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Landscape monitoring studies of the North Caucasian geochemical province

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The data on the geochemical features of the bedrocks and soils of the province are given. Considerable attention is paid to regional abundances, as well as enrichment and dispersion factors of the chemical elements in landscapes. Using the example of the North Caucasus, it is shown that for such indicators as phytomass, geological, geomorphological, and geobotanical features, it is possible to make a preliminary outlining of regional structures corresponding to geochemical provinces. At the same time, a subsequent geochemical study of these structures remains mandatory. Upon determining certain geochemical associations, geochemical provinces can be basically distinguished; to a large extent, geochemical properties of these accumulated and scattered associations of elements contribute to the regional soil geochemistry. The results of long-term monitoring studies of the North Caucasus geochemical province have shown that the key features of the regional landscapes are due to the composition of bedrock and the presence of a large number of ore deposits and occurrences. The data obtained are the basis for assessing the state of the environment in conditions of increasing anthropogenic impact, and the established regional abundances can be used to assess the degree of pollution in agricultural, residential, and mining landscapes.

Key words: abundances and distribution of elements; substance migration; geochemical associations; phytomass; enrichment factors; depletion factors

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Introduction. The geochemical heterogeneity of the Earth's surface required the zoning of large territories for various scientific and economic purposes as the areas may differ by several geochemical and subsequently environmental features. Initially, the land zoning was supposed to facilitate the study of the development of various tectonic-magmatic processes and the search for mineral deposits. Thus, even in the century before last, the allocation of metallogenic and petrographic provinces was justified. Later, mainly after the works of A.E.Fersman, the term “geochemical province” was used. It usually includes two previously mentioned provinces (metallogenic and petrographic) and is characterized by certain associations of chemical elements that are in high or low concentrations in rocks, as well as, respectively, in soils and organisms. The latter, to a certain extent, allows you to include biogeochemical provinces in a geochemical province.

Thus, in addition to the basic geochemical features of rocks, climatic, geomorphological, biogeochemical (and, consequently, geobotanical), and pedochemical features of territories are taken into account when allocating a geochemical province. In view of this, one can largely focus on terrain features and plant associations for the preliminary contouring of geochemical provinces. They often determine the soil formation and migration of chemical elements, and sometimes even the occurrence forms in various components of geochemical landscapes of the province under consideration. After conducting a preliminary separation of potential geochemical provinces, it is necessary to proceed to actual studies to understand geochemical features of the isolated territories and analyze the development of certain mineral deposits within them, primarily ore ones.

The average content of chemical elements in geochemical systems such as rocks, soils, and living organisms in geochemical provinces are referred to as the corresponding regional or local abundances or Clarkes. The ratios to the abundances in the lithosphere (certain types of rocks), soils, and living matter were coined by V.I.Vernadsky as the Concentration Clarkes, which correspond to Enrichment

Factors, EFs [8]. If these values are less than one, the inverse ratio of global abundances to local values is calculated. The resulting figures are the Dispersion Clarkes or Depletion Factors, DFs.

Problem statement. Since the content of chemical elements in the listed geochemical systems of a province is affected by a large number of equally probable random independent factors, the distribution of element contents is usually approximated by the normal distribution. This makes it most relevant to use the arithmetic mean content for monitoring studies of the geochemical systems. In such cases, it usually coincides with the mode and median values. The mean square deviation and absolute dispersion of contents are important indicators that characterize the distribution of chemical elements within the boundaries of the landscapes of the North Caucasian geochemical province. In systems smaller than a geochemical province, the number of equally probable factors affecting the distribution of elements is not so large. In this case, the distribution is more often subject to a logarithmically normal law, which should be taken into account when conducting environmental monitoring of the state of landscapes.

Research techniques and materials. The results of landscape-geochemical mapping carried out with the participation and guidance of the authors were used in the preparation of the work. Monitoring landscape studies of the North Caucasian geochemical province in 2000-2016, covering the territory from the Middle Russian upland to the Black, Azov, and Caspian seas were carried out on a scale of 1:500,000 and included testing of soils, predominant plants, and, if possible, bedrock on a grid of 5×5 – 5×7 km. For this purpose, special wells were drilled and pits were studied.

Besides, almost every year, including 2019, the authors conducted area testing of soils and plants on separate, relatively small plots. Such monitoring studies were conducted on the sites of mined deposits of Hg, Cu, Zn, Pb, and construction materials, as well as urbanized areas and various agricultural lands [19, 20]. The results of extensive ecological and geochemical surveys show that mining, agricultural, and residential landscapes need to be considered on a larger scale [1, 9, 10, 12-18, 21, 23]. In these cases, the sampling step varied from 2-5 to 200 m. The research methodology is described in detail in monographs [2, 3, 5]. In total, more than 30,000 samples subjected to spectral emission analysis in a certified and accredited laboratory were used in the preparation of the work. In addition, quantitative X-ray fluorescence and neutron activation analyses were performed in part of the samples. Inner and external laboratory control analyses were conducted for 3-5 % of the regular samples. The laboratories of the Institute of Biosphere Geochemistry (Novorossiysk), Magadangeologia (Magadan), the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Biochemistry RAS (Moscow), and the Institute of Physical and Organic Chemistry and the Department of Soil Science and Land Assessment of the Southern Federal University (Rostov-on-Don) performed the external control.

Results and discussion. The mountainous territory of the North Caucasus is usually quite clearly separated from neighboring territories (Fig.1). The boundary between these territories is confirmed, especially in the Western part of the region, by a clear change in plant associations (Fig.2) and the biomass of living matter. Thus, in biogenic landscapes, during the transition from steppe to forest, the phytomass varies from 11-13 to 180-300 t/ha. Analysis of the structure of living phytomass of plant communities has shown a significant role of underground parts (roots) in all grass ecosystems. For the steppes of southern Russia, indicators of aboveground plant phytomass (shoots) were established, varying within 1.5-7.2 t/ha, while underground phytomass in these phytocenoses was 10.6-28 t/ha. In forest ecosystems, 50-75 % of the stand phytomass is stem wood [6, 7].

Thus, according to many indicators that characterize most of the living plant matter of the regions, the mountainous lands of the North Caucasus differ significantly from neighboring territories. However, we note that with the increasing research scale within the North Caucasus, quite a lot of landscapes are distinguished that differ from one another, including the development of various plant communities.

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Fig.1. Location map of the sites for detailed field studies within the North Caucasian geochemical province

1 – telethermal mercury deposits (Krasnodarsky Krai: 1a – *Sakhalinskoe*, 1b –*Perevalnoe*); 2 – pyritic copper-zinc deposit (Karachay-Cherkessia: *Urup*); 3 – hydrothermal lead-zinc deposit (North Ossetia–Alania: *Buron*); 4 – construction materials deposits (Krasnodarsky Krai: 4a – *Novorossiysk*; 4b – *Krymsk*, 4c – *Aderbievka*; Stavropolsky Krai: 4d – *Kinzhal*); 5 – tungsten-molybdenum deposit (Kabardino-Balkaria: *Tyrnyauz*)

The intensive anthropogenic activity has led to the formation of quite numerous, although small in area, technogenic geochemical barriers and landscapes in the studied region. The largest territory is occupied by agricultural landscapes. Vineyards have had the greatest impact on the transformation of biogenic landscapes. However, even if they are cultivated on the border of the North Caucasian geochemical province, this border remains quite clearly distinguished by the geomorphological and geobotanical features of the neighboring provinces (Fig.3). Thus, preliminary geological, geomorphological and Botanical studies allow us to confidently separate the territory of the North Caucasus.



Fig.2. Natural geochemical landscapes on the border of the North Caucasian geochemical province. Meadow-steppe communities are represented in the foreground, followed by sparse fragments of the oak-hornbeam forest, in the background are the oak-hornbeam and hornbeam forests of the low mountain forest belt

Let's consider the main geochemical features of the studied territory. Bedrocks and soil-forming rocks are a constant source of chemical elements entering the upper horizons of landscapes. Detailed studies in the specific conditions of the Western part of the North Caucasus have established a clear relationship between the contents of almost all elements in rocks, soils, and woody vegetation. It is illustrated by the results of monitoring studies, which evaluated the distribution and prevalence of some chemical elements, for example, Mn (Fig.4-6). The territory of the North Caucasus, potentially separated as a geochemical province, is composed of rocks that differ both in age and in geochemical features from the bedrocks of the Fore-Caucasus [4].

Since the geochemical features of the bedrock largely or even decisively determine both the landscape-geochemical and ecological-geochemical peculiarities of individual sections of the biosphere, special attention is paid to the geochemistry of rocks in the region during monitoring studies.



Fig.3. Agricultural landscape of vineyards on the border of the North Caucasian geochemical province

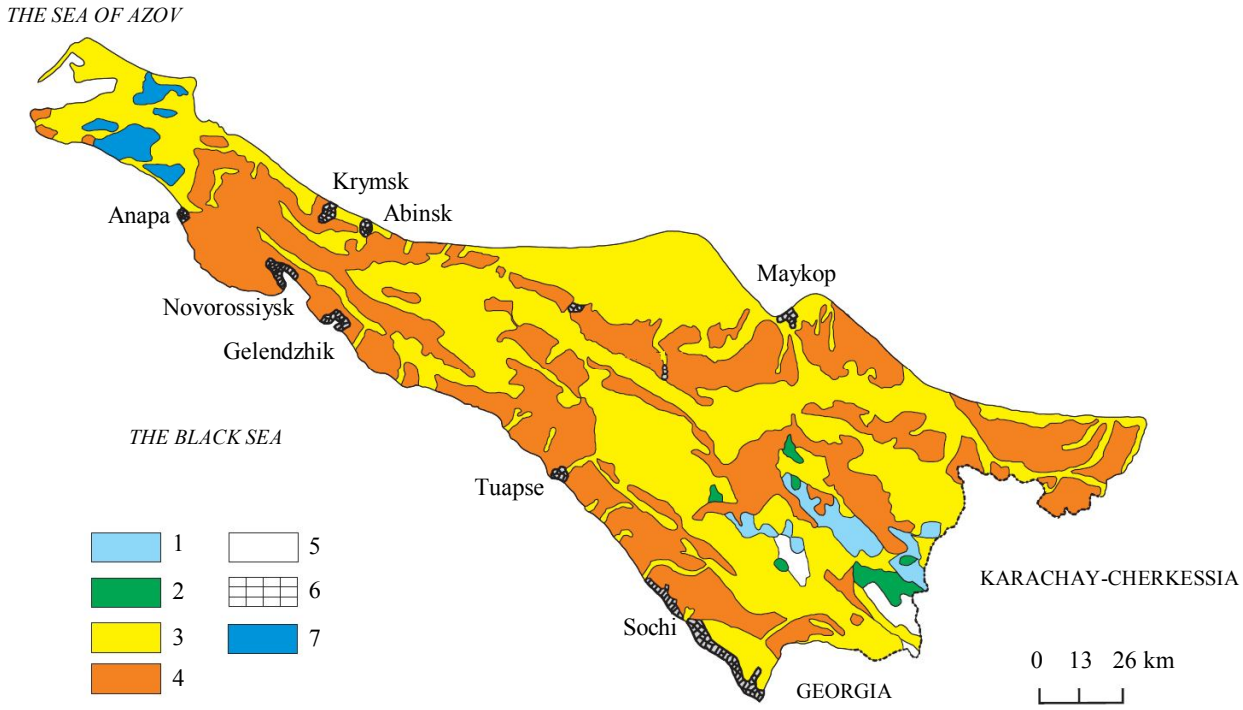


Fig.4. Map of mean background content of Mn ($n \cdot 10^{-3}$%) in the rocks of the western part of the North Caucasus

1 – 53.0 in terrigenous rocks; 2 – 64.2 in siliceous igneous rocks; 3 – 75.6 in terrigenous rocks; 4 – 78.2 in carbonate-terrigenous rocks; 5 – no reliable data on Proterozoic metamorphic rocks; 6 – urbanized areas; 7 – limans of the Taman Peninsula

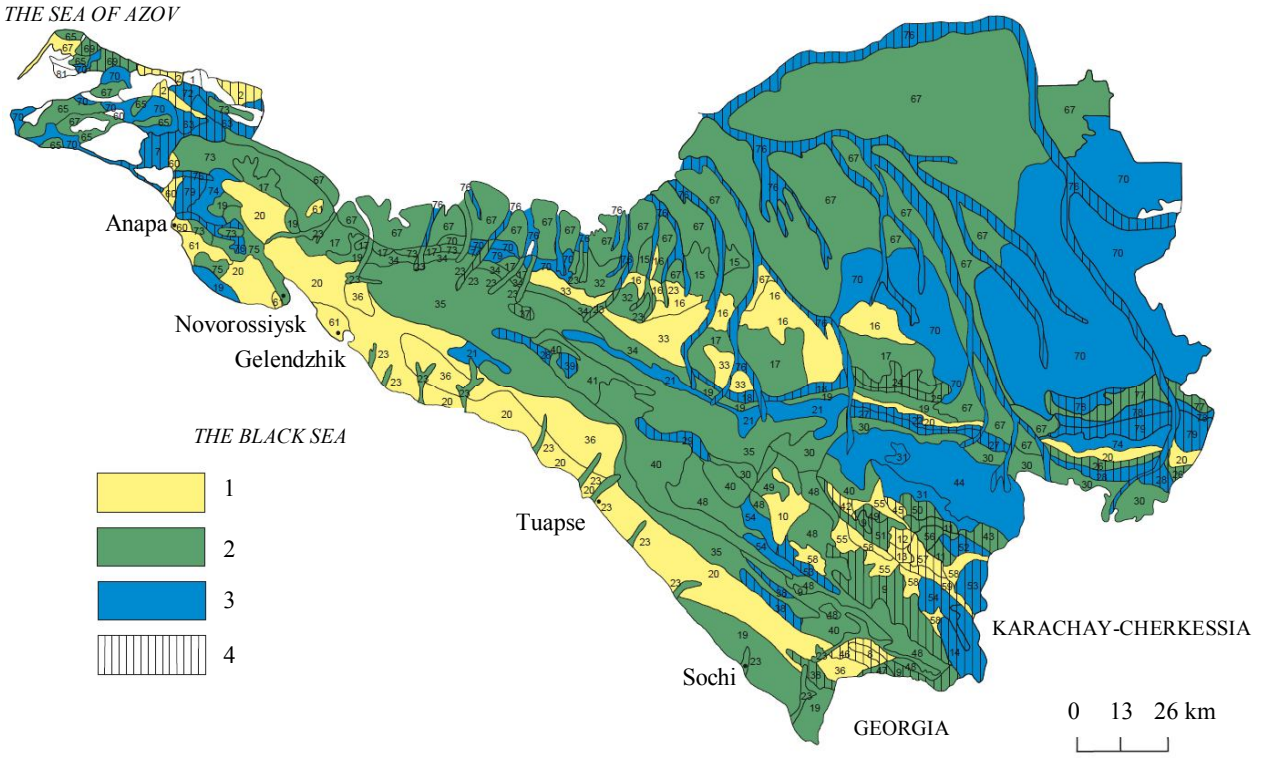


Fig.5. Map of mean background content of Mn ($n \cdot 10^{-3}$%) in the soils of the western part of the North Caucasus

1 – over 114; 2 – 85-114; 3 – 50-84; 4 – average levels

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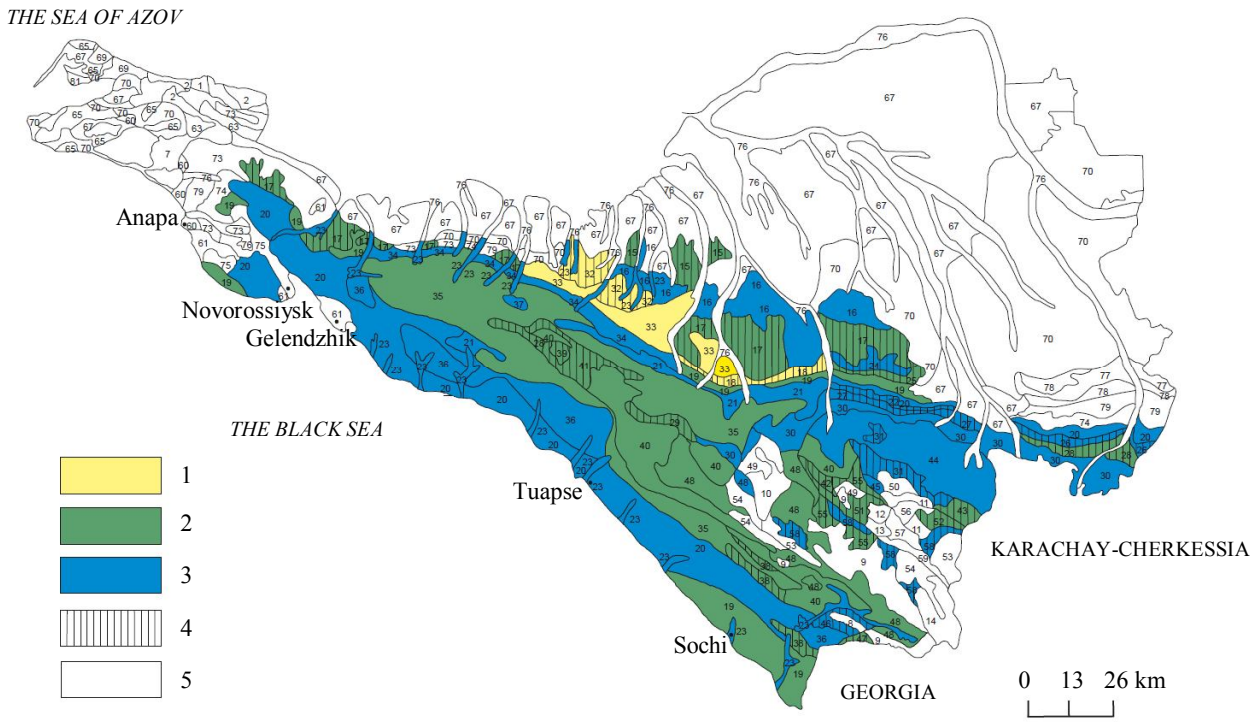


Fig.6. Map of mean background content of Mn ($n \cdot 10^{-3}$%) in the ashes of hornbeam leaves
1 – 725-850; 2 – 552-724; 3 – 80-551; 4 – average levels; 5 – landscapes with plant communities without hornbeam

The vast area of the considered territory of the North Caucasus is composed of sedimentary rocks. Clays, shales, sandstones, marls, limestones, and dolomites are among them. However, the mapping of all these varieties of sedimentary rocks becomes possible only with specially conducted detailed studies on separate, usually small areas. Such studies have shown that the ratio of clay, sand, and carbonate rocks in the region is the same as was established by L.B.Rukhin for sedimentary rocks of the lithosphere – 5:3:2. Due to the frequent layering of relatively thin horizons of all these rocks, as well as taking into account the significant content of terrigenous material in the carbonate layers, we have combined all the sedimentary rocks in the above-mentioned works into two important groups: terrigenous and carbonate-terrigenous. The average content of several chemical elements in the main groups of rocks in the region, established by the results of analyses of the samples we took in the North Caucasus, is shown in Table. These contents can be tentatively considered as local abundances for these types of rocks in the North Caucasian geochemical province.

With a certain degree of conditionality, given the data of K.H. Wedepohl and K.K. Turekian [22], and the above ratio of clay, sand, and carbonate rocks, we calculated the abundances of elements in terrigenous and carbonate-terrigenous rocks of the lithosphere (see table). We will try to identify the geochemical specialization of the regional rocks by comparing the abundances with the average content of chemical elements in rocks of the North Caucasus. Table also provides information about the content of a number of elements in siliceous igneous rocks found in a relatively small area in the eastern part of the province. EFs and DFs were used to compare with the abundances of the same rocks in the lithosphere.

As the data show, only the average contents of Mo have increased by more than 1.5 times in all varieties of rocks. The average contents of Zr(5.30), P (2.30), Sr (1.60), Mn (1.40), Ba (1.37), and Pb (1.30) are higher in carbonate-terrigenous rocks (EFs are given in brackets). The average contents of Be, Cr, and Zn are only slightly higher than the abundances. In terrigenous rocks, EFs greater than 1.4 are found for Mo (2.15), V (2.73), Pb (1.76), Mn (1.64), Zn (1.40), and Zr (1.40). In siliceous igneous rocks, EFs greater than 1.4 are typical for Ag (1.57), Ba (1.40), Be (2.00), Cr (3080), Li (1.60), Mn (2.20), Nb (2.00), Ni (1.50), Pb (2.20), Sn (3.00).

Patterns of chemical element concentrations ($n \cdot 10^{-3}$ %) in the prevailing rocks of the North Caucasian geochemical province

Element	Element number	Rocks											
		Carbonate-terrigenous				Terrigenous				Siliceous igneous			
		Abundances in the lithosphere	Abundances of the North Caucasus	EFs	DFs	Abundances in the lithosphere	Abundances of the North Caucasus	EFs	DFs	Abundances in the lithosphere	Abundances of the North Caucasus	EFs	DFs
Ag	47	0.008	0.006		1.37	0.008	0.0075		1.07	0.0051	0.008	1.57	
Ba	56	41.7	57.5	1.37		51.9	58.6	1.13		42	58.5	1.4	
Be	4	0.18	0.20	1.11		0.20	0.27	1.35		0.2	0.4	2	
Co	27	1.01	1.0		1.01	1.26	1.328	1.05		0.7	0.8	1.14	
Cr	24	6.27	6.5	1.04		7.6	10	1.31		2.2	8.4	3.81	
Cu	29	4.43	3.8		1.16	5.44	5.0		1.09	3	3.6	1.2	
Ga	31	1.94	0.03		3.08	2.32	1.59		1.46	1.7	2.04	1.2	
Ge	32	0.13	0.11		1.18	0.16	0.17	1.06		0.13	0.15	1.2	
Li	3	3.6	2.9		1.24	4.3	4.65	1.08		2.4	3.9	1.6	
Mn	25	57	80	1.40		43.75	71.9	1.64		54	53		1.01
Mo	42	0.11	0.18	1.64		0.13	0.28	2.15		0.1	0.22	2.2	
Nb	41	1.01	0.70		1.43	1.25	1.50	1.2		2	1.5		1.3
Ni	28	5.21	2.12		2.46	6.01	3.87		1.55	1.5	2.3	1.5	
P	15	13.1	30.2	2.30		54.5	63.8	1.17		92			
Pb	82	1.39	1.8	1.3		1.5	2.64	1.76		1.5	3.3	2.2	
Sc	21	0.55	0.53		1.04	0.66	0.81	1.22		1.4	2.0	1.4	
Sn	50	0.53	0.35		1.51	0.64	0.47		1.36	0.15	0.45	3	
Sr	38	35.3	57.1	1.62		28.9	30	1.03		44	2.4		1.6
Ti	22	278	247		1.13	338	408	1.2		340	360	1.05	
V	23	7.5	3.8		1.97	3.88	10.6	2.73		8.8	8.0		1.1
W	74	0.16	0.14		1.14	0.19	0.19	1	1	0.13	0.17	1.3	
Y	39	3.3	1.2		2.75	3.38	1.64		2.06	3.5	2		1.7
Yb	70	0.28	0.1		2.8	0.34	0.18		1.88	0.35	0.2		1.7
Zn	30	4.85	5.3	1.09		5.56	7.86	1.41		6	6.4	1.06	
Zr	40	16.9	89.0	5.26		20.8	14.4	1.44		14	10		1.4

These data allow us to present with a certain degree of conditionality a general association of chemical elements that are in high concentrations in the rocks of the North Caucasus in the following row: Mo → Pb → Ba→ Cr → Zn→ Be. The average contents of Sr, Zr, Mn, V, Cu, Zn, and Ni are often higher in certain areas and certain rocks.

Describing the rocks of the North Caucasus from the geochemical point of view, it is also necessary to distinguish associations of chemical elements that are in lower average contents compared to the contents in similar rocks of the lithosphere. As can be seen from Table, for Y and Yb, the average content in all varieties of the selected rocks of the North Caucasus was set, decreased by 1.5 times or more. The average contents of Ag, Cu, Ga, and Ni are often lower. In some areas, sedimentary rocks have lower concentrations of Cu and Sn; Sr levels are lower in igneous rocks.

We can assume that the described geochemical pattern was formed as a result of special conditions of various geochemical processes in the region (from tectonic-magmatic to sedimentation and weathering processes). It is this pattern that largely contributed to the creation of the North Caucasian geochemical province. These features of rocks undoubtedly influenced the soil formation, as well as geobotanical and biogeochemical features in the further geochemical history of the region. The greatest influence could be exerted by chemical elements that are in significantly increased (reduced) concentrations in rocks.

All six of the above-mentioned chemical elements, which are in high concentrations in different regional rocks (Mo, Pb, Ba, Cr, Be, and Zn) belong to the water migrants according to the A.I. Perelman's classification [11]. Of these, for four (Mo, Ba, Be, and Zn), biogenic accumulation plays a significant role in the element's history, while Mo, Zn, Pb, Ba, and Be are mobile and slightly mobile in an oxidizing environment. Consequently, these elements can pass into an ionic form and

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move as solutions in the oxidizing supergene zone. According to the ionization potential (and therefore the energy required for the formation of a cation), the elements most common in rocks (relative to the abundances in the lithosphere) can be grouped as follows: 1 –Ba (5.19); 2 – Cr (6.74), Mo (7.35), Pb (7.40); 3 – Be (9.50), Zn (9.35).

Except for Ba, this sequence of elements, depending on the ionization potential, practically corresponds to the position of elements that are in high concentrations in rocks. This can be a sign of a large role of ion migration in the formation of the modern geochemical peculiarities of the regional rocks. The role of ion migration is also important for these elements in the processes of further rock weathering.

This is also evidenced by the values of the Cartledge ionic potential. For Ba, Pb, and Zn the potentials are below three, and, therefore, they are characterized by migration in the form of cations that do not form complex ions. The size of the radii of the ions and their energy coefficients allow us to assume that the migration distance of these elements should be approximately the same.

Conclusion. The preliminary mapping of territories classified as geochemical provinces should be carried out taking into account the complex of general geological, geomorphological, and botanical features with the subsequent mandatory geochemical study of rocks, soils, and plants. Geochemical studies should include the calculation of the relations between regional and global abundances, the identification of associations of elements that are in high and low concentrations, and the determination of the values of absolute dispersion of average contents.

The main peculiarity of the provinces is determined by the bedrock geochemistry and the presence of a large number of ore deposits and occurrences. To a large extent, depending on the geochemical properties of elements in associations of high and low content, geochemical features of soils, as well as geobotanical and biogeochemical features of vegetation lead to the formation of the corresponding provinces.

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