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# Trace element accumulation by soils and plants in the North Caucasian geochemical province

**Vladimir A. ALEKSEENKO[1,2,3]✉, Natalya V. SHVYDKAYA[4], Jaume BECH[5], Alexander V. PUZANOV[3], Aleksey V. NASTAVKIN[2]**
[1] *Admiral Ushakov Maritime State University, Novorossiysk, Russia*
[2] *Southern Federal University, Rostov-on-Don, Russia*
[3] *Institute for Water and Environmental Problems of Siberian Branch of the Russian Academy of Sciences, Barnaul, Russia*
[4] *Kuban State Agrarian University, Krasnodar, Russia*
[5] *University of Barcelona, Barcelona, Spain*

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***Abstract*.** Long-term studies of the North Caucasian geochemical province allowed to establish regional abundances and calculate accumulation (dispersion) factors for chemical elements in rocks, soils, and plants. Certain natural regional patterns characterize the province. Associations of elements in high and low concentrations are often determined by the predominant composition of rocks: carbonate-terrigenous, terrigenous, and igneous. The study of the average contents of several chemical elements in the soils of the province showed that the association of accumulated elements includes metals with different migration characteristics. Thus, despite the rather close values of the ionic radii, Pb, Zn, Cu, and Li (judging by the ionic potential) are characterized by the formation of cations, while Mn, Mo, and Zr form complex ions. Such elements as Zn, Cu, and Pb are mainly accumulated on hydrosulfuric barriers, while Mo, Co, and Mn are stopped by oxygenous barriers. For Cu, Zn, Mo, and Co, biogenic accumulation plays a significant role, while for Pb and Ni it is practically absent. The absolute dispersion of the elements did not reach environmentally hazardous values, although it indicates a fairly intensive migration. In woody plants, Ba, Nb, Sc, Sr, and Zn are accumulated most intensively. The specific natural conditions that characterize the North Caucasian geochemical province may affect the technogenic transformation of the environment.

***Key words*:** soil geochemistry; phytoaccumulation; geochemical associations; phytomass; regional geochemical background

**Introduction.** The study of chemical element accumulation by the soil and vegetation cover of geochemical provinces is of considerable theoretical and applied interest for the characterization of environmental conditions. The key phenomena of element migration in provinces are determined not only by the fundamental geochemical features of rocks but also by the climatic, geomorphological, biogeochemical, and soil-geochemical features of the territories.

The average contents of chemical elements in such geochemical systems as rocks, soils, and living organisms of geochemical provinces are called the regional abundances [1, 3]. V.I.Vernadsky coined the term "Concentration Clarkes" that corresponds to Enrichment Factors (EFs), i.e. the ratios to the abundances of the lithosphere, certain types of rocks, soils, and living matter [7]. If these values are less than unity, the inverse ratio of global abundances to local values is calculated and the resulting figures are the Dispersion Clarkes or Depletion Factors, DFs [1, 3].

The study area (especially the central and western parts) is characterized by the presence of a variety of numerous mineral deposits (polymetals, mercury, copper and zinc, gold, oil and gas, tungsten, and molybdenum). Most of them are located in remote areas of the North Caucasus. The development of these deposits was associated with the work of a significant part of the local population. Unfortunately, many of these deposits have already been worked out, and mining workers have become unemployed, which is a particular problem for this region. The search for new deposits is often hampered by the heavy-going forest landscapes and terrain features. Under these conditions, with the predominance of individual canyon-like valleys and sometimes seemingly good exposure, the geochemical data obtained, e.g., during the heavy mineral concentrate sampling and search for primary halos, are not informative enough. In this regard, geochemical prospecting for secondary lithochemical and biogeochemical halos are among the most promising in the region [2]. Therefore, the study of the processes of migration and accumulation of chemical elements in the soil and vegetation cover in the specific conditions of the landscapes of the North Caucasus (primarily forest ones) has become one of the most important tasks in the region.

It is important to study the accumulation of elements by the soil and vegetation cover and to delineate the secondary geochemical fields corresponding to the areas and nodes of mineral deposits. They were predicted by one of the authors (V.A.Alekseenko) and were first identified on a landscape-geochemical basis for the western and central parts of the North Caucasian geochemical province. This, as well as the establishment of the boundaries of the potential formation of deposits, explains the special attention to these parts of the province in this article.

Natural migration-concentration processes of chemical elements, and, consequently, their content and distribution, in many geochemical provinces, are affected by common geochemical barriers [17], often associated with mined deposits, developed agricultural production, and urban settlements [24, 26, 29], as well as by numerous other technogenic factors. Since rocks, soils, plants, and waters in different geochemical provinces differ in the associations of chemical elements that are in high and low concentrations, the consequences of the same technogenic process may differ significantly [23, 25, 27, 28]; often this applies even to the development of animal and human diseases. It is obvious that the study of the geochemical features of the provinces, in addition to scientific purposes and the search for deposits, is of great environmental importance.

**Materials and methods.** The basis of the work is the data obtained by processing the materials of landscape-geochemical mapping, twice carried out with an interval of 13 years, on the territory of the North Caucasian geochemical province at a scale of 1:500.000. These works included testing soils, bedrock, and major plants on a 5×5 – 5×7 km grid. In some areas of the province, almost every year, areal testing of soils of rocks and several plant species was carried out. In the areas completely covered with plants, the work was accompanied by a sampling of bedrocks and soils from more than 300 pits and small clearings. The size of the areas studied in detail varied widely: from a few kilometers at the mined-out deposits to the entire Black Sea coast of the Krasnodar Krai. At these sites, the sampling step varied from 2-5 m to 200 m. Sampling control was carried out in the amount of 3-5 % of the number of ordinary samples. Its result allows us to consider the work outcomes as reliable. All fieldwork was carried out under the supervision and with the direct participation of the authors of the article.

According to the results of the first landscape-geochemical mapping carried out on a large territory at a scale of 1:500.000, maps of geochemical landscapes were published in 1988 and in 2000 [13, 14]. Only with their use, it became possible, based on the results of analyses of samples taken at a scale of 1:500.000, to reveal secondary lithochemical and biogeochemical fields corresponding to the areas of mineralization.

In total, over 30.000 samples were taken during the work (including the control ones). Of these, rocks made up more than 3.800, soils accounted for more than 8.200, and the number of plant species was over 15.000. All rock, soil, and plant ash samples were subjected to spectral emission analysis in the certified Central Testing Laboratory of the North Caucasus Production Geological Association. Internal and external laboratory control was conducted for 3-5 % of the number of ordinary analyses. Laboratories of the Research Institute of Biosphere Geochemistry (Novorossiysk), Magadangeology (Magadan), the Institute of Ore Deposit Geology (Moscow), and the Research Institute of Physical and Organic Chemistry of the Southern Federal University (Rostov-on-Don) were selected for external control. The calculation of the analysis errors allowed us to consider the work of the laboratory as reliable. The research methodology used is described in detail in [1, 3].

In addition to the own research, the published works of other authors were used [8-12]. During the analysis of the obtained material, such well-known geochemical indicators as ion radii, energy coefficients, Cartledge ionic potentials, and ionization potentials, and the absolute spread of chemical elements in the geochemical system (in this case, the spread of the average contents in the soils of the provincial landscapes) were used.

A large number of various deposits and ore occurrences [4] is one of the features of the North Caucasian geochemical province; a significant part of them is found in the western and central parts of the region (Fig.1). The ore deposits of the province are considered in detail in the monograph of S.B.Yashchinin [22].

**Results and discussion.** Deposits create primary ore fields of concentration and redistribution of elements corresponding to mineralization areas. Within such fields, the generally increased background levels of chemical elements in rocks are often accompanied by extreme unevenness of element distribution with the appearance of small negative anomalies. This unevenness is considered by many researchers as a geochemical revitalization of areas, often leading to the formation of deposits.

The uneven degree of plant cover did not allow to limit individual primary ore fields, although a large number of samples of bedrock (about 4.000) allows us to establish the main geochemical features of the rocks of the province with a high degree of confidence. Since rocks are the main and permanent sources of chemical elements accumulated by the soil and vegetation cover, we will consider these features (Table 1). According to A.E.Fersman [20], geochemical provinces are characterized by certain associations of chemical elements that are in high and low concentrations, often distributed relatively homogeneously.

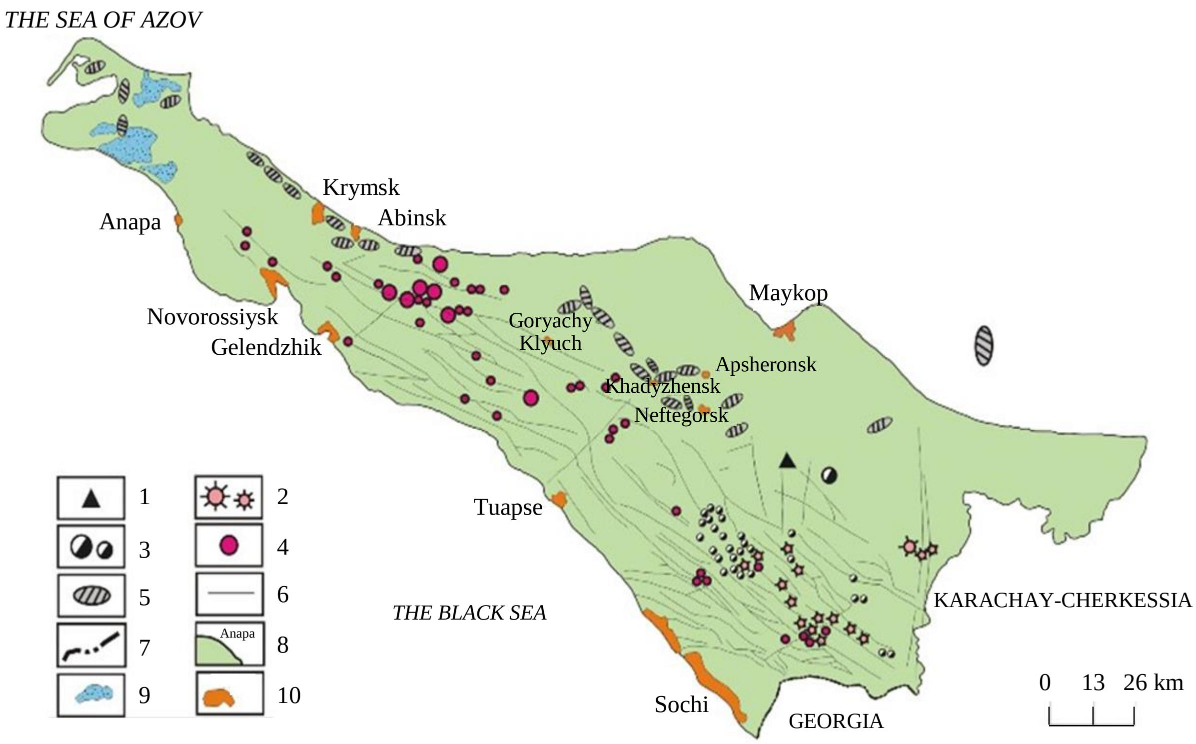


Fig.1. Map of mineral deposits in the central and western parts of the North Caucasian geochemical province

1 – gold deposits; 2 – copper deposits and ore occurrences; 3 – polymetal deposits and ore occurrences; 4 – mercury deposits and ore occurrences; 5 – oil and gas deposits; 6 – discontinuities; 7 – state border; 8 – border of the studied region; 9 – estuaries; 10 – settlements

*Table 1*

**Geochemical characteristics of the rocks of the North Caucasian geochemical province**

| Ag | Ba | Be | Co | Cr | Cu | Ga | Ge | Li | Mn | Mo | Nb | Ni | P | Pb | Sc | Sn | Sr | Ti | V | W | Y | Yb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Content in carbonate-terrigenous rocks of the lithosphere ($n\cdot10^{-3}$ %) | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.008 | 41.7 | 0.18 | 1.01 | 6.27 | 4.43 | 1.94 | 0.13 | 3.6 | 57 | 0.11 | 1.01 | 5.21 | 13.1 | 1.39 | 0.55 | 0.53 | 35.3 | 278 | 7.5 | 0.16 | 3.3 | 0.28 | 4.85 | 16.9 |
| Content in carbonate-terrigenous rocks of the province ($n\cdot10^{-3}$ %) | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.006 | 57.5 | 0.20 | 1.0 | 6.5 | 3.8 | 0.03 | 0.11 | 2.9 | 80 | 0.18 | 0.70 | 2.12 | 30.2 | 1.8 | 0.53 | 0.35 | 57.1 | 247 | 3.8 | 0.14 | 1.2 | 0.1 | 5.3 | 89.0 |
| Enrichment factors in carbonate-terrigenous rocks | | | | | | | | | | | | | | | | | | | | | | | | |
| – | 1.37 | 1.11 | – | 1.04 | – | – | – | – | 1.40 | 1.64 | – | – | 2.30 | 1.3 | – | – | 1.62 | – | – | – | – | – | 1.09 | 5.26 |
| Depletion factors in carbonate-terrigenous rocks | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.37 | – | – | 1.01 | – | 1.16 | 3.08 | 1.18 | 1.24 | – | – | 1.43 | 2.46 | – | – | 1.04 | 1.51 | – | 1.13 | 1.97 | 1.14 | 2.75 | 2.8 | – | – |
| Content in terrigenous rocks of the lithosphere ($n\cdot10^{-3}$ %) | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.008 | 51.9 | 0.20 | 1.26 | 7.6 | 5.44 | 2.32 | 0.16 | 4.3 | 43.75 | 0.13 | 1.25 | 6.01 | 54.5 | 1.5 | 0.66 | 0.64 | 28.9 | 338 | 3.88 | 0.19 | 3.38 | 0.34 | 5.56 | 20.8 |
| Content in terrigenous rocks of the province ($n\cdot10^{-3}$ %) | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.0075 | 58.6 | 0.27 | 1.328 | 10 | 5.0 | 1.59 | 0.17 | 4.65 | 71.9 | 0.28 | 1.50 | 3.87 | 63.8 | 2.64 | 0.81 | 0.47 | 30 | 408 | 10.6 | 0.19 | 1.64 | 0.18 | 7.86 | 14.4 |
| Enrichment factors in terrigenous rocks | | | | | | | | | | | | | | | | | | | | | | | | |
| – | 1.13 | 1.35 | 1.05 | 1.31 | – | – | 1.06 | 1.08 | 1.64 | 2.15 | 1.2 | – | 1.17 | 1.76 | 1.22 | – | 1.03 | 1.2 | 2.73 | 1 | – | – | 1.41 | 1.44 |
| Depletion factors in terrigenous rocks | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.07 | – | – | – | – | 1.09 | 1.46 | – | – | – | – | – | 1.55 | – | – | – | 1.36 | – | – | – | 1 | 2.06 | 1.88 | – | – |
| Content in felsic rocks of the lithosphere ($n\cdot10^{-3}$ %) | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.0051 | 42 | 0.2 | 0.7 | 2.2 | 3 | 1.7 | 0.13 | 2.4 | 54 | 0.1 | 2 | 1.5 | 92 | 1.5 | 1.4 | 0.15 | 44 | 340 | 8.8 | 0.13 | 3.5 | 0.35 | 6 | 14 |
| Content in felsic rocks of the province ($n\cdot10^{-3}$ %) | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.008 | 58.5 | 0.4 | 0.8 | 8.4 | 3.6 | 2.04 | 0.15 | 3.9 | 53 | 0.22 | 1.5 | 2.3 | – | 3.3 | 2.0 | 0.45 | 2.4 | 360 | 8.0 | 0.17 | 2 | 0.2 | 6.4 | 10 |
| Enrichment factors in felsic rocks | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.57 | 1.4 | 2 | 1.14 | 3.81 | 1.2 | 1.2 | 1.2 | 1.6 | – | 2.2 | – | 1.5 | – | 2.2 | 1.4 | 3 | – | 1.05 | – | 1.3 | – | – | 1.06 | – |
| Depletion factors in felsic rocks | | | | | | | | | | | | | | | | | | | | | | | | |
| – | – | – | – | – | – | – | – | – | 1.01 | – | 1.3 | – | – | – | – | – | 1.6 | – | 1.1 | – | 1.7 | 1.7 | – | 1.4 |
| Absolute spread in rocks and soils of continents | | | | | | | | | | | | | | | | | | | | | | | | |
| 13.5 (3) | 4000 | 12 (6) | 1500 | 800 | 21.7 | 20 | 25 (10) | 132 | 32.4 | 13 | 700 | 1000 | 6.5 | 20 | 30 | 20 | 610 | 46 | 12.5 | 3.7 | 100 (80) | 14 | 8.67 | 26.3 |
| Absolute spread of average contents in rocks of the provincial landscapes | | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | 1.9 | 3.3 | 3.0 | 3.3 | 3.7 | 4.9 | 1.6 | 2.3 | 2.4 | 6 | 3.0 | 3.0 | 2.5 | 2.1 | 1.9 | 3.1 | 6.3 | 2.40 | 3.9 | 2.5 | 2.7 | 2.5 | 4.2 | 2.7 |

As can be seen from Table 1, regional abundances of sedimentary and igneous rocks often exceed the corresponding abundances of the lithosphere by more than 1.5 times. The regional abundances of Zr, Mo, and Sr in carbonate-terrigenous rocks exceed the lithospheric abundances by more than 1.5 times too. Their EFs are equal to 5.26; 1.64; 1.62 respectively (Table 1). Values of EF greater than 1.5 are established for Mn(1.64), Mo(2.15), Pb(1.76), and V(2.73) in terrigenous rocks, and for Be(2.00), Cr(3.81), Li(1.60), Mo(2.20), Ni(1.50), Pb(2.20), and Sn(3.00) in felsic rocks. Summary of all information about the elements (Table 1) allows to arrange the chemical elements that differ most in content from the abundances of the lithosphere in the following order: Mo→Pb→Ba→Cr→Zn→Be.

In some areas and certain rocks, the average contents of Sr, Zr, Mn, V, Cu, and Ni are often increased. Judging by the ionization potentials, the six most different elements should get into ionic state and then migrate as solutions in the following sequence: Ba(5.8) – Cr(6.8) – Mo(7.1) – Pb(7.4) – Be(9.3) – Zn(9.4) (in parentheses, the energy factor required to separate an electron from an unexcited atom). According to the classification of A.I. Perelman, Ba, Zn, and Be are cationic elements with a significant role (as for Mo) of biogenic accumulation. For Pb and Cr, biogenic accumulation is insignificant.

The sedimentation of these elements, migrating as solutions, often occurs at different geochemical barriers. Thus, Zn, Ni, Pb, as well as Cu coming from weathering deposits, which are mobile in acidic waters of oxidative and gleyic environments, are deposited on alkaline barriers, Mo, which is relatively mobile in oxidative environments, is deposited on gleyic and hydrosulfuric barriers, Ba is a low-mobility water migrant, and Cr migrates mainly with organic complexes in a strongly acidic environment.

Comparing to the abundances of the lithosphere, contents of certain elements are lower: Y, Yb, Ga, V, Sn, and Ni in carbonate-terrigenous rocks of the province, Ni, Y, Yb, Ga, and Sn in terrigenous rocks, and Sr, Y, and Yb in igneous rocks.

These features of the prevalence of chemical elements in the most common rocks (Table 1) largely determined the accumulation of elements by the soil and vegetation cover of the North Caucasian geochemical province.

Let us consider the geochemical features of the soils of the region, and hence the features of element accumulation by this biomineral system (Table 2). Of the 25 elements, 13 have EFs greater than unity. These are Ba, Co, Cu, Li, Mn, Mo, Ni, P, Pb, Sc, Ti, V, and Zn. Of these, five have EFs over 1.5: Pb(3.70), Cu (2.65), Zn(2.40), Co(2.25), and Li (1.80). The established association is closest to the association of polymetallic deposits. If we add to these elements those with EFs slightly greater than unity, we practically get an association of elements of secondary lithochemical fields corresponding to the regions and nodes of mineral deposits in the region (Fig.2). The element association includes metals with different migration characteristics. Thus, despite the rather close values of the ionic radii, Pb, Zn, Cu, and Li (judging by the ionic potential) are characterized by the formation of cations, while Mn, Mo, and Zr form complex ions. It should be noted that Li ions are alkalis, and Mn makes a strong base. The ionization potentials, and hence the energy required for the formation of these ions, ranging from 5.19 for Co to 9.35 for Zn. Such elements as Zn, Cu, and Pb are mainly accumulated on hydrosulfuric barriers, while Mo, Co, and Mn are stopped by oxygenous barriers. For Cu, Zn, Mo, and Co, biogenic accumulation plays a significant role, while for Pb and Ni it is practically absent.

Comparing the features of the prevalence of several elements in soils and rocks, we note that some of those accumulated in all the considered rocks (Mo, Pb, Ba, and Zn) are also higher in soils. In both systems, these elements are characterized by relatively large EFs. Some elements that are slightly accumulated in soils (Co, Li, Mn, Sc, and Ti) are also elevated in at least two of the three most common rocks in the region (Table 1). This indicates that the soils have largely inherited for these elements the features of their prevalence in the bedrock and the deposits known to date.

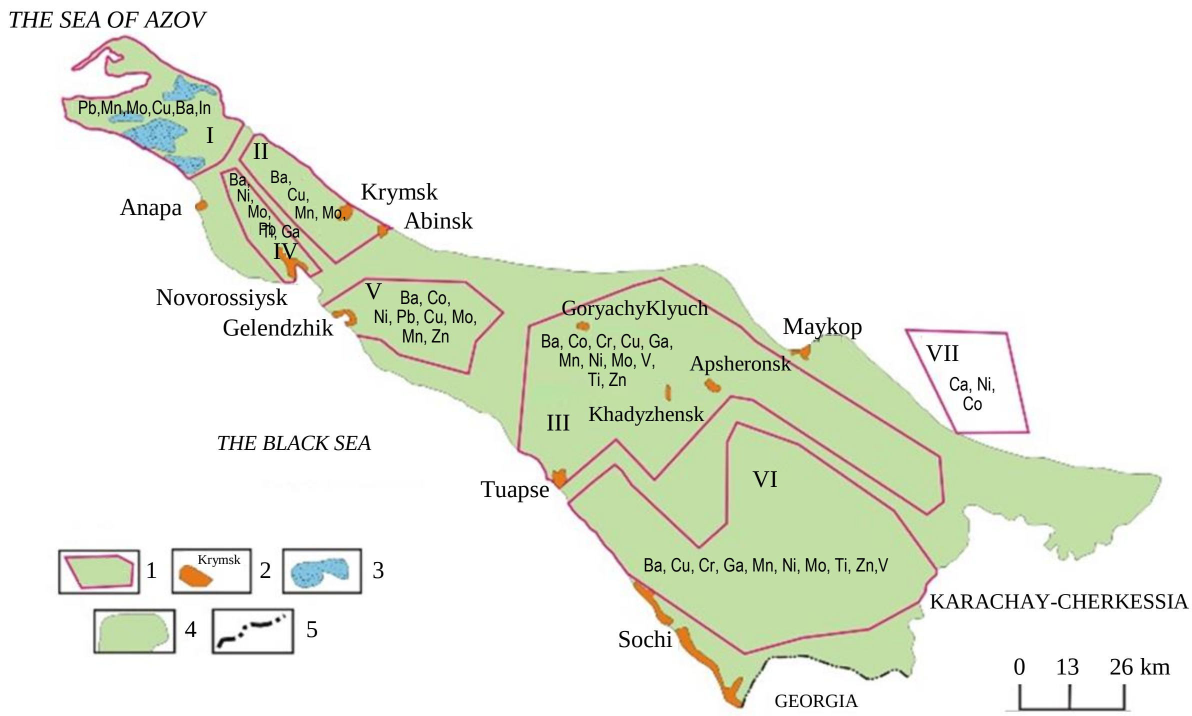


Fig.2. Map of secondary lithochemical fields corresponding to the areas and nodes of mineral deposits in the central and western parts of the North Caucasian geochemical province

1 – border of a lithochemical field; 2 – settlements; 3 – estuaries; 4 – border of the studied region; 5 – state border

As can be seen from the above data, the enrichment of the region's soils is associated with none of the ion migration factors. It can be assumed that the enrichment of the soils of the North Caucasian province, which is distinguished by non-geochemical features, corresponds to its tectonic-magmatic and metallogenic features [15]. It occurred mainly in the process of soil formation, and not due to subsequent changes in the soil associated with the introduction of certain metals.

In half of the chemical elements with decreased contents in the soils of the region, compared to the soils of the world, the contents are also lower in most of the rocks of the province (mainly in sedimentary ones). These are Ag, Ga, Ge, Y, and Sn.

The EFs are less than unity, i.e. the DFs are set for 9 elements (Table 2), and for all of them (except Sr) it is greater than 1.5: Ag(3.8), Y (2.5), Ge (2.3), Cr, Sn(1.8), Zn(1.6), Be(1.5), and Ga(1.5) (DFs in brackets). These elements (except for Zn) are not characterized by biogenic accumulation, and therefore by biogenic “pumping” from rocks to soils. Their transition to the ionic form requires more energy than that of accumulated elements. Judging by the values of the Cartledge potentials, Be, Cr, Ga, Ge, and Sn form complex ions. Only for Ag and Sr, migration in the form of true solutions can be common, although all the elements that make up this association are characterized by water migration.

Thus, according to the average content of 22 elements out of 24, the studied soils of the North Caucasus differ to a various extent from the soils of the world. Of these, the difference in the contents of more than 1.5 times is established for 14 chemical elements.

The Absolute Spread (AS) of the average chemical element content in the soils of individual landscapes of the province did not reach the values of AS in the rocks and soils of the continents (Table 2). This, as well as a relatively small area of landscapes with increased values of AS, allowed us to assume that the distribution of elements in the soils of the region does not reach values that significantly worsen the environmental geochemical situation. The relatively large AS of the average contents of Be, Mo, W, Ag, Yb, Ge, Cu, and Pb in the soils of the landscapes may indicate their rather intensive migration not only in the soils but also in the bedrock. Therefore, at certain geochemical barriers, their high concentration is possible, up to the formation of deposits.

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*Table 2*

**Geochemical characteristics of the soils of the North Caucasian geochemical province**

| Ag | Ba | Be | Co | Cr | Cu | Ga | Ge | Li | Mn | Mo | Nb | Ni | P | Pb | Sc | Sn | Sr | Ti | V | W | Y | Yb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Abundances in the Earth's soils * | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.05 | 50.0 | 0.6 | 0.8 | 20.0 | 2.0 | 3.0 | 0.5 | 3.0 | 85.0 | 0.2 | 1 | 4.00 | 80.0 | 1.0 | 0.7 | 1.0 | 30.0 | 460 | 10.0 | - | 5.0 | 0.3 | 5.0 | 30 |
| Regional abundances of the province** | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.013 | 60 | 0.4 | 1.8 | 11.0 | 5.3 | 1.9 | 0.22 | 5.30 | 120 | 0.28 | 1.86 | 4.7 | 110 | 3.7 | 1.0 | 0.57 | 29 | 540 | 11.0 | 0.25 | 2.0 | 0.25 | 12.0 | 19 |
| Enrichment factors as the rations of the regional abundances to the abundances in the Earth's soils ** | | | | | | | | | | | | | | | | | | | | | | | | |
| | 1.20 | | 2.25 | | 2.65 | | | 1.77 | 1.41 | 1.40 | | 1.18 | 1.38 | 3.70 | 1.43 | | | 1.17 | 1.10 | | | | 2.40 | |
| Depletion factors** | | | | | | | | | | | | | | | | | | | | | | | | |
| 3.85 | | 1.50 | | 1.82 | | 1.58 | 2.27 | | | | | | | | | 1.75 | 1.03 | | | | 2.50 | | | 1.6 |
| Absolute spread in rocks and soils of continents ** | | | | | | | | | | | | | | | | | | | | | | | | |
| 13.5 (3) | 4000 | 12 (6) | 1500 | 800 | 21.7 | 20 | 25 (10) | 132 | 32.4 | 13 | 700 | 1000 | 6.5 | 20 | 30 | 20 | 610 | 46 | 12.5 | 3.7 | 100 (80) | 14 | 8.67 | 26.3 |
| Absolute spread of average contents in soils of the provincial landscapes | | | | | | | | | | | | | | | | | | | | | | | | |
| 3.16 | 2.8 | 5.2 | 2.1 | 3.74 | 7.06 | 2.12 | 2.54 | 1.63 | 4.67 | 6.05 | 2.04 | 2.83 | 4.88 | 3.04 | 2.16 | 1.94 | 5.88 | 1.94 | 1.91 | 3.6 | 1.73 | 2.12 | 3.2 | 2.1 |

* After A.P.Vinogradov
** After V.A.Alekseenko

The considered geochemical features of soils are largely determined by the biogeochemical features of vegetation cover, which, according to the figurative expression of V.M.Goldschmidt, selectively pumps chemical elements to the surface from deeper horizons. The North Caucasus is characterized by a rich combination of many types of vegetation: forests (especially in the western part), meadows (alpine, subalpine, forest, post-forest, and floodplain), steppes, semi-deserts, and swamps.

The rugged terrain of the region largely influenced the zoning of vegetation, represented by nival, subnival, alpine, subalpine, mountain-forest, forest-steppe, and steppe types [18].

Significant differences in the biomass and productivity of the communities of the North Caucasian province determine their different contribution to the biological cycle. Thus, in biogenic landscapes, the lowest phytomass of higher plants is formed in alpine (0.7-2.0 g/ha) and subalpine meadows (2.0-5.0 t/ha) [4]. During the transition from steppe to forest landscapes, the stock of phytomass rarely changes and reaches 300 t/ha. From the above data, it can be seen that the overwhelming mass of chemical elements that are in biogenic form in the province is associated with forest landscapes. In them, the phytomass is hundreds of times higher than the phytomass of other landscapes. In the study of biogenic accumulation, woody vegetation was considered; it is developed in the forest landscapes of the mountain-forest belt at altitudes from 300 to 2600 m above sea level.

The main forest-forming species that form the vegetation cover of the upper, middle, and lower mountain-forest belt are oaks (*Quercus petraea* (Matt.) Liebl., *Q. robur* L.), hornbeam (*Carpinus betulus* L.), beech (*Fagus orientalis* Lipsky), chestnut (*Castanea sativa* Mill.), fir (*Abies nordmanniana* (Steven) Spach), pine (*Pinus kochiana* Klotzsch ex K. Koch), and birch (*Betula pendula* Roth). The upper sub-belt consists of coniferous (pine, fir, spruce) and deciduous (birch) forests. The middle sub-belt is formed by monodominant and mixed deciduous forests of primary (beech, fir-beech, and beech-hornbeam) and secondary (birch and hornbeam) origin. In the lower sub-zone, oak, oak-hornbeam, and fruit forests include pear (*Pyrus caucasica* Fed.), and apple (*Malus orientalis* Uglitzk.) [19].

Due to the economic development of the region, the processes of synanthropization have intensified in the vegetation cover of the province and manifested in the simplification, unification, and change of the biomass of phytocenoses. The creation of urbanized, agricultural, and other man-made systems instead of fragments of forest and steppe landscapes led to the development of anthropocenoses (including agrophytocenoses and communities of ruderal and spontaneous urban vegetation) with altered morphological, floristic, phytocenotic, productive, and biogeochemical properties [16, 21].

Considering the biogeochemical features of the region, we note that the EFs of chemical elements in the ash of plants differ in large values [2]. Thus, nine elements out of ten accumulated in plants in concentrations higher than the average for the ash of land plants, have EFs greater than 1.5 (Table 3).

For almost half of the elements under consideration, the average contents in the plants of the region exceed their global abundances in plants by more than seven times (Table 3). These include Ba(8.20), Nb(7.60), Pb(1.77), Sc(10.00), Sr(12.00), and Zr(7.00). We note that all these elements form independent deposits or large ore occurrences in the region.

The average content of 25 chemical elements in the ash of the most common woody plants in the region, in comparison with the average content in the ash of land plants of the world, is shown in Table 3. The contents established for the plants of the Earth, according to different authors, often differ. This can be explained, firstly, by the large variance of the contents in plants of different species, secondly, by the change in the contents in one species depending on the changing growing conditions, and thirdly, by the fact that not the entire plant, but only a certain part of it is usually subjected to testing. A number of researchers analyze not the ash, but a live or dehydrated (dry) plant. In this regard, it is advisable to use data on the content of land plants (or marine organisms) in various comparisons only as a kind of "reference points".

*Table 3*

**Geochemical characteristics of the vegetation of the North Caucasian geochemical province**

| Ag | Ba | Be | Co | Cr | Cu | Ga | Ge | Li | Mn | Mo | Nb | Ni | P | Pb | Sc | Sn | Sr | Ti | V | W | Y | Yb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Abundances in the Earth's crust | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.007 | 6.5 | 0.38 | 1.8 | 8.3 | 4.7 | 1.9 | 0.14 | 5.2 | 100 | 0.11 | 5.8 | 2 | 93 | 1.6 | 1 | 0.25 | 34 | 450 | 9 | 0.13 | 2 | 0.033 | 8.3 | 17 |
| Abundances in the Earth's living matter | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.0012 | 0.9 | 0.004 | 0.04 | 0.07 | 0.32 | 0.002 | – | 0.06 | 9.6 | 0.02 | 0.08 | – | 70 | 0.1 | – | 0.01 | 1.6 | 1.3 | 0.06 | – | 0.03 | – | 2 | 0.3 |
| Abundances in the terrestrial living matter ($n \cdot 10^{-3}$ %) | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.1 | 10.0 | 0.21 | 1.5 | 25.0 | 20.0 | 5.0 | 5.0 | 1 | 750.0 | 2.0 | 0.05 | 5.0 | 7.0 | 1 | 0.009 | 0.5 | 3.0 | 100.0 | 6.1 | 0.0005 | 0.1 | 0.01 | 90.0 | 0.5 |
| Abundances in the living matter of the North Caucasian geochemical province | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.07 | 81.8 | 0.07 | 0.35 | 4.79 | 6.6 | 0.13 | 0.1 | 1.66 | 367.8 | 0.13 | 0.38 | 4.35 | 944.0 | 1.7 | 0.09 | 0.2 | 36.1 | 99.7 | 1.2 | 0.23 | 0.21 | 0.03 | 12.6 | 3.5 |
| Enrichment factors as the rations to the abundances in plant ash | | | | | | | | | | | | | | | | | | | | | | | | |
| | 8.18 | | | | | | | 1.5 | | | 7.6 | | | 1.7 | 10 | | 12.0 | | | 460 | 2.1 | 3 | | 7 |
| Depletion factors as the rations to the abundances in plant ash | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.42 | | 3 | 4.28 | 5.2 | 3.0 | 38.4 | 50 | | 2.03 | 15.4 | | 1.15 | | | | 2.5 | | 1 | 5.08 | | | | 7.14 | |
| Average content in the ash of certain plant species | | | | | | | | | | | | | | | | | | | | | | | | |
| *Oak* | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.008 | 69.3 | 0.1 | 0.2 | 0.8 | 7.9 | 0.1 | 0.1 | 1.5 | 525.0 | 0.2 | 4.7 | 0.4 | 953.0 | 1.6 | 0.1 | 0.2 | 26.4 | 137.0 | 1.6 | 0.2 | 0.2 | 0.03 | 9.5 | 4.2 |
| *Beech* | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.003 | 96.7 | 0.07 | 0.1 | 1.6 | 8.4 | 0.1 | 0.1 | 1.5 | 571.4 | 0.1 | 0.4 | 5.1 | 969.0 | 1.8 | 0.07 | 0.2 | 29.3 | 120.0 | 1.3 | 0.2 | 0.2 | 0.03 | 13.8 | 4.2 |
| *Hornbeam* | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.003 | 64.1 | 0.1 | 0.2 | 1.0 | 6.5 | 0.2 | 0.1 | 1.5 | 476.6 | 0.1 | 0.4 | 4.4 | 926.0 | 1.9 | 0.1 | 0.2 | 36.4 | 157.0 | 1.7 | 0.3 | 0.3 | 0.03 | 6.6 | 4.5 |
| *Fir* | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.01 | 82.4 | 0.06 | 0.3 | 1.2 | 6.5 | 0.09 | 0.1 | 1.6 | 446.0 | 0.2 | 0.4 | 5.9 | 968.0 | 2.2 | 0.06 | 0.2 | 35.7 | 115.0 | 1.3 | 0.2 | 0.2 | 0.03 | 11.2 | 4.2 |
| *Pine* | | | | | | | | | | | | | | | | | | | | | | | | |
| 0.007 | 73.25 | 0.08 | 0.25 | 1.1 | 6.5 | 0.15 | 0.1 | 1.55 | 461.3 | 0.15 | 0.4 | 5.15 | 947.0 | 2.05 | 0.08 | 0.2 | 36.1 | 136.0 | 1.5 | 0.25 | 0.25 | 0.03 | 8.9 | 4.2 |
| *Hawthorn* | | | | | | | | | | | | | | | | | | | | | | | | |
| no data | 154.9 | no data | 0.47 | 26.7 | 5.4 | 0.14 | no data | no data | 35.5 | 0.08 | no data | 3.5 | no data | 1.08 | no data | no data | 198.5 | 17.9 | 0.29 | no data | no data | no data | 5.2 | no data |

Table 3 shows the average ash content of woody plants in the North-West Caucasus. They can be used as regional abundances of the territory. In comparison with the average content of land plant ashes, the contents of Ba, Li, Nb, P, Pb, Sc, Sr, W, Y, Yb, and Zr are higher in regional trees. The row can be continued by Cu, Mn, Mo, Ni, and (possibly) Zn. The last five are the basic indicator-elements to reveal secondary regional lithochemical fields (Fig.2) and reflect the general geochemical situation in the North Caucasus. As the review of the latest data [2] shows, their content in the ash of a number of terrestrial plants was overestimated by S.M. Tkalich. Thus, in living matter, the content of Cu is 0.30; Mn – 9.60; Mo – 0.02; Ni – 0.08; and Zn – 2.00 (all in $n\cdot10^{-3}$ %). The contents of these metals can't increase almost 100-fold during the ignition. Thus, the North Caucasus differs significantly in its biogeochemical features from the neighboring territories [2] and the land area of the biosphere.

Since geochemical provinces usually include biogeochemical ones, let's take a closer look at some of the biogeochemical features of the Western Caucasus. In the ash of the leaves of the tree species most common in the Western Caucasus, there are quite large fluctuations in the average contents of 6 of the 25 chemical elements considered. The maximum average content of Ag was observed in fir needles (0.01), the minimum – in hornbeam leaves (0.003); Co – maximum (0.47) in hawthorn leaves, minimum (0.1) in beech leaf ash; Cr – maximum (26.7) in hawthorn leaf ash, minimum (0.8) – oak; Mn – maximum (571) in beech leaves, minimum (35.5) – hawthorn; Sr – maximum (198) – in hawthorn leaves, minimum (26.4) – oak; Ti – the maximum (157) in the ash of hornbeam leaves, the minimum (17.9) – hawthorn (all contents in $n\cdot10^{-3}$ %).

The determination of biological cycles of metals contained in various morphological parts (first of all, in leaves) of trees is one of the most important biogeochemical issues. To establish the corresponding regularities, the results of analyses of biogeochemical samples taken in the region and the amount of biomass determined by N.I.Bazilevich and L.I.Rodin for different morphological parts of trees were used [5, 6].

Calculations have shown that in the middle-aged beech forest (approximately 160 years), more than 320 kg/km$^2$ of metals, in particular: Mn – 222; Ti – 44; Ba – 36; Sr – 9; Zn – 4; Cu – 3; Ni – 2; Pb – 0.7; V – 0.6; Cr – 0.5, are accumulated and temporarily extracted from the soil (before falling). In the leaves of oak forests of the same age, 130 kg/km$^2$ of heavy metals are accumulated annually: Mn – 84; Ti – 25; Ba – 12; Sr – 5; Cu – 2; Ni – 1; Zn – 1; V – 0.2; Pb – 0.2; Cr –0.1. In the leaves of a young hornbeam forest (about 50 years old) also, about 290 kg/km$^2$ of metals are accumulated annually, including Mn – 173; Ti – 69; Ba – 26; Sr – 14; Cu – 2.6; Ni – 1.8;Zn – 1; Pb – 0.9; V – 0.8; Cr – 0.2.

Mixed beech-fir forests occupy an intermediate position in terms of the mass of metals accumulated in leaves and needles: 46 kg/km$^2$ of metals (Mn – 33; Ti – 6; Ba – 3.5; Sr – 1.5; Zn – 0.7; Ni – 0.6; Cu – 0.4; V – 0.08; Pb – 0.06; Cr – 0.04). The pine needles accumulate about 13 kg/km$^2$ of metals (Ti – 8; Mn – 1.6; Ba – 1.1; Zn – 0.5; Cu – 0.3; Pb – 0.3; V – 0.2; Cr – 0.1; Ni – 0.04). In fir needles, more than 11 kg/km$^2$ of metals were determined in total (Mn – 8; Ti – 1.5; Ba – 0.9; Sr – 0.4; Zn – 0.2; Ni – 0.1; Cu – 0.1; V – 0.02; Pb – 0.01; Cr – 0.009).

Only 2-3 % (7 % in conifers) of the total amount of metals concentrated by wood species are accumulated in the leaves annually, and they are returned to the soil with the fall. However, over 100 years of the life of the tree species, both leaves and needles will involve more metals in the biological cycle several times than will be accumulated by plants as a whole, excluding leaves and needles.

The presence of a significant number of deposits and ore occurrences in the region affected the geochemical features of the province. The geochemical features of the deposits (worked out and spent) had a very significant impact on the biogeochemical characteristics of the province. In this regard, we point out some deposits that have had a significant impact on the accumulation of some metals by plants in the North Caucasus. These elements include Ba, Nb, Sc, Sr, and Zr, which enter the soil and vegetation horizons in significant quantities from deposits.

*Barium*. Barite is one of the main minerals in the polymetallic deposits of the Sadonsky and Bezengiysky (gold-polysulfide-barite) types.

*Niobium*. The ore occurrences of tantalum-niobates are mainly associated with the pegmatite bodies of the Tanadon granite massif and the aplite-porphyry dikes in the Kti-Teberda scheelite deposit.

*Scandium* was extracted from uranium-phosphate ores, "fish" layers in the Maikop clays. In the 70s and 80s, this source gave more than 90 % of the world's $Sc_2O_3$ production.

*Strontium*. The largest deposit Sinie Kamni with ore outcrops could meet the expected needs of Russia and European countries for decades (however, the demand for Sr, as well as for Sc, has fallen sharply). There are known Vitskhi and Kuli-Meer deposits with rich (more than 15 % of SrO) ores and large reserves.

*Zirconium* is found in the ash of plants in the region at an average concentration seven times higher than the corresponding abundance. Productive titanium-zirconium sands are exposed in the sides of river valleys and gullies of the Stavropol titanium-zirconium placer basin. The absence of high Ti content in plants is most likely due to insignificant biogenic accumulation of the metal and weak migration in a strongly acidic environment (zirconium migrates in an alkaline media). Beshpagirskoye and Kambulatskoye are the main deposits of the region. The depth of productive sands is from 0 to 30 m, which makes it possible to conduct biogeochemical searches for zirconium.

The DF values greater than five in the ash of plants in the region are established for six chemical elements: Cr (5.2), Ga(38.4), Ge(50.0), Mo(15.4), V(5.0), and Zn (7.1). This means that the content of every fourth element in plant ash is 5–50 times less than the corresponding abundance of the Earth's plants: V(5.0) →Cr(5.2)→Zn(7.1)→Mo(15.4)→Ga(38.4)→Ge(50.0). It is impossible to explain this by simple unidirectional changes in the concentrations of elements in rocks. Some of these elements in rocks are characterized by the high EFs, i.e. their content in rocks (sedimentary or igneous) is not lower, but higher than the abundances. Most likely, in these cases, the primary role is played by biogeochemical factors. An example of one of them is the relationship between the contents of Pb and Mo in plants; by using it, one of the authors discovered a polymetallic deposit in Kazakhstan [3].

**Conclusion.** The average contents of more than 20 chemical elements established for soils and woody vegetation of the North Caucasian geochemical province are local (regional) abundances for soils and living matter.

The formation of the EFs of the soil and vegetation cover of the province occurred under the significant, but not the only, influence of the regional abundances of rocks. Thus, the increased average contents of Zn, Pb, Mo, and Ba in the most common sedimentary and igneous rocks of the province coincide with the increased (relative to the Earth's soils) contents in the soils of the province. Their EFs in soils are respectively equal to 2.4; 3.7; 1.4; and 1.2. Despite the low content of Cu (an element with a significant role of biogenic accumulation) in the prevalent regional rocks, its average content in the soils of the province is higher than the abundance in the Earth's soils. The same pattern is established for Ni.

In Zr (an element with insignificant biogenic accumulation), with the predominance of increased contents in sedimentary rocks in the soils of the province, the content is even reduced, its DF is equal to 1.6.

The creation of a modern geochemical picture of soils is largely determined not only by the features of the rocks of the province, but also by the geochemical characteristics of the chemical elements, the specific landscape-geochemical situation, and the size of the geochemical barriers. Thus, the absence of accumulation (i.e., scattering) established for the eight chemical elements can be explained by the fact that they are not characterized by biogenic accumulation, and therefore by biogenic "pumping".

The concentrations of chemical elements in the ash of woody vegetation of the province (relative to the abundances of elements in the ash of terrestrial plants) were increased in 10 elements out of 24 studied. At the same time, in 7 of them, the average contents in the province exceed the abundances by more than 2 times Y(2.15), Yb(3.00), Nb(7.60), Ba(8.18), Sc(10.00), Sr(12.00), and W(460.00). Such a high concentration is not observed either in rocks or in soils.

The high degree of concentration of some metals in vegetation to date is not explained either by the values of the elements' indicators or by their role in the biogenic accumulation in the history of the element.

The absolute dispersion of chemical elements in the soils of the province is much less than in the rocks and soils of the continents, to which living organisms are accustomed.

Thus, the North Caucasian geochemical province has several geochemical features that must be taken into account when developing the region.

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***Authors*: Vladimir A. Alekseenko,** *Doctor of Geological and Mineralogical Sciences*, *Professor*, *vl.al.alekseenko@gmail.com*, *https://orcid.org/0000-0002-7874-8110* (*Admiral Ushakov Maritime State University*, *Novorossiysk*, *Russia*; *Southern Federal University*, *Rostov-on-Don*, *Russia*; *Institute for Water and Environmental Problems of Siberian Branch of the Russian Academy of Sciences*, *Barnaul*, *Russia*), **Natalya V. Shvydkaya,** *Candidate of Biological Sciences*, *Associate Professor*, *nepeta@mail.ru*, *https://orcid.org/0000-0003-0243-1480* (*Kuban State Agrarian University*, *Krasnodar*, *Russia*), **Jaume Bech,** *Doctor*, *Professor*, *jaumebechborras@gmail.com*, *https://orcid.org/0000-0001-9401-0266* (*University of Barcelona*, *Barcelona*, *Spain*), **Alexander V. Puzanov,** *Doctor of Biological Sciences, Director*, *puzanov@iwep.ru*, *https://orcid.org/0000-0002-1340-486X* (*Institute for Water and Environmental Problems of Siberian Branch of the Russian Academy of Sciences*, *Barnaul*, *Russia*), **Aleksey V. Nastavkin,** *Candidate of Geological and Mineralogical Sciences*, *Associate Professor*, *geo_alex@mail.ru*, *https://orcid.org/0000-0003-1472-9399* (*Southern Federal University*, *Rostov-on-Don*, *Russia*).

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