of the beach ridge. Novocaspian tier—Holocene N 42°48′24″ E 047°42′29″	2574	0.708326	0.000009
7	Azerbaijan, Palantekyan Mountain Ridge. Altitude 135 m. Clayey soils, clayed sand. Absheron stage—Eo-pleistocene. N 40°58′27″ E 046°30′33.97″	1411	0.707274	0.000009
8	Azerbaijan, Dzheiranchel. Altitude 440 m. Dry steppe. Clayey soils, alluvium of the Kura River tribuary. Neopleistocene—Holocene. N 41°20′02″ E 045°35′15″	1021	0.707395	0.000010
9	Azerbaijan, Bozdag (Garadzha) Mountain Ridge, 3 km to the east of Mingechaur. Altitude 130 m. Dry steppe of semi-desert. Clayey soils, clays. Absheron stage—Eo-pleistocene. N 40°47′51″ E 047°04′51″	1877	0.707669	0.000010

the eastern Caucasus is characterized by a contrasting distribution of rocks. Thus, the $^{87}Sr/^{86}Sr$ ratios at this territory and other rocks of the Palaeogene–Neogene can differ.

Samples from the central part of the Transcaucasia (7–9) from a separate group. They are characterized by a ratio from 0.70727 to 0.70766 (samples from the western part of Azerbaijan) and 0.70807 (Central Georgia). Samples 7–9 were collected at a distance of 150 km for rocks of different ages, from the Eopleistocene to Holocene. The mountain rocks of this area are dominated by terrigenous microfragmental rocks (clays, loamy soils, and sands), which can be repeatedly fragmented, undergo resedimentation, and accumulate again. On the whole, such characteristics of $^{87}Sr/^{86}Sr$ ratios can be found in all of the foothills that form a wide belt encircling the Caucasus from the

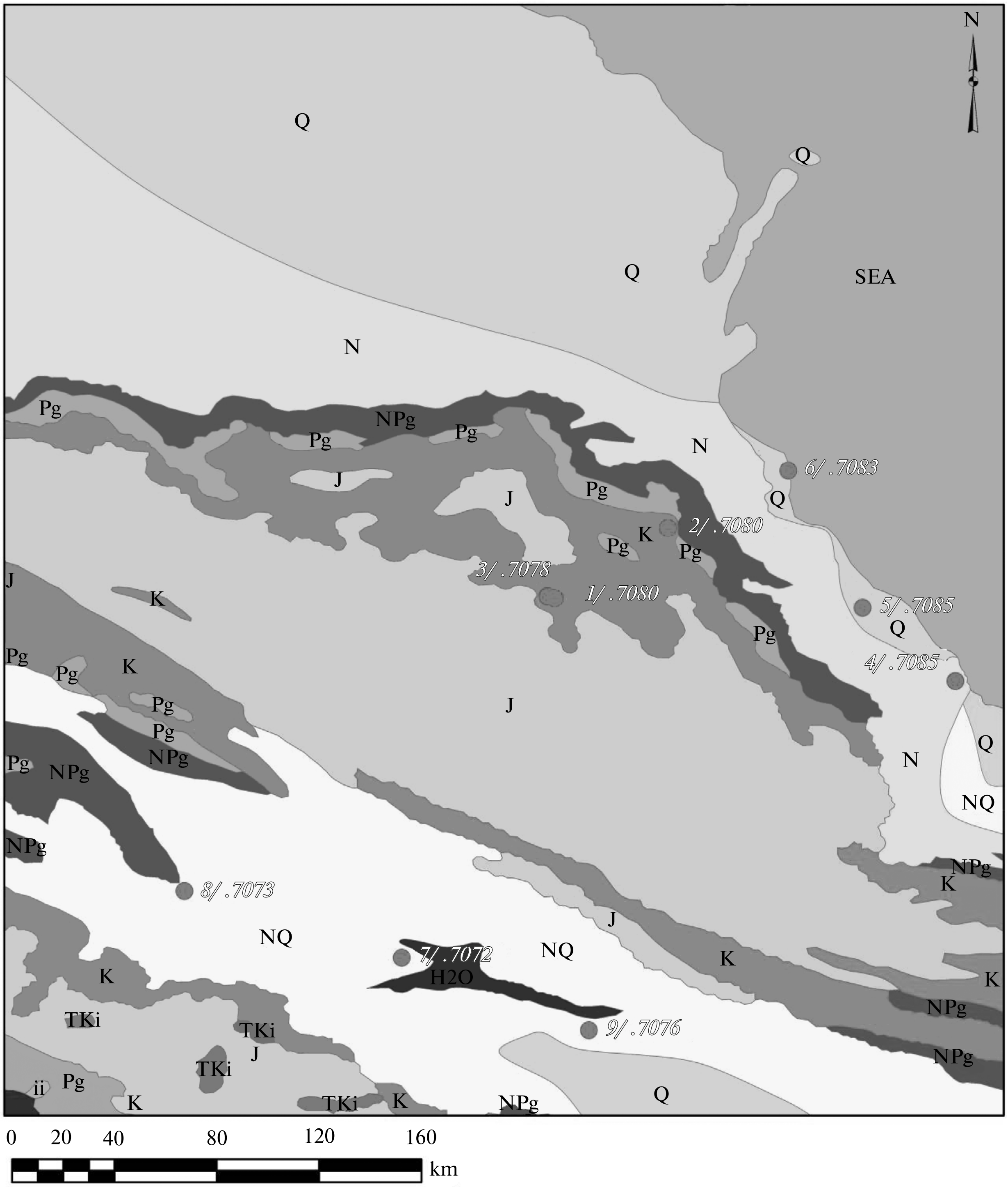

Fig. 2. Geological map of the eastern Caucasus.

south, as well as at the territory of the Kur-Araz Lowland, which is located southwards.

CONCLUSIONS

Variations in the $^{87}Sr/^{86}Sr$ ratios of contemporary snail samples from the eastern Caucasus complement data obtained previously from other regions of Russia. They show the $^{87}Sr/^{86}Sr$ ratios of particular large regions in the eastern part of Caucasus: Cretaceous limestones of Intermontane Dagestan, Late Pleistocene–Holocene marine terraces of the Caspian Sea, terrigenous rocks of Adzhinour region, and the entire southeastern periphery of the Caucasus. In other

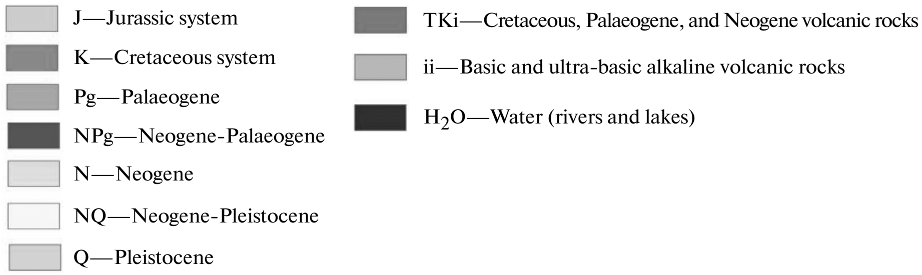

Fig. 3. Key to the geological map of the eastern Caucasus (see Fig. 2).

regions (the northeastern foothills of the Caucasus, the high-mountain zone of Jurassic rocks, Central Caucasus), further research should be done with the collection of samples from areas with different geological structures the. The revealed specifics of ^{7}Sr/^{86}Sr ratios in samples collected from different rocks prove their certain diversity and the possibility of singling out large regions with the same type of isotopic ratios, as well as in the preparation of the Atlas of Variations in ^{87}Sr/^{86}Sr Ratios in contemporary samples. These data would be helpful during the interpretation of natural-historic events.

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