Geochemistry of ultramafic-alkaline rocks of the Ziminsky complex (on the example of the Bol’shetagninsky and Beloziminsky massifs) (Eastern Sayan)

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Abstract. The paper compares the elemental composition of alkaline silicate rocks of the Bol’shetagninsky and Beloziminsky massifs, which are part of the Ziminsky complex of ultrabasic rocks and carbonatites. The rocks of the Bol’shetagninsky massif belong to the potassium series and are distinguished by increased concentrations of large ionic lithophilic elements; in the rocks of the Beloziminsky massif, the rocks of the sodium series predominate and the contents of highly charged elements are increased. Judging by the lack of correlation between the highly charged elements in alkaline and subalkaline rocks of the Bol’shetagninsky massif, their formation, in contrast to the rocks of the Beloziminsky massif, is not associated with the process of fractional crystallization.

1. Introduction
Despite their insignificant occurrence among the erupted rocks, the alkaline rocks are actively studied by the researchers. The largest deposits of phosphorus, niobium, tantalum, beryllium, zirconium, strontium, barium and rare-earth elements of great strategic importance, as well as apatite, phlogopite and fluorite are connected with the alkaline–carbonatite complexes. The specific feature of the alkaline–carbonatite complexes is their diverse and complex mineralization. At the same time, the mechanisms of distribution of ore components and formation of deposits of rare-earth elements and niobium are unclear yet. This work presents new data on the content of petrogenic components and trace elements in alkaline silicate rocks of the Bol’shetagninsky massif in comparison with the rocks of the Beloziminsky massif, compares the distribution of chemical elements, including ore components, and considers possible sources of matter for both massifs.

2. Object and methods
The Beloziminskiy and Bol’shetagninskiy massifs belong to the Ziminsky complex of ultramafic rocks and carbonatites, located in the Eastern Sayan at the intersection of the Uriksko-Iysky graben and the Taimyr-Angarsky paleorift. In addition to the mentioned massifs, the complex includes the Sredneziminsky massif and the Yarminskaya vein above-intrusive zone of the hidden massif [1].

Beloziminskiy massif belongs to the complex Nb–REE deposits. A large number of works have been devoted to geology, mineralogy, petrography, and the isotopic composition of the rocks of this
massif, an overview of which is given in [2, 3]. The massif is a central–type multiphase intrusion with an outlet area of about 18 km² and is controlled by the Beloziminsky fault of the northwestern strike. The host rocks are metamorphosed sandstones and schists of the Ingashinskaya formation of the Upper Proterozoic with quartzite layers and diabase dikes. The central part of the massif is composed of calcite, calcite-dolomite and ankerite carbonatites, in which ore mineralization is concentrated. The main niobium concentrator is pyrochlore; rare-earth elements, apart from pyrochlore, are also concentrated in synchysite, bastnaesite, monazite, ankylite, burbankite, apatite and zirconolite. Carbonatites are surrounded by alkaline silicate rocks: melteigites, ijolites, and nepheline syenites.

The Bol’shetagninsky massif is a niobium deposit, characterized by a wide distribution of subalkaline microcline syenites, which intrusion caused intensive metasomatism of earlier alkaline rocks. In contrast to the Beloziminsky massif, pyrochlore mineralization here is associated with metasomatites, but not with carbonatites. The host rocks are represented by sandstones and schists of the Ignashinskaya formation of the Upper Proterozoic and the Urikskaya formation of the Lower Proterozoic. Like the Beloziminskii massif, the Bol’shetagninskiy massif has a circular shape with a zonal-ring structure; carbonatites and subalkaline syenites are most widely spread, but pyroxene-nepheline rocks (ijolites, melteigites, urtites) are evolved locally and mainly represented by ijolites [4]. Moreover, outcrops of picritic porphyrites are observed, which compose a series of dikes.

The sampling of rocks of the Bol’shetagninsky massif was carried out by the authors during an expedition in 2019. The samples of ijolite, melteigite, urtite, aegirine syenite, nepheline and feldspar syenite were studied. The chemical composition of the samples was studied at the Institute of the Earth Crust, SB RAS, Irkutsk by methods of silicate analysis (analyst Samoilenko M.M.), ICP–MS (analyst Panteeva S.V.) at the Collective Use Centre "Ultramicroanalysis" on a quadrupole mass spectrometer Agilent 7500 (Agilent Technologies Inc,) according to the method [5] and by X-ray fluorescence analysis (analyst Khudonogova E.V.). In addition, the analyses given in the work of Kozhevnikov O.K. [6] were used. Data on the composition of the rocks of the Beloziminsky massif (ijolites, melteigites, nepheline syenites) were taken from the work of E.V. Khromova [2].

3. Results and discussion

Ijolites of the Beloziminskii massif are composed of nepheline and clinopyroxene; garnet, magnetite, mica, calcite, perovskite and apatite are present in smaller amounts [2]. The mineral composition of the ijolites of the Bol'shetagninsky massif is characterized by diopside, aegirine–diopside, and nepheline; melanite and apatite, single grains of biotite are also present. The rocks are often potassium-feldsparitized, carbonatized, and biotitized. The aegpaitic coefficient (Cagg) is 0.58, the sum of Na₂O and K₂O alkalis is 5.9 at a highly variable and generally low Na₂O/K₂O ratio (0.03-0.83) due to superimposed microclorization. For the ijolites of the Beloziminsky massif Cagg and sum of alkalis are higher (0.75 and 7.53, respectively), as well as the Na₂O/K₂O ratio (0.26-2.24), and the SiO₂ content in the ijolites of both massifs practically does not differ (38.04 and 38.83 wt %). The ijolites of the Beloziminsky massif have higher contents of TiO₂ (2.32), FeO (10.01), MgO (7.02), Na₂O (3.48) (wt %), V (405), Co (40), Cu (91), Zr (592), Cs (2.07), Tb (3.5), Hf (9. 73), U (1.7) (ppm), and the rocks of the Bol'shetagninsky massif differ by increased contents of CaO (14.75), K₂O (6.71)(wt %), Zn (162), Rb (78), Sr (1819), Nb (126), Ba (424), total REE (239), Pb (3.71) (ppm).

Melteigites of the Beloziminsky massif are composed of clinopyroxene, nepheline, perovskite, and magnetite; phlogopite, amphibole, apatite, titanite, garnet, and ilmenite are also present [2]. Melteigites of the Bol'shetagninsky massif are represented by single sample. The sample is composed of aegirine diopside, calcite, and, in small amounts, nepheline replaced by muscovite, hylalophane, and celsian. Compared to the melteigite sample of the Bol'shetagninsky massif, the melteigites of the Beloziminsky massif differ by the increased V (366), Cu (103), Ge (1.5), Zr (562), Nb (457), total REE (632), Hf (13), Ta (24) and Th (10) (ppm) concentrations, whereas the melteigite sample of the Bol'shetagninsky massif shows a high content of Ba (20806 ppm).

The nepheline syenites of the Beloziminsky massif are composed of potassium feldspar, nepheline, and clinopyroxene; alkaline amphibole, phlogopite, calcite, and apatite are also present. Nepheline
syenites of the Bol’shetagninsky massif are composed of nepheline, potassium feldspar, often replacing nepheline, pyroxene diopside and titanium augite; biotite, calcite, apatite, ore minerals and garnet are also present. In nepheline syenites of the Beloziminsky massif, the sum of Na₂O+K₂O alkalis is 15.14 at Cagp 1.13, Na₂O/K₂O 0.96, FeO_total 4.63. In nepheline syenites of the Bol’shetagninsky massif the sum of alkalis and Cagp are two times lower (7.4 wt % and 0.6, respectively). The Na₂O/K₂O ratio is low (0.02–0.17), which is caused by superimposed microclinization. The nepheline syenites of the Beloziminsky massif have higher SiO₂ (51.44), Al₂O₃ (18.08), Na₂O (7.31) (wt %), Ta (9.6), Th (6.3), U (12.5) (ppm), and the nepheline syenites of Bol’shetagninsky have increased concentrations of TiO₂ (1.77), Fe₂O₃ (8.53), CaO (11.76) (wt %), V (347), Cr (23), Co (13), Ni (7), Cu (18), Zn (256), Sr (1297), Ba (3513), REE (418), Y (45), Pb (45) (ppm).

The urtite sample of the Bol’shetagninsky massif is composed mainly of cancrinitized nepheline; biotite, garnet, and apatite are also present. At the lowest silica SiO₂ content (32.8) as compared with other silicate rocks of this massif, urtite is distinguished by the highest Na₂O/K₂O ratio (4.1) and the highest contents of TiO₂ (2.4), Al₂O₃ (15.7), MgO (3.4), Na₂O (7.5) (wt %), F (0.6) and Ta (6.1) (ppm).

Potassium-feldspar syenites (microclinites) of the Bol’shetagninsky massif are almost entirely composed of potassium feldspar with minor admixture of apatite, biotite, hematite and ore minerals (rutile, pyrite, sphalerite). The SiO₂ content is 47.3 wt % with the sum of alkalis 10.7; Na₂O/K₂O ratio varies from 0.52 in albitized syenites to 0.01, CaO content varies in a wide range from 0.7 to 10.6. The apatite ratio is 0.96, with a higher silica ratio (in contrast to nepheline syenites). In comparison with other silicate rocks of this massif, the potassium–feldspar syenites are characterized by the highest contents of K₂O (8.8 wt %), Cu (25), Rb (215), Nb (392), Cs (1.9) and U (3.4) (ppm).

As for rare and rare-earth elements, the highest total REE contents are observed for melteigites of the Beloziminsky massif (632) and nepheline syenites of the Bol’shetagninsky massif (418) (ppm), while in nepheline syenites of the Beloziminsky massif the REE content is 4 times lower (101). The REE spectra for all studied samples have a negative inclination, indicating the depletion of heavy REE (Figure 1). In all investigated varieties of silicate alkaline rocks, light lantanides prevail over the heavy ones (La₉/Yb₉ from 5.14 for the ijolites of the Beloziminsky massif to 286 for egirine syenite of the Bol’shetagninsky massif with Gd/Yb from 1.47 for the ijolites of the Beloziminskaya massif to 5.73 for melteigites of the same massif). La₉/Sm₉ for the rocks of the Beloziminsky massif varies from 2.04 in the ijolites to 4.84 in nepheline syenites; in the varieties of silicate rocks of the Bol’shetagninsky massif, from 5.01 in the ijolites to 10.24 in nepheline syenites and 16.79 in feldspath syenites. Minor europium anomaly is noted only for the spectra of potassic syenites of the Bol'shetagninsky massif, which may indicate that during the formation of rocks plagioclase remains in the source as a result of fractional crystallization or partial melting.

The graphs of rare element contents normalized to the primitive mantle show negative anomalies of Th, Ce, Pr, Nd, Sm for most rocks of Bol’shetagninsky massif, and Ta anomalies for aegirine syenite; and positive anomalies of Nb, P, Pb and Zr for most rocks, and Ba for nepheline syenites and melteigite sample, U for aegirine syenite and Ti for feldspar syenite (figure 1). Negative anomalies of Pb and Ti and significant variations of Ba, Nb, Ta, Zr, and Hf are observed for the silicate rocks of the Beloziminsky massif.
4. Conclusion
The obtained data show that the silicate rocks of both massifs have some differences in their chemical composition despite their general similarity. Among the aluminosilicate rocks of the Bol'shetagninsky massif, the rocks of the potassic series (Na₂O/K₂O<1) prevail, but among them there are rocks of the natrium series (urtite); and the rocks of the natrium series (Na₂O/K₂O≥1) prevail in the Beloziminsky massif. The ijolites of the Beloziminsky massif are more ferruginous and titanic and contain more transitional elements (V, Cr, Co, Cu), and the same rocks of the Bol'shetagninsky massif contain more Ca and large–ionic lithophile elements (Rb, Sr, Ba, Pb). In melteigites of the Beloziminsky massif, the content of highly charged elements (Th, Hf, Nb, Ta, REE) is increased, and, the content of Ba is increased in melteigite of the Bol'shetagninsky massif. In nepheline syenites of the Beloziminsky massif the content of highly charged elements (Ta, Th, U) is increased, and in nepheline syenites of the Bol'shetagninsky massif the content of large-ion (Ba, Sr, Pb) and transit (V, Cr, Co, Ni, Cu, Zn, Fe, Ti) elements is increased. In Bol'shetagninsky massif at the general similarity of spectra of rare elements distribution in alkaline and subalkaline rocks (minimum by Th, maximum by Nb, Pb, P, Sr,
Zr), subalkaline feldspathic syenites in comparison with feldspathoidal rocks are characterized by general depletion of rare-earth elements and especially heavy lanthanides, more fractionated distribution of light REE (LaN/SmN = 14–28 in feldspar syenites and mainly 3–8 in ijolites, urtite and nepheline syenites), the presence of negative Eu-anomaly (Eu/Eu* = 0.33–0.75). In addition, compared with ijolite–urtite and nepheline syenites in them is generally lower content of Ti, Zr, Y, Sr, P, Pb, but higher Nb, U. For the Beloziminsky massif the formation of silicate rocks is associated with the process of fractional crystallization, and the evolution of these rocks is expressed in a change in the chemical composition of the main rock-forming minerals [2]. For the Bol’shetagninsky massif, the absence of correlation between highly charged elements in alkaline and subalkaline rocks [8] does not allow us to associate the formation of these rocks with fractional crystallization of the alkaline potassium–sodium melt. At the same time, the geochemical features of subalkaline syenites indicate the probable presence of titanium garnet in the source or its fractionation.

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References
[1] Frolov A A and Belov S V 1999 Geol. Ore Depos. 41 109–30
[2] Khromova E A 2020 Age and petrogenesis of rocks of the alkaline-ultrabasic carbonatite Beloziminsky massif (Eastern Sayan) Dissertation for the degree of candidate of geology and mineralogy sciences, speciality 25.00.04 (Ulan-Ude: BSC SB RAN) p 164
[3] Khromova E A, Doroshkevich A G and Izbrodin I A 2020 Geosph. Stud. 1 33–55
[4] Frolov A A and Bagdasarov Yu A 1967 Sov. Geol. 12 80–93
[5] Panteeva S V, Gladkochoub D P, Donskaya T V, Markova V V and Sandimirova G P 2003 Spectrochimica Acta B 58 341–50
[6] Kozhevnikov O K, Kukhrinkova N V and Tugolukova G A 1974 Bolshe-Tagninsky Massif of Ultramafic Alkaline Rocks and Carbonatites Endogenous Minerals of the Sayan-Baikal Mountain region ed K A Savinsky (Irkutsk: East Siberian Book Publ.) pp 134–63
[7] Sun S, McDonough W F 1989 Geol. Soc. Special Publ. 42 313–45
[8] Bazarova E P, Savelyeva V B and Danilova Yu V 2021 Geochemistry of Ultramafic-alkaline Rocks and Carbonatites of the Bol’shetagninsky Massif (Eastern Sayan) Proc. of the Fersman Scientific Session of the Geological Institute KSC RAS 18 31–6