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Paleosols Of Archaeological Sites In The Sochi Black Sea Coast

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Abstract

The paper provides the distinctive characteristics of several paleosols of the Sochi Black Sea coast of Russia. The authors explored two paleoalluvial soils (Histosoils (Folic)) in the open archaeological pits of ancient encampments (aged 8.3 and 24.5 thousand years) and the middle argic horizon Acrisols (Clayic) buried under the foundation of an ancient fortress (at the age of about 1600 years). Traditional soil methods were employed to reveal the morphological, chemical, microbiological properties of paleosols. Mass-spectrometry and atomic emission analyses with inductively coupled plasma enabled examination of their content for 61 chemical element. Comparison of paleoalluvial soils with their modern analogs revealed: 1) a reduced content of humus (1.4 times on average) and actual soil acidity (pHaq changed from 7.3 to 7.8 on average); 2) a decreased species richness of prokaryote microbiome (the index of operational taxonomic units was reduced 1.7 times on average) and a stable inhibition of a species of the Thermoleophilia class, Gaiellaceae family; 3) an increased content of some elements (Ca, Zn, Ba, Cu, Sr 3.0, 2.9, 1.8, 1.8, 1.7 times on average, respectively); 4) an increased content of exchangeable phosphorus (2.3 times on average), an additional source of which was bone remains of ancient animals hunted by humans. It is unique that the effect of rare earth element fractionation in organomineral horizons of paleoalluvial soils manifested itself as a positive europium anomaly (Er/Er*=1.3–1.1). All the examined paleosols showed lower contents of the rare earth elements group (REE) versus modern soils, due to the specific formation of their complex compounds. REEs are more active than other microelements in forming organic complex compounds with the nonspecific acids, which are released by living roots and generated during fresh plant litter decomposition. Hence, serving as ligands, REEs are accumulated in the complex compounds in modern soils. In paleosols their content is decreased.

Keywords: The Sochi Black Sea coast, paleosols.

1. Introduction

The paleosols of archaeological sites characterize the climatic conditions of their formation time, reflect the specifics of soil diagenesis, determined by transition of soils to a buried state. In addition, these relict objects bear evidence of particular activities of ancient human beings.

Archaeological soil science is an international, interdisciplinary research area, actively developing since the 80-90s of the last century at the intersection of paleosol science and archaeology (Gubin, 1984; Demkin, 1997; Demkin et al., 1992, 2007; Retallack, et al., 2003; Sheldon and Tabor, 2009).

Research studies of paleosols in archaeological sites have shown a wide variety of key aspects of soil formation history due to a space-temporal variability of environmental factors. Scientists identified the peculiarities of the genesis of the Late Pleistocene and Holocene soils, related to climatic changes and terrain-formation processes. There were conceptual models of the Holocene evolution of soils; they were proposed for many natural areas (Mikharevich et al., 2020; Reider, 1980; Wu, 2012; Wenxiang et al., 2013; Rouza et al., 2021; Suleymanov et al., 2020). Among the most extensively studied problems, there are genetic-evolutionary patterns of steppe soil formation, as well as the issues linked to the history of environmental development in Eurasian semiarid and arid regions. Researchers found regularities in the processes of solonetz and humus formation and profile textural differentiation; they established the directions and rate of migration of salts, gypsum and carbonates (Demkin, 1997; Khokhlova et al., 2001, 2007; Demkin et al., 2007; Tatyanchenko et al., 2013; Zolotareva and Demkin, 2013).

They also revealed particular features of transformation in paleosols, occurring during their burial. Soil diagenesis in paleosols contributes to a significant decrease in humus content due to organic matter mineralization, a reduction in soil acidity, a decline in their microbiological activity (Zolotareva and Demkin, 2013; Tatyanchenko et al., 2013; Retallack et al., 2003; Sheldon and Tabor, 2009, Ivanov et al., 2009, Alekseeva et al., 2019).

Various elements of paleosol transformation, related to human activities, are indicative of some distinctive traits of the past anthropogenic impact on the environment. For instance, the comparison of paleosols with natural soils of the same age at the locations of medieval settlements in the South-Eastern Romania and the Czech Republic showed a decline in the acidity of settlement soils and accumulation of P, K, Ca, Mg, Mn, Fe, Cu, Zn, Sr and Rb (Radu et al., 2020; Asare et al., 2021). High content of both total and plant-available phosphorus, as well as respective good resistance to leaching, was observed in agricultural soils of the Neolithic Age (from 4400 to 2200 B.C.E.) and the Bronze Age (from 2200 to 700 B.C.E.), in loess areas of Central and Western Germany (Lauer et al., 2013). In the East Mediterranean (Israel), the paleosols of medieval settlements showed presence of specific calcite minerals of non-natural origin, which indicated soil alkalization due to human life activities (Itkin et al., 2016). In the Danish Forest area, modern distribution of soils demonstrates their previous land use in the Bronze and Iron Ages (Kristiansen, 2001).

The history of anthropogenesis is reconstructed according to the inherent properties of variously aged soils. For example, abundant traces of fossil roots are linked to a long period of steady conditions, associated with the absence of people in the German Middle Franconia in the Early Bronze Age (Sprafke et al., 2020). The urban landscapes of the Mayan epoch settlements demonstrate that this civilization employed engineering methods and landscape modifications that preserved soils in urban conditions (Evans et al., 2021).

Despite the data about the origins of palesols are extensive, the questions of their geography in different historical epochs and diverse climatic zones remain poorly studied. There are almost no works devoted to the paleosols in the territory of the humid subtropical zone of Russia (the Black Sea coast near the city of 0Sochi). However, this region has abundant archaeological artefacts of various epochs (from ancient encampments to medieval archaeological objects) and representatives of indigenous ethnic groups and numerous migrating peoples. Medieval monuments here are very common, including castles and other facilities of worship. Their foundation rests on structural-metamorphic horizons (the argic clay horizon) of zonal soils - zheltozems (Acrisols (Clayic)), developed in the coastal marine area, and brown soils (Cambisols (Clayic)), spread away from the sea. Generally, there are no organomineral horizons in such buried soils. However, it is also quite relevant to examine the middle clay argic horizon, which characterizes the subtropical type of soil formation and became buried about 500-1800 years ago.

In addition to commonly encountered medieval objects, there are many ancient encampments in the river valleys of the Black Sea coast near Sochi. These are caves and grottos adjacent to riverbeds. Early men used them as a temporary shelter during hunting for animals' slaughtering and primary carcass cutting. The age of these encampments (for well-known objects, thoroughly explored by archaeologists) varies widely from the Pleistocene to the Middle Holocene (Voronov, 1979). Here, in the necks of caves and grottos, alluvial soils are likely to be found, buried by the natural processes of terrain formation.

In the wide arsenal of genetic soil analysis used in paleosol studies, not inferior to the study of daytime soils, it is hard to find an in-depth examination of their composition for the content of rare and dispersed elements. Meanwhile, soil diagenesis, primarily accompanied by mineralization of organic matter with no supply of fresh organic litter, can occur with a change in geochemical properties of soils (Ivanov et al., 2009; Tatyanchenko et al., 2013; Zolotareva and Demkin, 2013; Alekseeva et al., 2019). For example, it is of interest to examine the behavior of Rare Earth Elements (REE). These are known to be good indicators of changes in conditions and are closely related to acids of a non-specific nature, formed during primary decomposition of fresh organic litter that is absent in paleosols.

The work aims at characterizing the main indicators (morphological, chemical, microbiological properties) of paleosols of the archaeological sites located along the Black Sea coast near Sochi. It also involves an in-depth analysis of the composition of soil elements, including a broad spectrum of rare and dispersed chemical elements, to identify the specifics of transformations in geochemical properties of paleosols due to their transition to a buried state.

2. Location, material and methods

The research was carried out at three archaeological objects of the Sochi Black Sea coast. Two of them are ancient encampments located in the Akhtsu grotto and the Akhshtyrskaya cave within a hillslope of the right-bank terrace of the Mzymta River, in its middle reach. The Mzymta River flows in the Adler region of Sochi. It begins in a small lake at the altitude of 2440m and flows into the Black Sea (Fig.1). The valley in the upper reaches of the river is V-shaped. The bottomland along the riverbed in its middle reaches is ~50-70m wide, upwards of which there are steep slopes with a gradient of 30–35° and sometimes 40–50°. Upon reaching the Adler lowland, the Mzymta River flows across a wide, well-developed valley. The river is characterized by a pronounced seasonal flood during the warm period of the year, frequent autumn floods, and a steady winter low-water season.

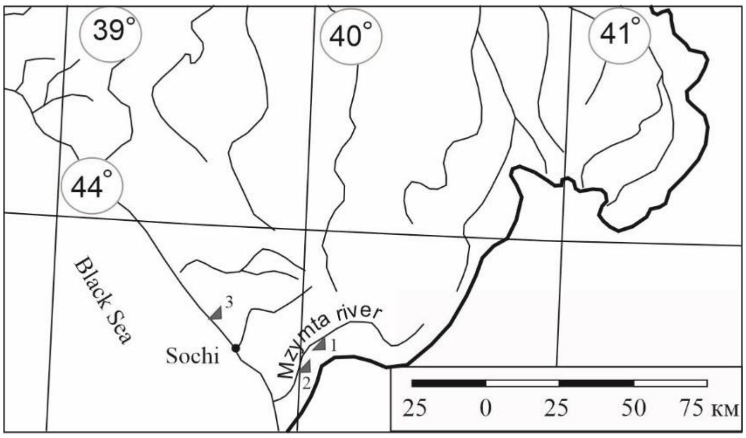

Fig. 1 Schematic map of the study area, 1 – the Akhtsu grotto, 2 – the Akhshtyrskaya cave, 3 – the Mamai-Kale fortress.

This part of the river valley is formed by sedimentary deposits. Paleogene and Neogene clays, marl clays with siltstones underlie recent alluvium (Lavrischev et al., 2002). The river basin is characterized by the development of polymetallic, lead, zinc, and gold ore mineralization with lateral extension (tens and hundreds of square kilometres) (Bogush and Cherkashin, 2012). There is a developed dispersed sulphide mineralization in both sedimentary and intrusive rocks (Karelina et al., 2017). Paleogene subalkaline basic and intermediate rocks with rare-metal–rare-earth specialisation are also present (Gazeev et al., 2018).

The Akhtsu grotto is located 20km from the sea coastline and about 70m from the Mzymta River waterline. Its absolute elevation above sea level is 133m, elevation above the river level is 12m (Kulakov et al., 2017). The grotto is a small cavity in the river valley slope, well heated by the sun. The grotto neck (of about 5m^2) is covered by cave loose sediments. The ancient encampment in the Akhtsu grotto, as well as its ancient things made of flint, was first discovered by A. Kizilov in 2014. Later, in the culture-bearing layers of the grotto neck deposits, scientists found fragments of ancient stone ware and remnants of early animals (brown bear, red deer, wild goat, moufflon, marten, fox, birds, and fish), obtained by humans while hunting. The results of archaeological surveys made it possible to classify the grotto as the Stone Age monument and name it the “cave encampment in the Akhtsu grotto” (Kulakov et al., 2017).

The studies, carried out as part of this work, were undertaken on the open pit made during archaeological surveys in 2015. In the scarfed pit outcrop, located at the grotto edge, at the depth of 12-30 cm, archaeologists found paleosol formed in a finely disintegrated rock of cave deposits. The top of the paleosol was overlain by a horizon of dense calcareous rock. The calcareous rock had deposited during destruction of the grotto walls and ceiling and had potentially been exposed to hydrothermal processes, as witnessed by its considerable compaction (cementation).

The pedogenic nature of the very dry, loose, spall-containing horizon, occurring at the depth of 12-30 cm, was confirmed by its crumby structure, high content of humus (3.85%, Table 1) and presence of individual fragments of well-preserved rhizoliths (ancient roots). Concerning its mesomorphological properties (studied under ×10 magnifier), the paleosol was a loosely formed dark-brown amorphous material, bonded in clumpy blocks. The age of the layer, where the paleosol was found, was defined during archaeological studies using radiocarbon method by the bones of ancient animals; it was 8.3 thousand years (Kulakov et al., 2017).

The second object of the studies was the widely recognized Akhshtyrskaya cave, positioned downstream from the grotto, 15km from the sea coastline. The early mana’s encampment in the Akhshtyrskaya cave was discovered in 1936 by S. Zamyatin and repeatedly examined by subsequent archaeological expeditions (Voronov, 1979). The soil studies in the scarfed wall of the pit made during archaeological studies in 2008 identified a paleosol buried at the depth of 20-37 cm beneath cave deposits of crushed calcareous rock. According to the numbering specified by archaeologists, such paleosol is common within the 3rd excavation horizon in layer 2/3 (Kulakov and Kulkova, 2017). The morphological, mesomorphological, physical and chemical soil properties were similar to those of the above-described paleosol of the Akhtsu grotto. It differed from the latter in abundant inclusions (of up to 30%) of the crushed material of limestone spalls in the horizon mass. The age of the layer, where archaeologists had found an organomineral horizon using radiocarbon “carbon-like lens” dating, was about 24.5 thousand years (Kulakov and Kulkova, 2017). The lower part of the archaeological section was represented by different mineral horizons - from pebbly material to loam soils, and clays, deposited here during the Pleistocene period as a result of alluvial processes.

Examination of the morphology, properties, and location across the terrain helped to classify the soils of the described objects as alluvial grey -humus soil (Shishov et al., 2008). As per the World Reference Base for Soil Resources (WRB, 2014) and special paleosol classification of G. Mack (Mack et al., 1993), such soils are diagnosed as Histosoils (Folic). Modern analogs of these soils, with similar properties and mesomorphological characteristics, were tested in the immediate vicinity of the grotto and the cave, on the same slopes of the river valley under tall-grass and various-grass vegetation in the large-blocked rock fissures.

The third object of this study was the soil buried under the ruins of the ancient Mamai-Kale fortress. It is located in the boundaries of Sochi in the Mamaika micro-region close to the Psakhe river mouth on an elevated littoral terrace. The fortress was first mentioned way back in the 18th century by the French consul Jacques-Francois Gamba. He was recognised as the discoverer of Mamai-Kale (Voronov, 1979). Later, the fortress was repeatedly explored. There were numerous diverse hypotheses on the time of its construction. Recent research recognise that the fortress was built at the turn of III-IVth centuries C.E. to protect a local trade settlement (Argun, 2020). The present studies detected a material of a buried structural-metamorphic clayed Bmg horizon (clay argic horizon) of paleo zheltozem (Acrisols (Clayic)). It was found under the fortress foundation during archaeological excavations in 2003. The buried horizon had morphological and mesomorphological attributes similar to the analogous properties of Bmg horizons of modern Acrisols. About 1600 years ago, the middle and lower part of Acrisols profile, typical of the Russian subtropical zone (devoid of the upper organomineral horizon during the fortress construction), was buried under the building foundation. To study the specifics of the buried soil transformation, the authors explored modern Acrisols (Clayic) soil that is frequently encountered in the immediate surroundings at identical altitudes.

The pH of aqueous and salt (1 N KCl) soil extract (the ratio “soil: solution” – 1:2.5) were determined using the potentiometric method (state technical standards GOST 26423-85, GOST 26483-85, respectively). The content of humus was defined using the Tyurin methodology, as modified by CINAO (GOST 26213-91), with selection of plant residue during sample preparation and colorimetric termination. Hydrolytic acidity was defined by means of titrimetric analysis, using the Kappen method as modified by CINAO (extract 1 N CH3COONa, in the ratio of “soil: solution” – 1:2.5, GOST 26212-91). The content of exchangeable forms of calcium and magnesium was found trilonometrically with the extraction of 1 N NaCl (GOST 26487-85), exchangeable forms of phosphorus and potassium - using the Olsen and Maslova methods, respectively.

The samples of buried soils for microbiological metagenomic analysis were selected with the use of sterile gloves and knives. They were further placed into sterile plastic tubes with a sealed cover. These tubes were frozen in a freezer compartment at t=-20°C; after several days, they were delivered frozen to the laboratory for follow-up studies. The 16S rRNA gene sequencing method was employed for the metagenomic analysis. Metagenomic libraries were prepared pursuant to the “Preparing 16S Ribosomal RNA Gene Amplicons for the Illumina MiSeq System” Protocol. 16S rRNA V3-V4 region was amplified employing prokaryotic primers: upstream – TCGTCGGCAGCGTCAGATGTGTATAAGAGACAGCCTACGGGNGGCWGCAG; downstream – GTCTCGTGGGCTCGGAGATGTGTATAAGAGAC AGGACTACHVGGGTATCTAATCC, with further indexing of amplicons. Sequencing was performed on the Illumina MiSeq platform (USA) (the mode of pair reading of 300 base pairs). The algorithm for classifying operational taxonomic units (OTU) with open reference (Open-reference OTU) was used while processing the sequencing data. Similarity classification threshold was taken as 97%, which usually corresponds to a species. The results of analysing OTU representation in the samples allowed computing the biodiversity indices of Shannon (Shannon, H) and Chao1 (estimation of the OTU real number in microbiome): $H = -\Sigma p_i \ln p_i$ (p_i – percentage of the i^{th} species in the community; S_{est} (ChaoI) = $S_{obs} + a^2/2b$ (S_{est} – estimated number of OTU, S_{obs} – observed number of OTU, a – number of OTU, revealed one time, b – number of OTU, revealed exactly twice).

The total contents of 61 chemical element in soils were defined using quantitative methods. These involved mass-spectrometric and atomic emission analyses with inductively coupled plasma (ICP-MS and ICP-AES), made according to the attested methodology of ABAA[1] No.499-AES/MS “Determination of elemental composition of rocks, soils, grounds and bottom sediments using atomic emission method with inductively coupled plasma and mass-spectral method with inductively coupled plasma”. The equipment in use was: a mass-spectrometer with inductively coupled plasma Elan-6100 ("PerkinElmer", USA), an atomic emission, inductively coupled plasma spectrometer Optima-4300 DV (“PerkinElmer”, USA).

Decomposition of samples was carried out in an open system, with the use of HF, HNO_3, HCl and $HClO_4$. Decomposition stages of each sample were under control employing stable isotopes. Standard samples confirmed accuracy of the analysis. Usually, such a method for dissolving samples provides a 90–100% chemical yield of all defined elements. The use of these methods and external standard gives a ≤6% error in defining chemical elements. The method detection limits for soils are: two decimal places of microgram per gram for microelements and two decimal places of a per cent for macrocomponents. The techniques of decomposition and further analysis of the obtained solution using the ICP-MS + ICP-AES methods were described in detail in 2007 (Karandashev et al., 2007).

To estimate differences in elemental compositions of paleosols and their modern analogs, coefficients of concentrations of chemical elements (CC) were calculated as the ratios CC = Cipa / Cim, where Cipa is the content of an element in the paleosol and Cim is its concentration in the modern soil. With allowance for potential variations in the concentrations of elements in soils, determined by random

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factors, significant differences in contents of elements in soils were considered within the $1.5 \geq CC \geq 0.5$ range.

To evaluate the specifics of the behaviour pattern of rare earth elements in the examined soils, the REE contents were normalised in relation to the North American Shale Composite (NASC). The Eu anomaly value was calculated by the formula: $Eu_{an} = Eu_n / (Sm_n \cdot Gd_n)^{1/2}$ (Haskin et al., 1968; Gromet et al., 1984).

3. Results and discussion

3.1 Chemical properties of soils

As compared to modern soils, the paleoalluvial soils show a 1.3-fold and 1.5-fold decrease in humus content (in the grotto and cave soils, respectively) (Table 1). This transformation is determined by soil diagenesis, which is considered as a stage of physical and chemical equilibration of the soil body, occurring due to transition of soils to a buried state (Gubin, 1984). Mineralization of organic matter in paleosols, accompanied by gradual decrease in humus content, is recognized to be one of the most significant processes among diagenetic alterations (Demkina and Demkin, 1994; Retallack et al. 2003; Sheldon and Tabor, 2009; Tatyanchenko et al., 2013; Zolotareva and Demkin, 2013; Alekseeva et al., 2019). It was found that the loss of humus over the first 1700 years is equal to 50%. In the period of up to 1 million years, humus content in paleosols remains relatively constant at the rate of 0.3% (or 6-7% of the original content). In this case, during diagenesis, the type of humus and its elemental composition s preserved (Ivanov et al., 2009).

With the foregoing data as a background, the examined paleoalluvial soils show a very minor decrease in the humus content compared to modern soils. This fact can be explained by two factors. The first one is the composition of local rocks. It is known that in the soils, formed on clayey argillites and shales, C_{org} associated with clay minerals of the silt fraction of soils remains unchanged for a long time (Ivanov et al., 2009, Prikhodko et al., 2020). Moreover, the process of organic matter mineralization is manifested to a lesser degree in peat-like and hydromorphic paleosols (Retallack et al. 2003; Sheldon and Tabor, 2009). The latter should involve the examined alluvial paleosols, formed in the vicinity of the riverbed in conditions of regular over-moisturizing.

Another significant element of transformation of the studied paleosols is a steady decrease in their actual acidity. An increase in pH of paleosols is mostly connected with a growing content of exchangeable forms of Ca in them (1.5 and 2.2 times in soils of the grotto and the cave, respectively). These easily leach from soils. Contrariwise, the hydrolytic soil acidity of the paleosols is lower. It characterizes the total content of hydrogen and aluminum ions, including those tightly bound in the soil adsorption complex. A lesser degree of leaching of Ca exchangeable forms in paleosols, on the one hand, can be indicative of drier and colder climatic conditions of the period, when they were formed. On the other hand, it may reflect the specifics of the soil diagenesis, accompanied by more alkaline conditions, due to the lack of supplying fresh organic litter to paleosols. The processes of primary decomposition of organic matter are known to go along with formation of nonspecific acids (acetic, glycolic, lactic and others) with pH of 2-3 units (Nagao et al., 1998). These acids acidify the surrounding medium and facilitate leaching of the most mobile forms of chemical elements from the upper organomineral horizons of soils. Absence of nonspecific acids in buried soils contributes to a gradual decrease in actual acidity and an increase in the content of more mobile weakly bound forms of elements in them.

This factor can also be associated with a higher content of exchangeable forms of phosphorus and potassium in paleosols relative to modern soils. A substantial (3.1 times) difference between the content of phosphorus in the modern and paleoalluvial soils of the grotto can additionally be linked to abundant phosphorus-enriched bone remnants of ancient animals in them (Kulakov et al., 2017).

3.2 Elemental composition and microbiological properties of soils

From exploring the microbiological properties of the background alluvial soils by OTU, Shannon and Chao1 biodiversity indices, it was found that the studied soils exhibited an intense microbiological activity. The values of the mentioned indices were similar to those of the upper horizons of the alluvial soils developed in tropical climate (Chernov et al., 2019).

The paleosols demonstrated a significantly lower number of their prokaryote microbiome species as compared to modern soils (Table 2). The OTU number of prokaryotes in the soil of the grotto and the cave was 1.6 and 2.8 times lower than in modern soils. Shannon (H) and Chao1 biodiversity indices were 1.1 and 1.5 times lower in the grotto soils and 1.4 and 3 times lower in the cave soils, respectively.

To identify taxons-indicators of microbiome in the paleosols, we selected the phyla and species of prokaryotes (higher and elementary taxonomic units), which were dominant in bacterial cenosis and the DNA occurrence of which in the examined soils exceeded 1%. Life activity of the dominant forms of soil microorganisms defines the direction, in which the processes of transforming substances in carbon and nitrogen cycles take place (Dobrovolskaya et al., 2015). The qualitative composition of dominant bacterial phyla was akin for all the buried examined soils and their modern analogs. It can be confirmed by their similar genesis.

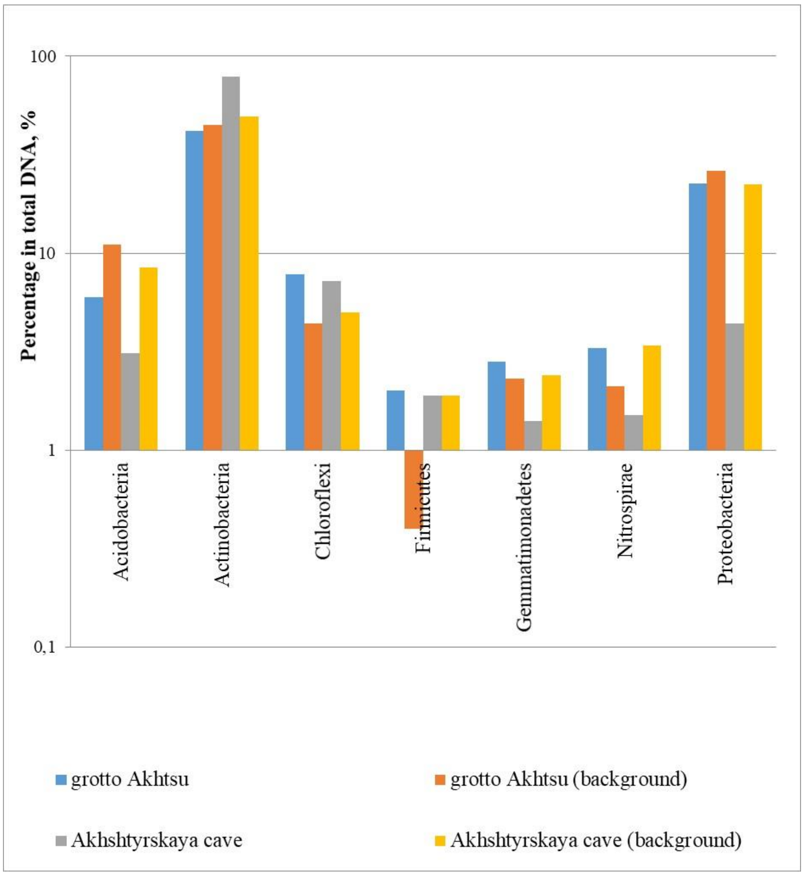


Fig. 2. DNA percentage (%) of the dominant phyla of bacteria in paleo and modern background soils.

Seven out of 37 detected phyla were dominant (Fig.2). The Actinobacteria phylum (42-79%) had a maximum percentage of the total DNA, which is inherent in southern soils (Chirak et al., 2013). The Proteobacteria phylum were developed to a smaller extent (4.4-26.3%). The percentage of Chloroflexi phyla (4.4-7.8%), Acidobacteria (3.1-11.1%), Nitrospirae (1.5-3.4%). Gemmatimonadetes (1.4-2.8%), Firmicutes (0.4-2%) had even lower shares in the total DNA. All the listed dominant phyla form a part of soil prokaryotic community of various types of soils. They form associations and are involved in disintegration of organic matter (Chirak et al., 2013; Chernov et al., 2018, 2019).

The ratio between Actinobacteria and Proteobacteria phyla can serve as a diagnostic indicator, showing both the degree of soil organic matter mineralization determined by soil diagenesis and the conditions for soil formation. In the grotto paleosol, the ratio “Actinobacteria / Proteobacteria” was comparable to modern background analogs. The values of this ratio for the cave soil were 9 times higher compared to modern soils, due to an increase in the percentage of actinobacteria (by 30%) and a decrease in the number of proteobacteria (by 18%). One of the factors, which considerably changed the structure of microbial community in the soils of the Akhshtyrskaya cave as compared to the grotto soils, is apparently a slightly higher degree of organic matter mineralization in them. In addition, it is likely that drier conditions of soil formation in the cave affected Actinobacteria and Proteobacteria content in the soil. The

Akhshtyrskaya cave is situated in rock outcrops high up off the river waterline. The Akhtsu grotto neck is positioned much closer to the surface of a low terrace rising above the river floodplain at a rather low hypsometric elevation. Most likely, the grotto soils were formed under more hydromorphic conditions and were exposed to bottomland processes more than the cave soils.

It is common knowledge that the main physiological features of Actinobacteria species, mostly gram-positive spore-forming bacteria, are their orientation towards hardly accessible organic substrates (cellulose, chitin), including humic acids (k-strategists), and their drought-resistance and ability to develop even more actively during dry periods (Chernov and Zhelezova, 2020). Proteobacteria species (the largest group of gram-negative bacteria, 1534 species or about one third of all known species) are characterized by the ability to quickly grow and reproduce on easily accessible substrates (sugars, organic acids, amino acids) (r-strategists) and sensitivity to arid conditions (Zvyagintsev et al., 2005). It explains a considerable increase in the Actinobacteria /Proteobacteria ratio in more ancient soils of the Akhshtyrskaya cave, formed in less hydromorphic conditions.

The lack of differences in the Actinobacteria / Proteobacteria ratio in the grotto paleosols and their modern analogs can be also associated with the effect of a complex of factors. It includes the process of organic matter mineralization, which is less manifested in hydromorphic paleosols, and more humid conditions of their formation and burial.

The content of remaining dominant phyla in paleosols and their modern analogs differed insignificantly. There was a noticeable tendency towards a higher content of Chloroflexi (by 3%) and a decline in Acidobacteria (by 5%) in the buried soils. However, these changes can hardly serve as the indicators of temporal (evolutionary) re-formation of the microbiome structure, because they correspond to the level of seasonal fluctuations in the content of these groups of microorganisms in soils (Chernov and Zhelezova, 2020). On the other hand, alterations in the chemical parameters of the paleosols, namely, alkalization during diagenesis, could lead to a decline in the number of Acidobacteria, since they are known to have an inverse correlation with the indicator of soil acidity (Chirak et al., 2013; Chernov et al., 2019).

The study of the species structure of bacterial cenosis showed that all the identified dominant species (16 of 522 sampled) represented the dominant phyla. To make a discussion of results convenient, each species was given a sequence number. Actinobacteria (numbers 1-11) prevailed; it once more attested predominance of this group of microorganisms in southern soils of alluvial type. One species each belonged to the Proteobacteria, Chloroflexi, Nitrospirae, Firmicutes phyla. The qualitative and quantitative compositions of dominant types in the modern soils and in the soils sampled from the grotto and the cave were identical. It again confirms the unity of the genesis of soils formed in the coastal zone of one mountain river. The paleosols of the grotto had identical composition of dominant species as compared to modern background analogs. However, the content of most of them was a little higher (by 0.8–4.9 %). It may relate to both seasonal fluctuations and a more intense mineralization of paleosol complex components (including those related to human activities). The exception was species no. 7 and 8 (Actinobacteria phylum, Thermoleophilia class) from a specific group of microorganisms that includes few species with sensitivity to temperature factor (meso- and thermophiles) (Albuquerque et al., 2011). A lower content of these species of Actinobacteria in the paleosol is likely to be related to colder climatic conditions (relatively the existing ones) of the Holocene period, during which the grotto soil was formed. The prevailing bacterial cenosis of the cave paleosol differed from modern analogs both quantitatively and qualitatively. There were no species no. 4 and 5 (Actinobacteria phylum, Micrococcaceae family, Arthrobacter genus) and 13 (Proteobacteria phylum, Sphingomonadaceae family, Kaistobacter genus). Actinomycetes from the Micrococcaceae family, including Arthrobacter genus, and Kaistobacter genus Proteobacteria are of widespread occurrence in modern fertile soils (Zverev et al., 2016). Chinese scientists defined the Kaistobacter genus as dominant in the soils of parks and gardens (Wei et al., 2018). Their disappearance from the cave is evidently conditioned by a greater degree of organic matter mineralization (a decline in soil fertility) and more arid conditions. A slightly higher content of humus, sufficient humidification and more neutral ambient of the grotto paleosol facilitated preservation of these bacteria forms therein.

The species of interest were those whose content differed considerably (by more than 5%) in the cave buried soils and modern analogs. Thus, the content of species no. 1, 2 (Actinobacteria phylum, Pseudonocardiaceae family) and 6 (Nocardioidaceae family) in the cave soils was higher by 16, 22 and 5.2%, respectively. Actinomycetes of the Pseudonocardiaceae and Nocardioidaceae families are characterized by the ability to use complex organic substances as substrates. Moreover, they are drought-resistant, which defined their considerable predominance in the cave paleosol.

The percentage of species no. 7 (Actinobacteria phylum, Thermoleophilia class, Gaiellaceae family) were lower, as compared to modern analogs, in the paleosols of both the cave (by 11.4%) and the grotto (by 2.8%). Inhibition of the the named family species (which species identity requires better specification) can be considered as one of the diagnostic attributes of subtropical paleoalluvial soils.

3.3 Elemental composition of soils

In analyzing the total elemental composition of paleosols, it is more correct to speak about its transformation, occurred due to soil diagenesis. This indicator will to a lesser degree reflect various conditions of soil formation during different Holocene or Pleistocene periods. The reason is that it mostly depends on the composition of soil-forming rocks, which is invariant throughout geological eras. In various periods (namely, in the Upper Pleistocene, the Middle Holocene and at present time), the soil elemental composition of the Mzymta River middle reach and the Psakhe river mouth was formed and is formed owing to the chemical composition of Jurassic limes in the first case, and Oligocene clays with beds of silt stone – in the second case. Different geochemical properties of paleosols, as compared to modern soils, should be considered as a short-term (from the point of view of geology) transformation. The latter relates to a change in redox conditions, alteration and mineralization of organic matter, a decline in microbiological activity of soils, etc.

A comparative analysis of the elemental composition of paleosols and their modern background analogs confirms the invariability of the rock composition (Table 3). In all studied paleosols, the contents of most chemical elements were similar to the contents in modern soils.

For the paleosols of the Akhtsu grotto, CC of 32 chemical elements of the examined 54 were close to 1 (Table 4). In the paleosols of the Akhshtyrskaya cave, this indicator was even more apparent – 47 elements of 54. In the structural- metamorphic horizon of the Mamaika district paleosol, there were only 3 elements with CC higher than 1.5.

The group of elements with CC ≤ 1.5 for the paleosol of the Mzymta River valley incorporates Ca (3.9, 2.1), Zn (2.4, 3.4), Ba (2.1, 1.5), Cu (1.7, 1.8), Sr (1.4, 2.0) (the CC values in parentheses are given for the grotto and cave soils respectively), As (1.5) for the grotto soils, Mo (CC=7.3), K (1.6) and Na (1.5) for the cave soils. In the mineral horizon of the Psakhe river valley paleosol, CC ≤ 1.5 is found only for Ca (16.9), Cd (1.7) and Sr (1.6).

On the one hand, higher contents of some elements in the paleosols can be attributed to the lack of primary decomposition of fresh organic litter that acidifies the surrounding medium and facilitates leaching of more mobile forms of chemical elements. Concurrently, it should be noted that the spectrum of elements with high CC in the Mzymta River paleosols indicate their potential connection with the geochemical anomalies of the rocks developed at predominant elevations of the territory. As per the scheme of mineragenic zoning (Lavrischev et al., 2002), there are several mineragenic zones and ore districts near and within the watershed boundary of this segment of the river valley. Two geochemical anomalies are characterized by excessive values of Zn and Cu in the soil composition. There are also zones of auric sulfide mineralization, which always contain As as an accessory mineral (Saet et al., 1990). The area also shows presence of barites, whose associated elements are Sr and Ca (Saet et al., 1990).

In such conditions, increased contents of the listed chemical elements are likely to appear in the soils of the nearest territories. The paleosols of the Mzymta River valley were both formed on the local soil-forming rocks and overlapped with the crushed redeposited material of these rocks. They could accumulate greater amounts of elements than their modern analogs formed on the steep slopes of terraces on the surface of dealluvial deposits.

3.4 Rare earth elements

The most interesting point in estimating the geochemical indicators of paleosols is the specifics of rare earth element distribution in them. Rare earth elements have comparable chemical properties and simultaneously are good geochemical indicators of changing conditions (Haskin et al., 1968; Gromet et al., 1984). Due to high REE sensitivity to changes, e.g., to reductive-oxidative processes, the REE group can undergo fractionating and show positive or negative anomalies of individual elements, expressed in their higher or lower content relatively to the other elements of the group.

No.	Phylum	Class	Order	Family	Specie
1	Actinobacteria	Actinobacteria	Actinomycetales	Other	
2	Actinobacteria	Actinobacteria	Actinomycetales	Pseudonocardiaceae;	
3	Actinobacteria	Actinobacteria	Actinomycetales	Pseudonocardiaceae;	Pseudonocardia
4	Actinobacteria	Actinobacteria	Actinomycetales	Micrococcaceae	
5	Actinobacteria	Actinobacteria	Actinomycetales	Micrococcaceae	Arthrobacter
6	Tinobacteria	Actinobacteria	Actinomycetales	Nocardioidaceae	
7	Actinobacteria	Thermoleophilia	Gaiellales	Gaiellaceae	
8	Actinobacteria	Thermoleophilia	Solirubrobacterales		
9	Actinobacteria	Acidimicrobiia	Acidimicrobiales		
10	Actinobacteria	MB-A2-108			
11	Actinobacteria	MB-A2-108	0319-7L14		
12	Nitrospirae	Nitrospira	Nitrospirales	0319-6A21	

13	Proteobacteria	Alphaproteobacteria	Sphingomonadales	Sphingomonadaceae	Kaistobacter
14	Chloroflexi	Gitt-GS-136			
15	Firmicutes	Bacilli	Bacillales	Bacillaceae	Bacillus
16	GAL15				

All the territory of Sochi, including the Mzymta River valley, has a particular specificity of REE distribution in natural environments (Zakharikhina and Litvinenko, 2019). The sedimentary rocks of most of the Sochi Black Sea coast are characterized by high REE content. Therefore, the river waters, e.g., the Mzymta River, are significantly enriched with rare earth elements. In summer, REE concentrations in the river waters are 10-100 times higher than their medium contents in continental waters. Contrariwise, the soils and bottom sediments in the region are REE-depleted. At that, the general geochemical specificity of the discussed environmental components is defined by similar well-conditioned configuration of REE concentration spectra (normalized in relation to the North American Shale Composite (NASC)) with steadily prevailing middle group of REE (MREE) (Zakharikhina and Litvinenko, 2019).

The background soils formed in the immediate vicinity of the examined paleosols are characterized by predominance of the middle REE group (Nd, Sm, Eu, Gd) as well. They also have a pronounced La maximum that can be linked to the local conditions of this part of the river valley (Fig. 3).

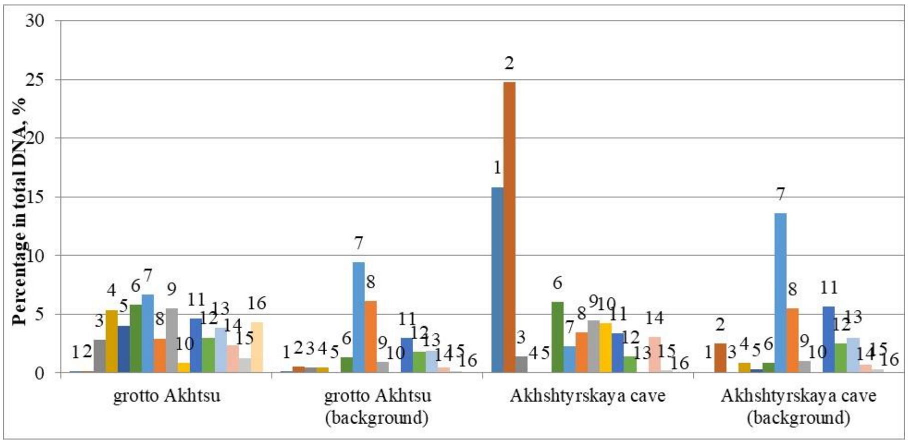


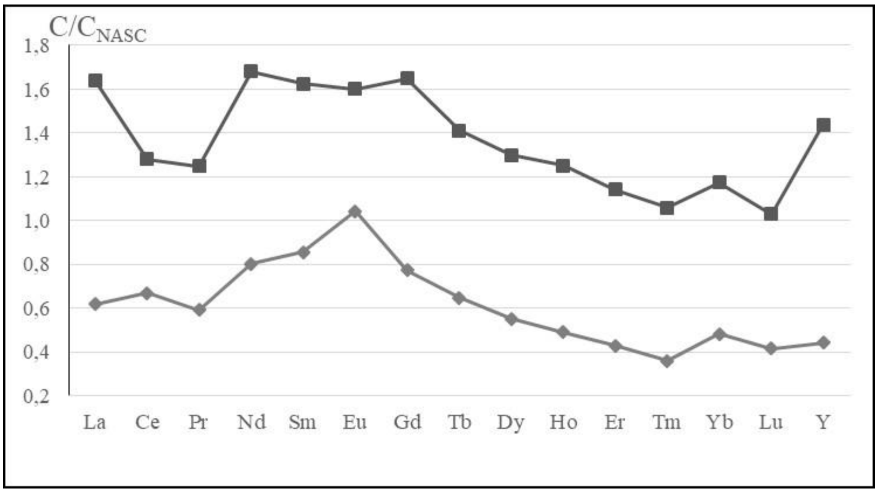
Fig. 3. DNA percentage (%) of dominant species in paleo and modern background soils

The most notable difference between all the studied paleosols and their modern analogs was a reduced content of the entire group of REE in them. The sum of REE for the paleosols was lower than the identical indicator for the background analogs: 2.3, 1.2 and 1.8 times lower for the soils of the grotto, cave and Mamai-Kale, respectively (Table 2, the last line).

A steady decrease in the REE contents in the paleosols is likely to be due to their complex formation. REE are known to interact more actively than other microelements with non-specific organic acids of various classes: monobasic (acetic, glycolic, lactic), dibasic (oxalic, malonic, succinic, glutaric, adipinic, pimelic, azelaic, sebacic), dibasic unsaturated (maleic, fumaric, citraconic), oxyacids - dibasic (tartaric, mucic, saccharic) and tribasic (tricarballylic, aconitic, citric), amino acids (aminoacetic, α-alanine, aspartic, glutamic), aminopolyacetic (nitrile triacetic and ethylene diamine tetra acetic), sulphonic acids (anthraquinone sulphonic, α-amino-β- sulphonic-acid, naphthalene trisulphonic) (Ryabchikov and Terenteva, 1960). The latter characterize the primary process of soil formation; they are the products released by living roots and formed when a fresh organic litter decays; they are associated with life activity of microorganisms and are contained in greater amounts in the modern soil. In paleosols, with no living root system, no supply of fresh organic matter, and reduced microbiological activity, the amount of nonspecific organic acids is less; it is evidenced by an increased pH of the paleosols as compared to the background soil. It clarifies a steady decrease in the content of all the REE group in paleosols, where there is lowered or no content of nonspecific acids, with which REE are able to form organic complex compounds, serving as ligands.

Comparing the two buried soils of ancient encampments showed that the difference of REE contents in the younger paleosol of the Akhtsu grotto (formed after the last glacial period) and the background soil is more significant than the difference of REE contents in the older Upper Pleistocene paleosol of the Akhshtyrskaya cave and the background soil. In addition, in the paleosol of the Akhtsu grotto, REE fractionation, occurred due to the soil diagenesis, was more intense. The reason for this seemingly illogical regularity is in the different distance between the grotto and cave necks and the open surfaces of terraces. The Akhtsu grotto neck is still located close to the open surface of a low terrace, rising above the river floodplain at a rather low hypsometric elevation. It is not fully closed with the grotto “ceiling”. Contrast temperature, redox conditions in the open grotto neck obviously led to a greater transformation of the segment paleosols. The Akhshtyrskaya cave is located in rock outcrops high up off the river waterline; its neck extends to the depth of the rock. Since there are no Holocene soils there, it was closed with the “ceiling” of the cave at the Upper Pleistocene pre-glacial age. The deep-seated neck of the Akhshtyrskaya cave was likely to serve as some preservative factor for its paleosol - geochemical transformation of specific REE distribution here is less noticeable.

The REE distribution graphs, normalized in relation to North American Shale Composite (NASC) show that among the most prominent signs of the REE behavior changes in the grotto paleosols, as compared to modern soils, are pronounced lanthanum amd yttric minima, and europium maximum (Fig. 4 a).


C/C_NASC
1,8
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Ho
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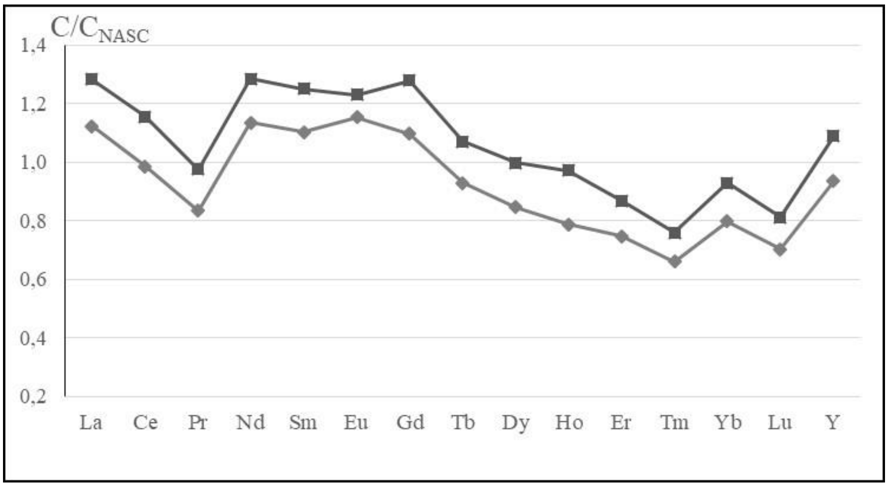
Y

a)


C/C_NASC
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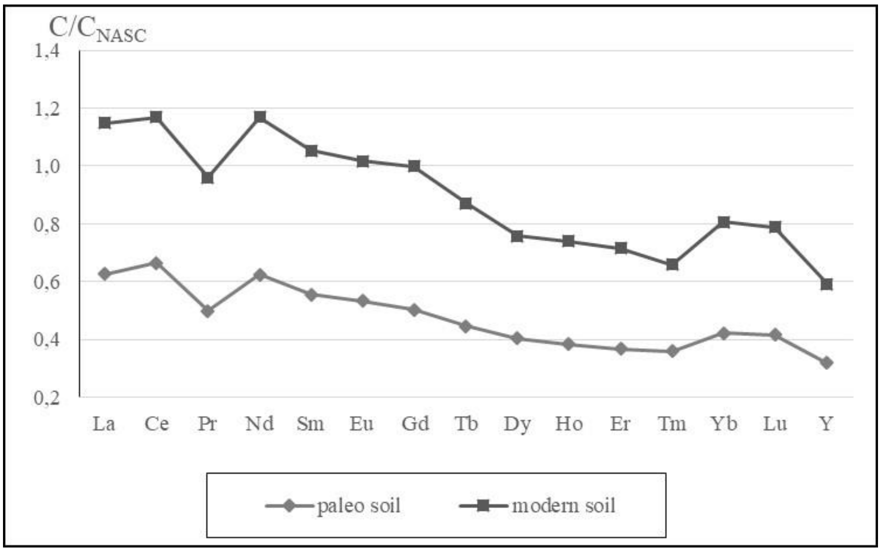
b)


C/C_NASC
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La
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Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Y
paleo soil
modern soil

c)

Fig.4. Spectra of REE concentrations in the paleosols and their modern (background) analogs, normalized in relation to North American Shale Composite (NASC), a – the Akhtsu grotto, b – the Akhshtyrskaya cave, c – the Mamai-Kale fortress.

The europium anomaly found in the organomineral horizons of the paleosols of the grotto (E/Er*=1.3) and the cave (Er/Er*=1.1) (Fig.4 a, b) represents a known phenomenon. However, it is described mostly for the rocks, where it appears both in deficiency of the element and in its excess content in comparison with other REE (Vodyanitskii, 2012).

There is no unified commonly accepted hypothesis on the reason for europium anomaly. The issue remains a subject of discussions. Positive europium anomalies are explained by occurrence of plagioclase or feldspars - europium concentrates. The phenomenon is also associated with a change in redox conditions and specific features of acid-alkaline properties of the element. Eu is an element with mixed valence. Eu^{2+} is a strong reducing agent. It forms EuO oxide with stronger alkaline properties. Eu^{3+} forms Eu2O3 oxide with a higher acidity.

The observed positive Eu anomaly in the paleosols should be linked to several factors: 1) burial of soils and the associated change of redox situation to more reducing conditions, 2) mineralization of organic matter of the soils and absence of nonspecific acids in them, 3) relatively closer relationship between the element and the organic relict matter of the paleosols, 4) different conditions of paleosols formation before their burial.

The available small sampling of paleosols does not allow an explicit determination of the factor, which led to the occurrence of Eu maximum. The discussed objects substantially differ in the time of their burial. The conditions, in which they were formed and later remained buried, differ as well. However, most likely, Eu maximum characterizes the soil diagenesis that relates to organic matter mineralization in a redox situation changing towards more reducing conditions. The latter is borne out by the absence of Eu maximum in the buried mineral metamorphic BM horizon under the medieval fortress Mamai-Kale (Fig.4c).

The discovered phenomenon requires further research on more paleo-objects with different age-related characteristics and conditions of their formation. The numerical characteristics of Eu maximum in paleosols along with already existing methods may serve to identify the age of their burial.

Manifestation of the Eu anomaly only in paleosol organomineral horizons can be considered as a diagnostic attribute that differs them from mineral horizons (the BM horizon in this case). Identification of organomineral horizons and paleosols as such on relict objects in the rock mass, constitutes the first problem faced during paleosol studies. With no clear differentiation of soil with respect to genetic horizons, as, e.g., in alluvial soils, presence of rhizoliths (fossil roots) is often the only criterion for their detection

(Alekseeva, 2020). Eu maximum may become one more, supplementary, diagnostic attribute of organomineral horizons of paleosols.

Exploring the specifics of REE fractionation in paleosols is quite relevant, both to enhance the knowledge about the behavior of rare earth elements under changing conditions and to reveal indicative properties of paleosols and specifics of their formation and transformation under burial conditions.

4. Conclusion

All the examined paleosols demonstrated a decrease in actual acidity along with reduction of humus content. In the absence of fresh organic litter and the acids of nonspecific nature associated with its decomposition, the processes of leaching of mobile forms of elements in paleosols were less intense. Hence, paleosol pH index was insignificantly higher compared to modern soils, mainly due to a growing content of Ca exchangeable forms in paleo-objects (1.5, 2.2, 3.9 times in the soils of the grotto, the cave, and the Mamai-Kale fortress, respectively). Besides, a lower degree of leaching of Ca exchangeable forms in paleosols might be indicative of more arid and colder climatic conditions of their formation period.

The analysis of microbiological properties of paleosols relatively their modern analogs revealed a considerable decline in the species richness of prokaryote microbiome. The comparison of the taxonomic structure of microbial communities of variously aged subtropical paleoalluvial soils with their modern analogs indicated that physical and chemical factors such as the territory acidity/alkalinity, moisture content and temperature affect the biodiversity and structure of prokaryote microbiome to a greater extent than the temporal factor does.

The modern and paleoalluvial soils have a relatively similar composition of elements, but the latter have higher contents of some elements: Ca, Zn, Ba, Cu, Sr, as well as As (for the grotto soils) and Mo, K, and Na (for the cave soils).

Another common feature of the transformation of paleosols was a steady decline in the content of rare earth elements. Such decline is related to the absence of nonspecific acids in paleosols, with which REE form organic complexes more actively than other microelements. The paleoalluvial soils demonstrated the effect of a positive europium anomaly. Since this phenomenon is not inherent in the mineral horizon buried beneath the Mamai-Kale fortress, the europium anomaly is probably determined by soil diagenesis related to organic matter mineralization, in a changing redox environment towards more reducing conditions.

In the more ancient paleosol of the Akhshtyrskaya cave, formed prior to the last glaciation in the late Pleistocene, the observed geochemical differences versus the modern soil manifested themselves weaker than in the Middle Holocene paleosol of the Akhtsu grotto. This can be explained by different distances from the grotto and the cave necks to the open surfaces of terraces. The contrast conditions in the open neck of the grotto caused a more significant transformation of the paleosols in this segment, whereas a considerable depth of the cave neck served as a preservative factor for its paleosol.

Conflict of interest statement

The authors confirm that this work is original and has not been published or submitted for publication in or to any other journal. The authors declare no conflicts of interest in connection with this work.

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Tables Table 1. **Chemical properties of soils**

Soil location and age	Depth, cm	pH		Humus	Ca^{2+}	Mg^{2+}	Hydrolytic acidity	Degree of soils saturation with alkalis	P_2O_5 (acc. to Olsen)	K_2O (acc. to Maslova)
		water	KCl	%	cmol (equiv.)/kg			%	ppm wt	
Akhtsu grotto, 8.3 thsd. years ago	12 - 30	8.15	7.45	3.85	31.37	2.49	0.46	98.66	21.9	75.7
Akhtsu grotto	5 - 20	7.6	6.95	5.04	47.59	3.08	0.7	98.64	6.9	20.9

background										
Akhshtyrskaya cave, 25 thsd. years ago	20-37	7.4	6.97	3.21	25.2	5.00	0.46	98.50	137.5	563.6
Akhshtyrskaya cave, background	5 - 20	7.12	6.38	4.99	56.54	2.95	0.71	98.82	102.1	335.2
Mamaika, 1600 years ago	30 - 45	7.71	7.14	1.54	41.83	1.96	0.69	98.45	7.8	28.3
Mamaika, background	15 - 25	6.84	6.20	0.47	30.96	2.84	0.63	98.17	5.8	12.8

Table 2. Indicators of biological diversity of variously aged paleosols and their modern analogs

Indicators	Akhtsu grotto, 8.3 thsd. years ago	Akhtsu grotto, background	Akhshtyrskaya cave, 25 thsd. years ago	Akhshtyrskaya cave, background
Species richness, OTU	1732	2685	905	2555
Chao1	1940	2944	977	2978
Shannon, H	8.8	9.9	6.7	9.4

Table 3. Content of chemical elements in the paleosols and in their modern (background) analogs

	Akhtsu grotto, 8.3 thsd.	Akhtsu grotto background	Akhshtyrskaya cave, 25 thsd. years ago	Akhshtyrskaya cave, background	Mamaika, 1600 years ago	Mamaika background

	years ago					
Na	0.72	0.42	0.33	0.22	0.39	0.70
Mg	0.89	0.95	0.76	0.73	0.55	0.45
Al	6.67	7.46	5.66	6.51	6.03	6.19
K	1.51	1.56	1.89	1.20	0.72	0.97
Ca	10.36	2.64	14.79	6.90	6.04	0.36
Ti	0.26	0.41	0.26	0.25	0.31	0.47
Mn	0.11	0.24	0.15	0.29	0.08	0.06
Fe	4.08	3.83	3.29	3.43	3.39	3.31
Li	45.4	52.1	37.9	53.7	41.1	49.4
Be	1.54	2.01	1.49	1.63	1.1	1.62
Sc	14.4	17.6	12.6	15	10.7	12.8
V	111.9	123.8	114.4	105.2	108.4	105.4
Cr	76.2	87.5	74.8	84.3	70	69.1
Co	16.4	29.8	15.3	23.8	5.52	13.7
Ni	56.3	74.3	59.2	87.8	24.5	30
Cu	79.6	47.8	102	56.9	27.1	29
Zn	357.6	146.4	831.6	241.8	75.2	69.5
Ga	17.2	19.8	14.3	18.1	13.7	15.5
As	15.7	10.8	7.39	8.74	9.53	9.78
Rb	115.9	140.2	120.9	150.7	67.3	91.8
Sr	201.4	149.7	335.4	172.3	126.5	80
Y	15.5	50.3	32.7	38.1	11.2	20.7
Zr	47.6	133.4	96.2	98.4	95.3	162.4
Nb	8.48	17.2	10.8	11.2	11.1	17.2
Mo	0.57	0.7	6.41	0.88	0.79	1.23
Cd	0.4	1.24	2.51	2.79	0.19	0.11
Sn	2.56	3.28	2.44	2.63	2.25	2.65
Sb	1.07	0.98	0.88	1.1	0.52	0.87
Te	0.14	0.21	0.1	0.23	0.05	0.05
Cs	6.22	6.72	5.96	6.38	4.49	6.09

Ba	1309.6	611.3	616.6	415.1	280.9	287.3
La	19.2	51	34.9	39.9	19.5	35.7
Ce	44.6	85.5	65.7	77.1	44.4	77.9
Pr	4.67	9.87	6.59	7.7	3.94	7.58
Nd	22	46.1	31.1	35.2	17.1	32
Sm	4.78	9.09	6.16	6.99	3.11	5.89
Eu	1.23	1.89	1.36	1.45	0.63	1.2
Gd	4.02	8.57	5.7	6.65	2.62	5.19
Tb	0.55	1.2	0.79	0.91	0.38	0.74
Dy	3.2	7.54	4.91	5.79	2.34	4.4
Ho	0.51	1.3	0.82	1.01	0.4	0.77
Er	1.46	3.88	2.54	2.95	1.25	2.43
Tm	0.18	0.53	0.33	0.38	0.18	0.33
Yb	1.48	3.59	2.44	2.84	1.29	2.47
Lu	0.19	0.47	0.32	0.37	0.19	0.36
Hf	1.16	2.92	2.2	2.41	2.29	3.86
Ta	1.17	1.7	1.35	1.29	1.31	1.51
W	1.27	2.63	1.77	2.06	1.4	2.32
Tl	0.47	0.64	0.53	0.65	0.31	0.45
Pb	18.4	28.4	18.8	25.8	12.6	25
Bi	0.32	0.5	0.37	0.45	0.17	0.32
Th	7.23	13.4	9.15	11.3	7.74	12.7
U	1.33	1.59	1.85	1.4	1.31	2.47
∑ REE	123.57	280.83	196.36	227.34	108.53	197.66

Note: Na, Mg, Al, K, Ca, Ti, Mn, Fe are indicated in %, other elements - in ppm wt. The contents of Se, Rh, Pd, Te, Re, Ir, Pt, Au are below the method detection limit: < 0.2. 0.01. 0.05. 0.05. 0.008. 0.01. 0.05. 0.05 ppm wt, respectively.

Table 4. The geochemical formulas for the paleosols by the CC = Cipa / Cim index

Chemical elements with CC > 1.5 (CC value is given in parentheses)	CC = 1.5 – 0.5	Chemical elements with CC > 0.5 (CC value is given in parentheses)
Akhtsu grotto, 8.3 thsd. years ago		
Ca(3.9)-Zn(2.4)-Ba(2.1)-Na, Cu(1.7)-As(1.5)	Sr, Sb, Fe, K, Mg, Cs, V, Al, Li, Cr, Ga, U, Rb, Sc, Mo, Sn, Be, Ni, Tl, Ta, Te, Eu, Pb, Bi, Ti, Co, Th, Sm, Ce, Nb, W, Nd, Pr, Gd, Tb, Mn	Dy, Yb, Lu, Hf, Ho, La, Er, Zr(0.4)-Tm, Cd, Y(0.3)
Akhshtyrskaya cave, 25 thsd. years ago		
Mo(7.3)-Zn(3.4)-Ca(2.1)-Sr(1.9)-Cu(1.8)-K(1.6)-Ba, Na(1.5)	U, V, Ti, Ta, Mg, Zr, Nb, Fe, Eu, Cs, Sn, Be, Hf, Cd, Cr, Nd, Sm, La, Al, Tm, Tb, Lu, Al, Tm, Tb, Lu, Er, W, Yb, Y, Gd, Pr, Ce, Dy, As, Sc, Bi, Tl, Ho, Th, Ho, Th, Rb, Sb, Ga, Pb, Li, Ni, Co	Mn(0.5)-Te(0.4)
Mamaika, 1600 years ago		
Ca(16.9)-Cd(1.7)-Sr(1.6)	Mn, Mg, Zn, V, Fe, Cr, Te, Ba, As, Al, Cu, Ga, Ta, Sn, Sc, Li, Ni, K, Cs, Rb, Tl, Be, Ti, Nb, Mo Th, W, Sb, Hf, Zr, Ce, Na, La, Tm, Y, Nd, Dy, Bi, U, Sm, Lu, Eu, Yb, Pr, Ho, Er, Tb, Gd, Pb	Co(0.4)

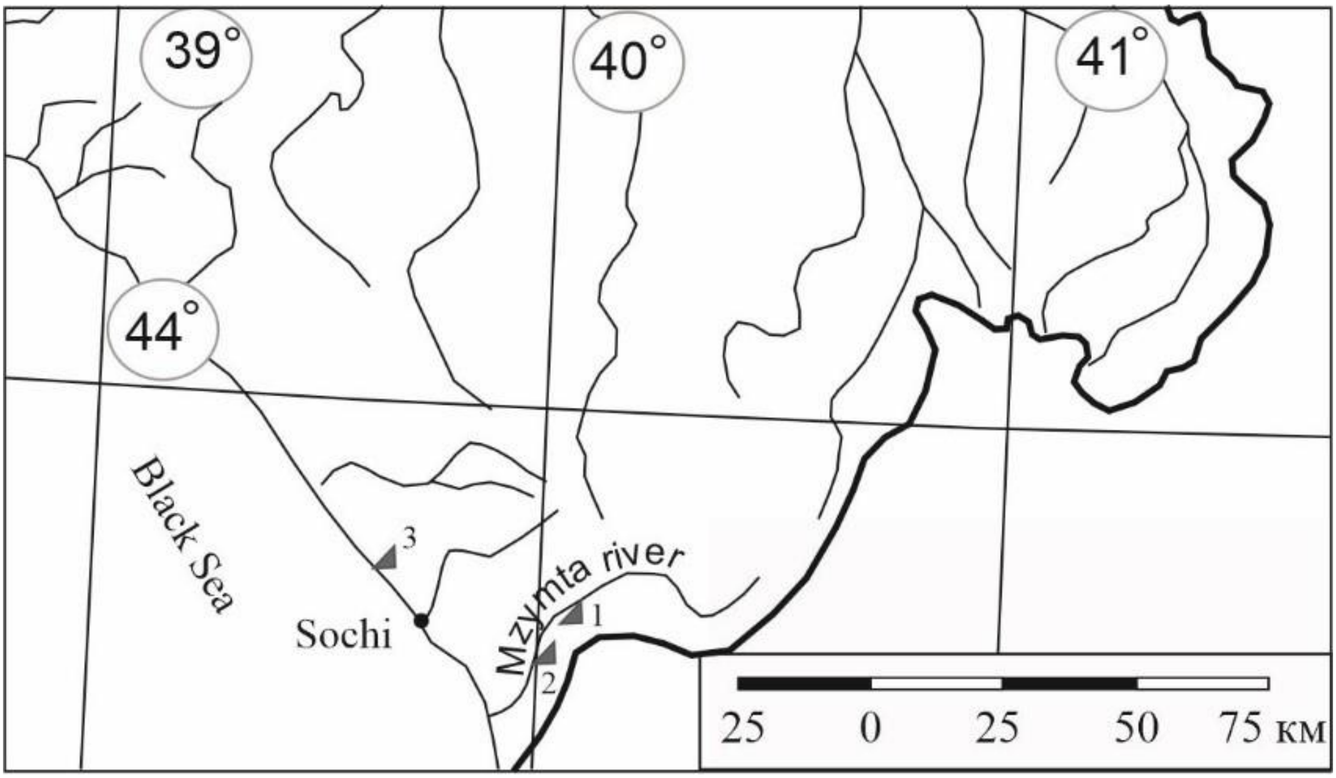

Fig. 1 Schematic map of the study area, 1 – the Akhtsu grotto, 2 – the Akhshtyrskaya cave, 3 – the Mamai-Kale fortress.

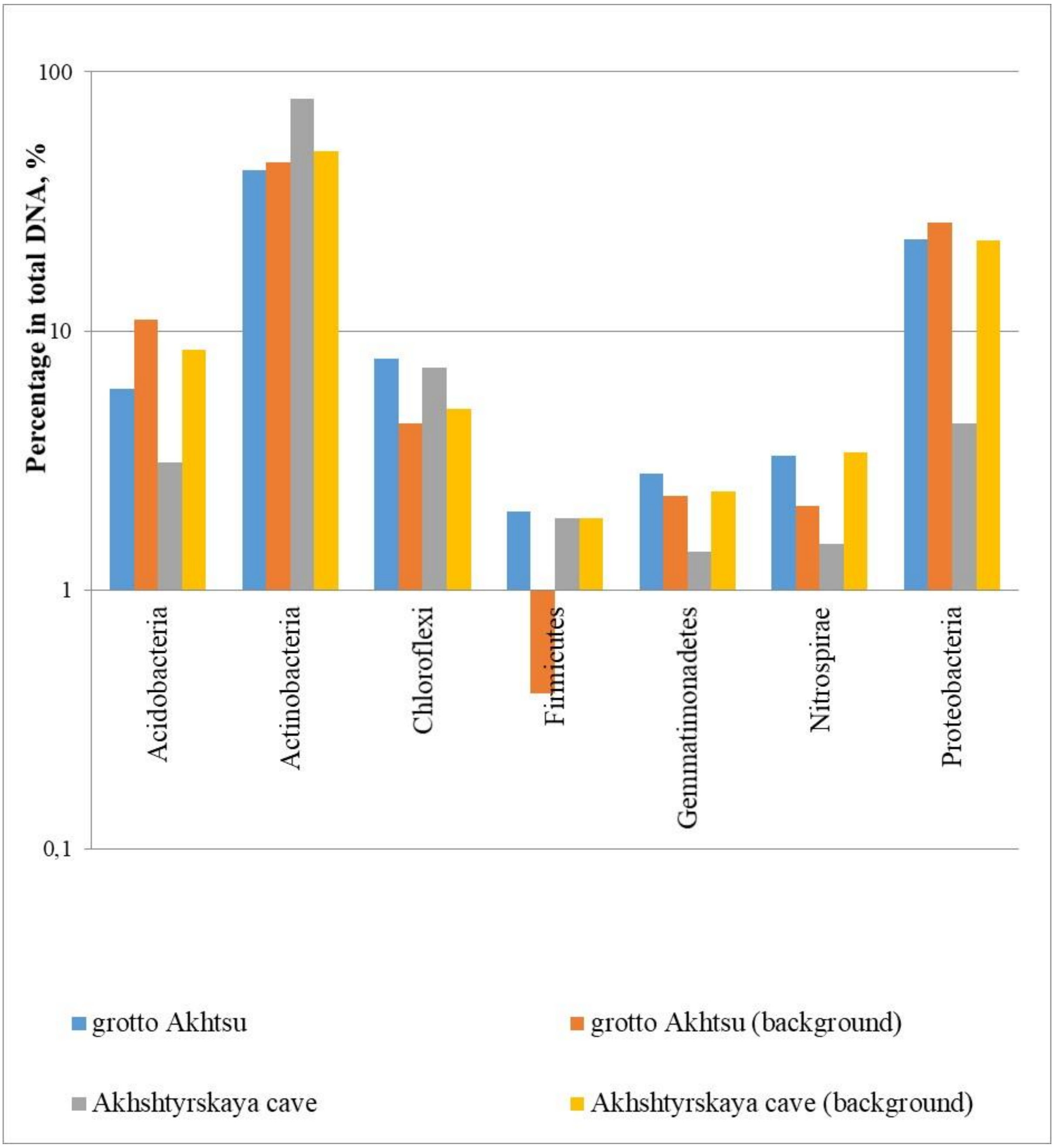

Fig. 2. DNA percentage (%) of the dominant phyla of bacteria in paleo and modern background soils.

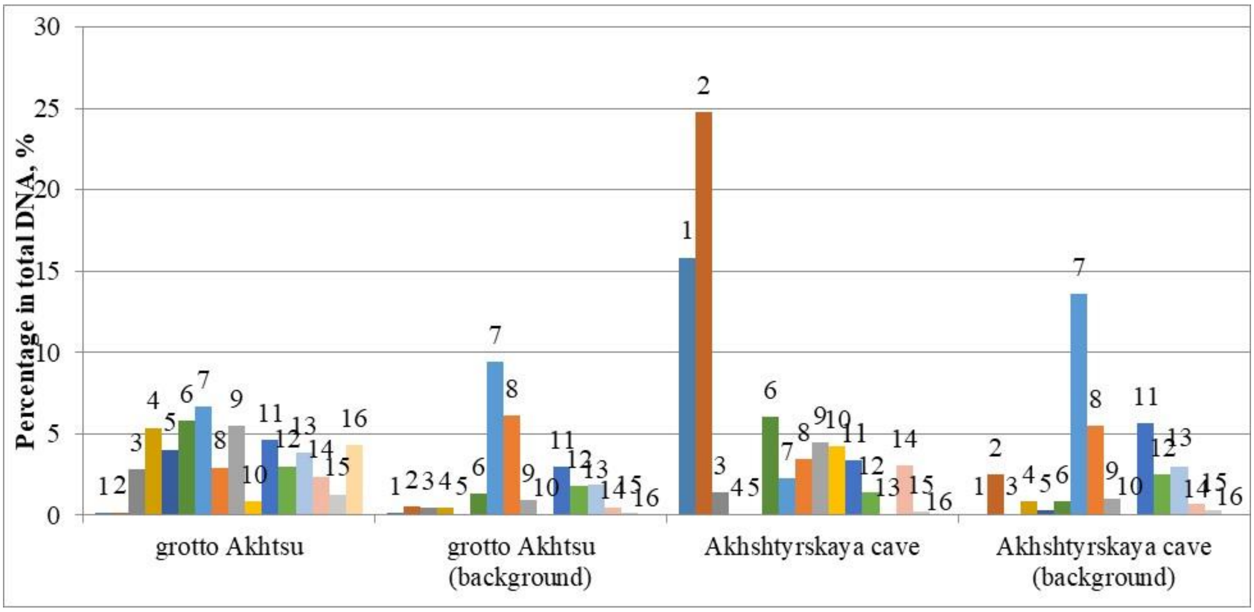

Fig. 3. DNA percentage (%) of dominant species in paleo and modern background soils

No.	phylum	class	order	family	specie
1	Actinobacteria	Actinobacteria	Actinomycetales	Other	
2	Actinobacteria	Actinobacteria	Actinomycetales	Pseudonocardiaceae;	
3	Actinobacteria	Actinobacteria	Actinomycetales	Pseudonocardiaceae;	Pseudonocardia
4	Actinobacteria	Actinobacteria	Actinomycetales	Micrococcaceae	
5	Actinobacteria	Actinobacteria	Actinomycetales	Micrococcaceae	Arthrobacter
6	Tinobacteria	Actinobacteria	Actinomycetales	Nocardioidaceae	
7	Actinobacteria	Thermoleophilia	Gaiellales	Gaiellaceae	
8	Actinobacteria	Thermoleophilia	Solirubrobacterales		
9	Actinobacteria	Acidimicrobiia	Acidimicrobiales		
10	Actinobacteria	MB-A2-108			

11	Actinobacteria	MB-A2-108	0319-7L14		
12	Nitrospirae	Nitrospira	Nitrospirales	0319-6A21	
13	Proteobacteria	Alphaproteobacteria	Sphingomonadales	Sphingomonadaceae	Kaistobacter
14	Chloroflexi	Gitt-GS-136			
15	Firmicutes	Bacilli	Bacillales	Bacillaceae	Bacillus
16	GAL15				

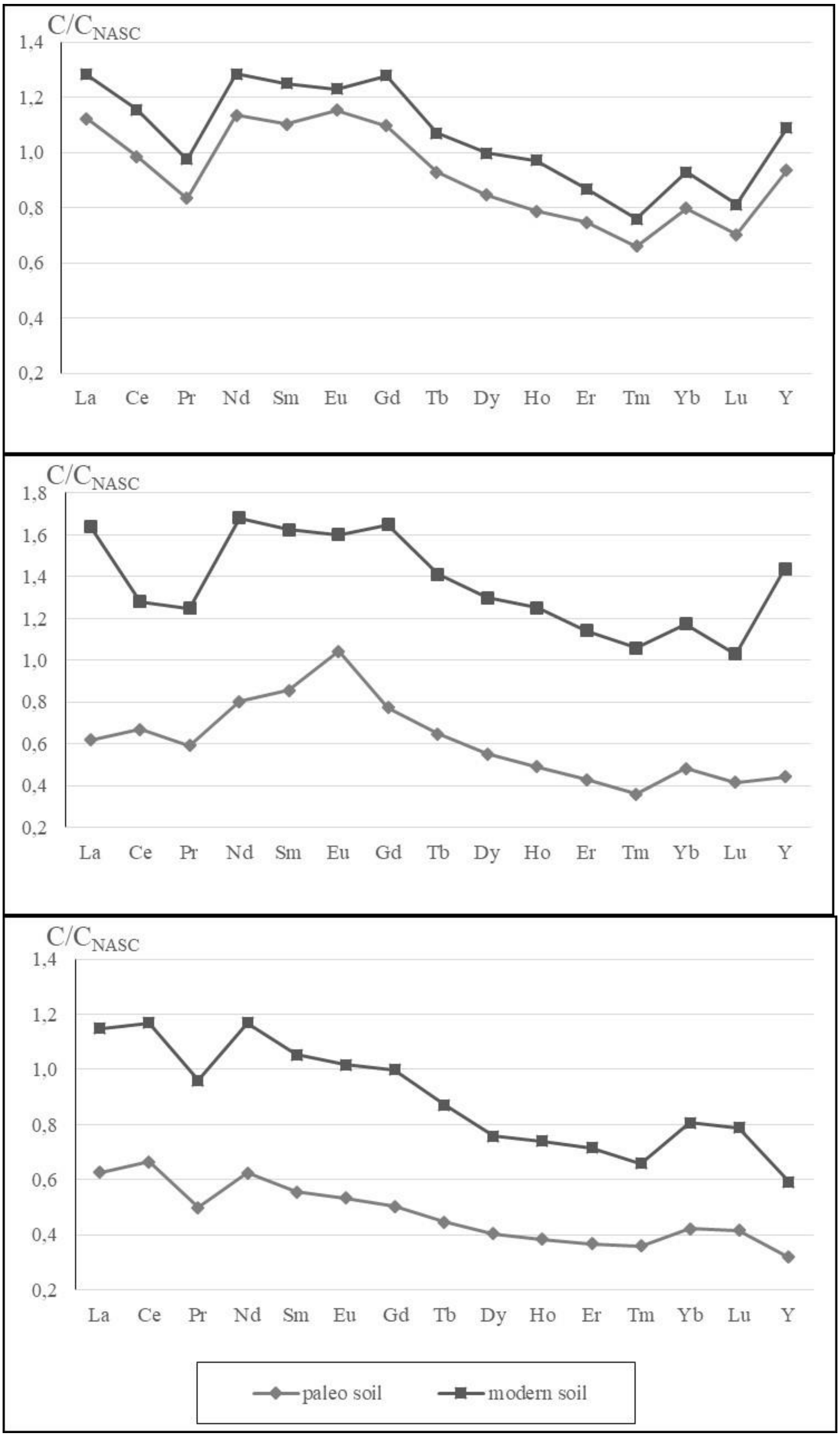

Fig.4. Spectra of REE concentrations in paleosols and in their modern (background) analogs, normalised in relation to North American Shale Composite (NASC), a – the Akhtsu grotto, b – the Akhshtyrskaya cave, c – the Mamai-Kale fortress.