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MIGRATION FORMS OF CHEMICAL ELEMENTS IN THE INTRUSIVE ROCKS OF THE EASTERN DESERT (EL SELA AREA, EGYPT)

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In the Egypt's Eastern Desert intrusive rocks with U-REE mineralization (two-mica granites, microgranites, dolerites, and bostonites) are developed. We estimated the content of chemical elements in reference samples of intrusive rocks and also in their water-soluble (colloid-salt) fraction. This fraction is water-extracted from the rock under certain conditions. The rock sample and its colloid-salt fraction are analyzed using ICP-MS.

The chemical characteristic of the extracted fraction reflects the mobile migrating part of the chemical elements in the composition of the rocks. Comparison of the obtained data allows us to estimate the share of migrating and weakly migrating elements.

Key words**:** uranium; rare earths elements; intrusive rocks; migration forms of chemical elements; Eastern desert; Egypt

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Introduction. The region of the Egypt's Eastern desert belongs to the U-REE province, within which intrusive rocks enriched with U, REE, and chalcophile elements are widely distributed. Economically valuable U and REE ore occurrences are genetically related to two-mica leucogranites with an age of 560 Ma [10, 11, 13, 16]. These leucogranites are transversed by microgranites, dolerites and bostonites dikes confined to fault zones. The deposits of uranium and rare earth elements are of the vein type and are also confined to the linear zones of mineralization in tectonic areas composed of hydromica-kaolinite metasomatites with iron hydroxides impurities.

The El Sela region landscape is characterized by high mountain chains, which form a series of plutons with distinct boundary with host rocks. Intrusive rocks form a hilly landscape, which protrusions are represented by intrusive bodies and dikes.

The physical and chemical weathering of rocks causes a formation of desert sands. A significant day and night temperature changes lead to the moisture accumulation in the rocks pore space. The accumulated moisture contributes to the chemical elements transition into a mobile state and their migration to the surrounding areas.

The question of the elements forms in rocks is important for studying the weathering of rocks. It is known that a significant part of chemical elements can be found in minerals as isomorphous impurities, replacing mineral formula elements in the crystal lattice. Some of them are accumulated in gas-liquid inclusions, and some occur in the colloid-dispersed form in the rocks pore space. It is a well-known fact that the lower is the average content of the chemical element in the earth's crust, the greater is its share in the dispersed form. Weathering leads to the rocks disintegration and washing out of chemical elements from the pore space, which results in the new physical and chemical conditions conducive to the further rocks destruction.

Environmental pollution is closely related to the mobility of elements in natural systems. Heavy metals and radionuclides may be involved in a range of complex chemical and biological interactions. The most important factors affecting the mobility of elements are pH, sorption, the presence of organic and inorganic ligands, including humic and fulvic acids. Redox reactions are of great importance in chemical weathering of rocks, which include variable valence and chalcophile elements such as U, Th, REE, Cu, Ni, Zn, and Pb.

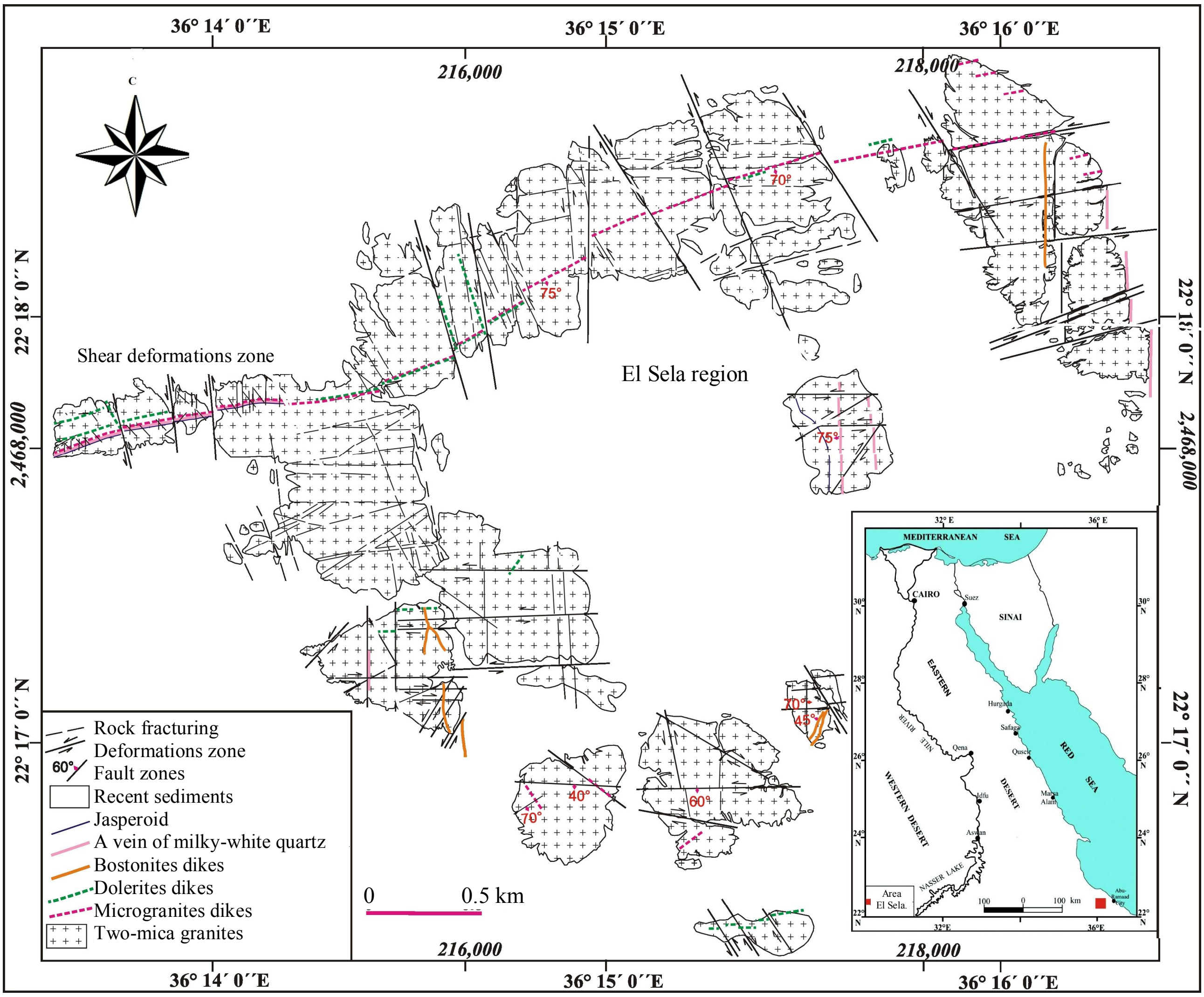

Fig.1. Geological map of El Sela, Eastern Desert, Egypt
(Abdel-Meguid et al., 2003; Ibrahim et al., 2007; Ali, 2011; Abdel Gawad et al., 2015)

To determine the risk of environmental pollution, the mobility of uranium and pathfinder elements contained in the intrusive rocks of the U-REE province is of particular importance. Despite the developed general concepts of mobile and tightly bound forms of elements in rocks and methods for their extraction, there are not enough experimental quantitative data to assess the behavior of micro elements mobile forms in rocks.

The aim of the study is to drain out the pore solution (colloid-salt fraction) from intrusive rocks, determine the content of trace elements in it and compare it with the intrusive rocks composition.

Geological settings The El Sela area is located in the Eastern desert of Egypt along the Red Sea coast with uneven topography and moderate to high relief (up to 560 m). Precambrian uranium-containing granites are exposed in the southern part of the Eastern Desert (Fig.1).

Based on field observations, the rocks in the studied area have the following formation sequence: two-mica granites, dikes (microgranites, dolerites, and bostonites), quartz and jasperoid veins [1, 6-10, 12-16, 19].

Two-mica granites compose a large part of the studied area in the form of rounded granite plutons (3 × 5 km). They are intersected by two perpendicular zones of shear deformation. The first shear deformations zone extends in the direction of E-SE. Zone length and width are of about 1.5 km and 5-40 m, respectively. This zone is intersected by the tectonic zone of the NW-SE strike.

The microgranite and dolerite dikes, as well as jasperoid veins, are characteristic of this shear deformations zone.

Microgranite dikes intersect two-mica granites along the ENE-WSW shear deformations zone and have a south dip of 72-83°. This dike, composed of fine-grained rock, varies from 3 to 20 m in width and extends over 6 km in the SW direction.

Dolerite dikes have an ENE-WSW and NNW-SSE directions. The dikes strike is N 75° and the dip is S 68-81°.

Bostonites dikes cut granite plutons along the N-S and NNE-SSW tectonic zones. The rocks form a sheetlike body with a thickness of 0.5 to 2 m. Bostonite is a fine-grained, reddish-brown, massive rock.

Materials and research methods. We have studied the intrusive rocks of the El Sela region (two-mica granites, microgranites, dolerites, and bostonites) and their colloid-salt fraction.

The mineral composition of various intrusive rocks is unique (Table 1). Two-mica granites consist mainly of quartz, potassium feldspar, plagioclase, muscovite, and a small amount of biotite. The accessory minerals are presented by thorium-bearing ones (thorite, uranothorite, phosphothorite), zircon, ilmenite, titanite, and apatite. Secondary alterations are expressed in pelitization of potassium feldspar, sericitization of plagioclase and biotite, as well as in the occasional presence of fluorite and sulfides.

Table 1

The mineral composition of the intrusive rocks of the El Sela region

Minerals	Two-mica granites	Microgranites dikes	Dolerites dikes	Bostonites dikes
Rock-forming minerals	Quartz K-feldspar Plagioclase Muscovite Biotite	Plagioclase K-feldspar Quartz Sericite	Plagioclase Pyroxene Olivine Quartz	Microcline Albite Quartz Aegirine
U and Th-bearing minerals	Thorite Uranothorite Phosphothorite	Coffinite Uranophane Autunite Kasolite	Coffinite Uraninite Autunite	Coffinite
REE-bearing minerals	Bastnaesit Monazite Xenotime	Monazite	Monazite	Monazite Bastnaesite
Other minerals	Zircon Ilmenite Titanite Galenite Rutile Apatite Barite Fluorite Hematite	Zircon Apatite $\text{Ni}_{\text{native}}$ $\text{Fe}_{\text{native}}$ $\text{Cu}_{\text{native}}$ $\text{Au}_{\text{native}}$ Barite Pyrite Chalcopyrite	Zircon Magnetite Barite Pyrite Chalcopyrite Fluorite	Zircon Ilmenite Titanite Galena Rutile Apatite Barite Fluorite Hematite

Microgranite consists of plagioclase, to a lesser extent potassium feldspar, and quartz. The rock is significantly altered; a large amount of sericite and sulfides appears, as well as $\text{Ni}_{\text{native}}$, $\text{Cu-Ni}_{\text{native}}$, and barite. Coffinite, uranophane, autunite, and kasolite are also presented. Accessory minerals are zircon, monazite, and apatite.

Dolerite dikes consist mainly of plagioclase and pyroxene, less often olivine and quartz, zircon, titanomagnetite, and barite. Secondary minerals are presented by chlorite, sericite, fluorite, calcite, and sulfides. Among the uranium-bearing minerals are uraninite, coffinite, uranophane, and autunite.

Bostonite dikes consist of microcline and albite, quartz and aegirine are less common. The set of accessory minerals contains zircon, rutile, ilmenite, titanite, and apatite. U-REE mineralization is represented by coffinite, bastnaesite, and monazite.

The chemical composition of rock samples was determined by the standard complete decomposition model using concentrated nitric, hydrogen fluoride, and perchloric acids. Analysis of the solutions was carried out on the ICP-MS mass spectrometer «ELAN-6100 DRC» (PERKIN ELMER).

To study the water-soluble component of the pore solution, we used the method of extraction and analysis of the rocks submicron fraction, which is enclosed in the pore and intergranular space, in which chemical elements are in ionic, molecular, and colloidal forms. The basics of the method are described in a number of publications and patents [2-4].

A substance extracted by water is not considered as an aqueous extract, which characterizes exclusively «truly soluble» forms of elements, but as an independent fraction, having a weight (weight fraction) and a specific particle size (up to 1 μm). To distinguish it from other fine fractions, it was called the submicron fraction (SMF) in accordance with the particles dimension. Particle size less than 1 μm in colloidal chemistry is the conditional boundary of the colloidal state, above which the substance is released into a separate solid phase [5].

The technique for SMF extraction included crushing and abrasion of samples to a particle size of < 74 μm. In the case of an experiment with rocks, their preliminary grinding is necessary for pores and microfractures opening in order to ensure the access of the extractant (water) to free and adsorbed salts and colloidal particles.

A weighed quantity of the pre-grinding sample was filled up with heated deionized water, periodically stirred during 5 h and kept for 24 h to stabilize the resulting colloid-salt solution. The solution was taken with a syringe and infiltrated through Sartorius membrane filter, which guarantees the transmission of particles less than 1 μm. The obtained solution is colorless, transparent, colloidal and shows Tyndall effect.

Analysis of the solutions on the NanoSight nano-sizer showed that the modal value of the pore colloid particle size is 679 nm in two-mica granite, 566 nm in microgranite, 571 nm in dolerite, and 580 nm in bostonite. A part of the solution was evaporated in a pre-weighed Petri dish in order to determine the proportion of the submicron fraction in the sample. Another part of the solution was analyzed by ICP-MS.

Compliance with the chosen experimental conditions ensures a high reproducibility of the analysis results and the possibility of determining a wide range of chemical elements (up to 75 elements). Analysis of aqueous solutions allows maximizing the potential of the ICP-MS method. The absence of injected acids or other solvents prevents the possibility of uncontrolled isobaric overlays. This fact leads to elements detection limits decrease by 2-3 orders of magnitude in submicron fraction analysis, compared to the bulk analysis, especially in case of the rare elements.

Results and discussion The intrusive rocks contain a wide range of trace elements (Table 2). The highest uranium contents are characteristic of microgranite and dolerite. Two-mica granites are enriched with thorium. Chalcophile elements accumulate in various intrusive rocks in different ways: two-mica granite contains minimal amounts; microgranite accumulates Zn, Pb, Cu, REE, and Y; dolerite and bostonite are enriched in Ni, Zn, REE, and Y.

Experiments on the submicron fraction extraction have shown that its content in intrusive rocks varies from 1.31 to 1.78 wt% (Table 3). The highest value is characteristic of two-mica granite, which has the most coarse-grained structure.

Table 2

Trace elements composition of the intrusive rocks of the El Sela region, ppm

Rock	U	Th	REE	Y	Ni	Cu	Zn	Pb	Rb	Sr	Ba
Two-mica granite	11.3	25.3	43.5	5.58	86.0	13.2	29.0	13.1	212	89.0	329
Microgranite	224	3.93	202	21.7	55.4	22.6	209	19.3	129.6	126	157
Dolerite	31.1	13.1	530	64.8	285	23.4	175	4.87	54.3	567	355
Bostonite	4.22	17.4	379	45.3	179	17.5	106	4.38	89.9	52.1	345

Table 3

The submicron fraction share in the Intrusive rocks and trace elements content in the submicron fraction

Rock	SMF share, wt %	Trace elements content, ppm										
		U	Th	REE	Y	Ni	Cu	Zn	Pb	Rb	Sr	Ba
Two-mica granite	1.78	1.80	1.10	16.3	1.40	256	45.0	164	0.50	113	77.0	304
Micrograníte	1.42	68.0	0.82	11.1	2.50	187	39.0	201	0.61	305	305	398
Dolerite	1.31	1.30	1.30	17.3	2.60	206	29.0	223	0.30	102	103	402
Bostonite	1.60	5.20	1.90	17.3	3.80	113	13.0	112	0.31	110	25.0	205

Table 4

The share of chemical elements in the submicron fraction of intrusive rocks, rel.%

Rock	U	Th	REE	Y	Ni	Cu	Zn	Pb	Rb	Sr	Ba
Two-mica granite	0.30	0.10	0.70	0.40	4.30	6.10	10.1	0.10	0.90	1.50	1.60
Microgranite	0.40	0.30	0.07	0.20	4.80	2.50	1.40	0.10	3.30	3.40	3.60
Dolerite	0.10	0.10	0.04	0.10	0.90	1.60	1.70	0.10	2.50	0.20	1.50
Bostonite	1.50	0.20	0.07	0.10	1.00	1.20	1.70	0.10	2.00	0.80	0.90

The results of the SMF analysis of intrusive rocks are shown in Table 3. High contents of trace elements in the SMF are as follows: uranium is characteristic of microgranite, chalcophile elements, as well as Rb, Sr, and Ba accumulate in all types of intrusive rocks.

To assess the degree of elements accumulation in the submicron fraction, we have calculated accumulation coefficient as the ratio of the content in the SMF to the content in the rock (Fig.2). Geochemical formulas are as follows: two-mica granite ($Zn_{5,7}$ – $Cu_{3,4}$ – $Ni_{2,5}$); microgranite ($Ni_{3,4}$ – $Ba_{2,5}$ – $Sr_{1,9}$ – $Rb_{1,8}$ – $Cu_{1,7}$); dolerite ($Rb_{1,9}$ – $Zn_{1,3}$ – $Cu_{1,3}$); bostonite ($Rb_{1,2}$). The highest values of elements accumulation coefficient are specific to two-mica granite. Zinc, copper, nickel, to a lesser extent barium, rubidium and strontium have shown the highest migration capacity. The uranium concentration in the microgranites submicron fraction is 68 ppm, but the accumulation coefficient

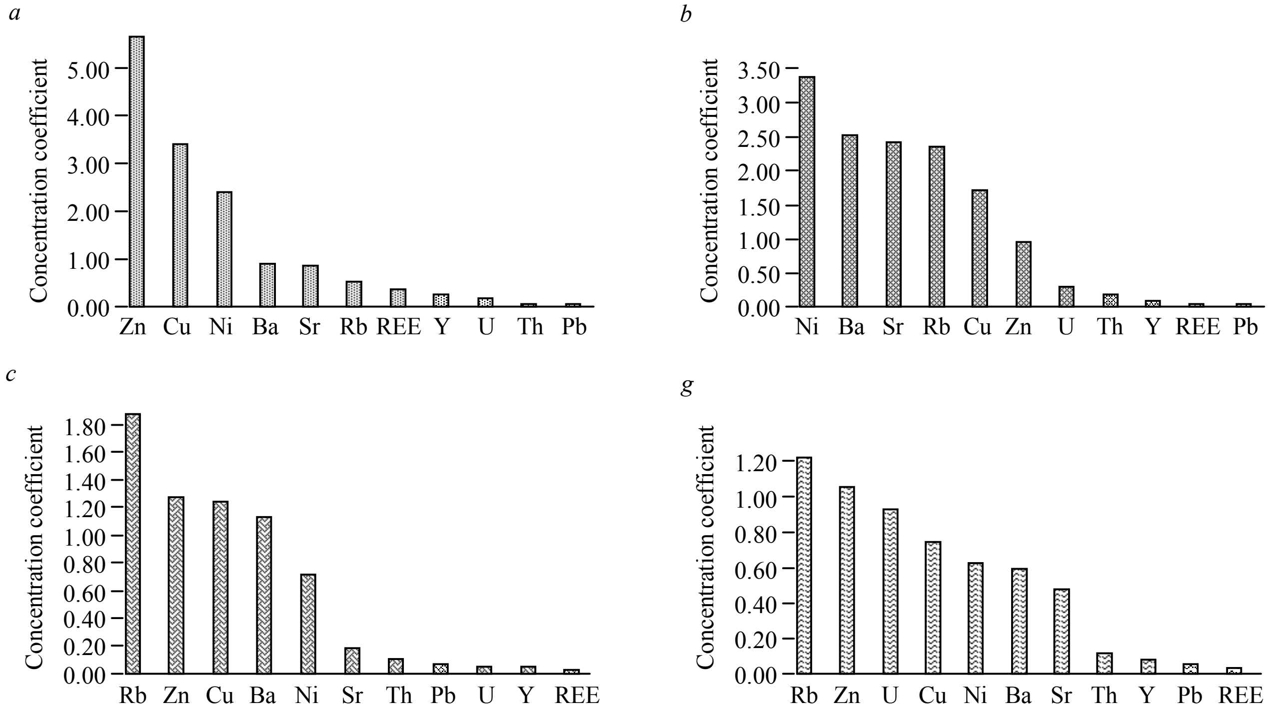

Fig.2. The concentration ratios of chemical elements in the colloid-salt fraction of intrusive rocks of the El Sela region: *a* – two-mica granite; *b* – microgranite; *c* – dolerite; *g* – bostonite

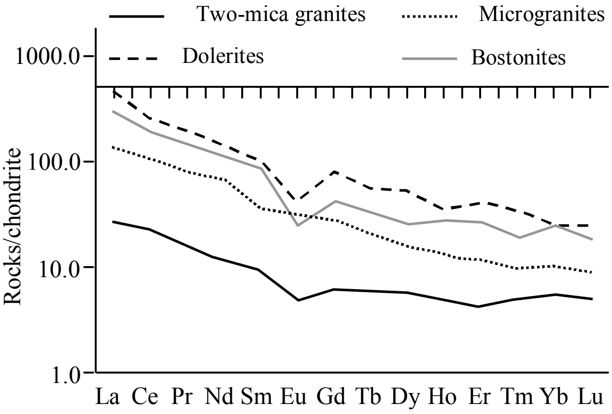

Fig.3. Chondrite-normalized REE content in the intrusive rocks of the El Sela region (normalized by Boynton, 1984).

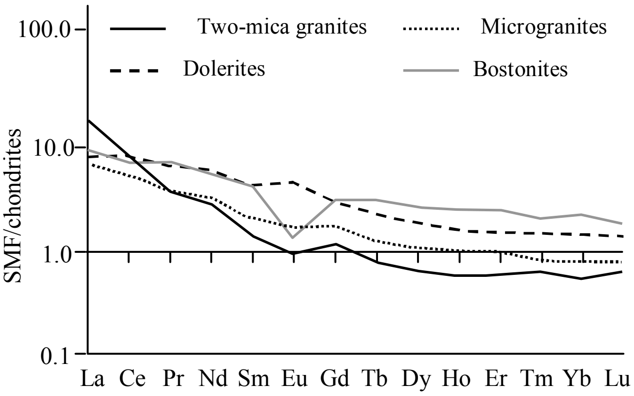

Fig.4. Chondrite-normalized REE content in the submicron fraction of intrusive rocks of the El Sela region (normalized by Boynton, 1984).

of this element is less than one. Apparently, this can be explained by the presence of secondary uranium minerals in the intrusive rocks, which do not convert into solution during the SMF extraction. Rare-earth elements, yttrium, thorium, and lead hardly convert into submicron fraction solution.

The REE content in various intrusive rocks is presented in Table 2. The highest values are characteristic of the dike complex (dolerite – 530 ppm, bostonite – 379 ppm, microgranite – 203 ppm). The REE content in two-mica granite is low 43.5 ppm.

The REE spectra are shown in Figure 3. In all cases, the content of light rare earth elements (LREE) is higher than that of heavy ones (HREE). Unaltered and slightly altered intrusive rocks have a Eu-minimum. The microgranite spectrum is characterized by the absence of Eu-minimum due to the rock secondary alterations.

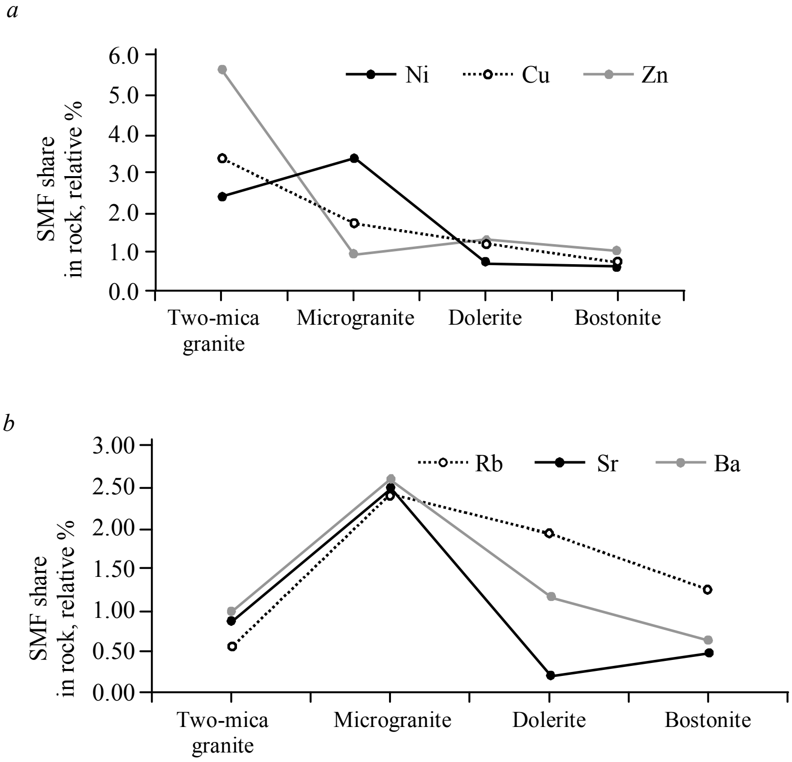

Fig.5. The share of chemical elements in the submicron fraction of the total content in the rock (according to table 4).

The ΣREE and yttrium contents in the rocks submicron fraction are presented in Table 3. The values are low, which indicates the weak mobility of these elements.

Figure 4 shows the REE spectrum in a submicron fraction of intrusive rocks. It is possible to trace the similarity and differences in the REE spectra of SMF and intrusive rocks (Fig.3 and 4). The REE spectra of microgranite and bostonite have not changed much. The europium anomaly disappeared from dolerite and two-mica granite spectra.

We have calculated the relative fraction of chemical elements contained in the submicron fraction, taking into account the weight fraction for each rock type (Table 4). hese tables show the relative fraction of elements that are in a mobile state in the rock. The highest values are characteristic of Zn, Cu, and Ni. These values are greater than one in all types of intrusive rocks (Fig.5, *a*). The mobility of rubidium, strontium, and barium is highest in microgranite, which is most susceptible to secondary alterations (Fig. 5,*b*). Uranium is accumulated in the SMF of bostonite. The least mobile elements are U, Th, Pb, REE, and Y.

Conclusions

We estimated the content of chemical elements in reference samples of intrusive rocks and also in their water-soluble (colloid-salt) fraction. This fraction is water-extracted from the rock under certain conditions. The rock sample and its colloid-salt fraction were analyzed by ICP-MS.

The chemical characteristic of the extracted fraction reflects the mobile migrating part of the chemical elements in the composition of the rocks Comparison of the obtained data allows us to estimate the share of migrating and weakly migrating elements.

1. Intrusive rocks of El Sela area (two-mica granites, microgranites, dolerites, and bostonites) are characterized by U and REE high contents. In addition, two-mica granites are enriched in Th; microgranites accumulates Zn, Pb, Cu, REE, and Y; dolerite and bostonite contain Ni, Zn, REE, and Y.

2. The share of submicron (colloid-salt) fraction of intrusive rocks varies from 1.31 to 1.78 wt%. The particle size of the SMF varies from 566 to 679 nm. The largest particle size and a high share of the fraction are characteristic for the most coarse-grained two-mica granite.

3. The trace element contents in the SMF of intrusive rocks have been measured: Uranium is characteristic of microgranite, chalcophile elements (Zn, Ni, Cu) and Rb, Sr, Ba accumulate in all types of intrusive rocks.

The relative fraction of chemical elements contained in the submicron fraction was calculated taking into account the weight fraction for each rock type. The highest values are characteristic for Zn, Cu, Ni. The mobility of rubidium, strontium, and barium is highest in microgranite, which is most susceptible to secondary alterations. Uranium is accumulated in the SMF of bostonite. The least mobile elements are U, Th, Pb, REE, and Y.

4. During the chemical weathering of intrusive rocks, a number of elements (Zn, Cu, Ni) become mobile and can migrate to the surrounding territories. Uranium, thorium, and lead form secondary minerals and do not accumulate in the colloid-salt fraction. The least mobile elements, REE and Y, are accumulated in minerals.

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