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## Rare elements in minerals of pegmatites of the Kolmozero deposit (Kola Peninsula)

To cite this article: L N Morozova *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **302** 012048

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## Rare elements in minerals of pegmatites of the Kolmozero deposit (Kola Peninsula)

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**Abstract.** The content of rare elements in the mineral composition can vary over a wide range. Therefore, the distribution regularities of impurity elements in crystalline phases are used to solve various petrological problems. Rare elements in minerals are indicators of PT-conditions for mineral formation or late superimposed processes. Rare elements that do not form their own phases, but are completely dispersed as an isomorphic impurity in the grids of rock-forming minerals, serve as reliable indicators of the development of mineral formation processes. For the pegmatite process, such microelements are: Rb, Cs, Ba, Sr, Pb and Tl. The main rock-forming pegmatite minerals are represented by quartz, plagioclase, microcline, spodumene and muscovite. The content of rare elements: Li, Be, Ta, Nb, Cs, Rb, Mn, Ti, Hf, Sr, Ba, Tl, Pb, Th, U, Y, Zr, Zn, Sc, V, Cr, Co, Ni, Cu, Ga, Ge, As, Cd, Sn, Bi, W in spodumene, plagioclase, microcline and muscovite from rare metal pegmatites of the Kolmozero lithium deposit was determined by mass spectroscopy method with inductively coupled plasma (ICP-MS). A distinctive feature of the composition of spodumene is the high content of Li, Mn, Rb, Ti, Bi and Sn. In plagioclase high concentrations are noted for Li, Mn, Ti, Rb and Cr. According to the set of rare elements, microcline and plagioclase are comparable with each other. However, rare elements – V, Cr, Hf, defined in the plagioclase, are absent in the microcline. In comparison with plagioclase and microcline, muscovite is characterized by higher contents of Li, Ta, Mn, Ti, Be, Zn, Ga, Sn, Ba and Tl. The presence of a large number of rare elements in the composition of spodumene, plagioclase, microcline and muscovite may be due to isomorphism processes and the presence of mineral inclusions. High contents of Li, Be, Nb, Ta, Cs, Ti, Mn, Zn, Rb in the studied minerals indicate the enrichment of the pegmatite melt with these elements in the process of pegmatite formation.

### 1. Introduction

Granite pegmatites are an important source of rare elements (Li, Cs, Nb, Ta, Be and Sn), muscovite, gems, ceramic raw material, etc. [1, 2, 3, 4]. Therefore, pegmatites attract the attention of researchers in the field of metallogeny, geochemistry and mineralogy [5, 6, 7]. However, despite the huge amount of researches on granitic pegmatites, many scientific questions remain unresolved up till now. This relates primarily to the problem of pegmatites genesis, their classification, and mineral formation processes. The material on the geochemistry of rare elements in pegmatite minerals is quite extensive [8, 9, 10, 11]. At the same time, the distribution of trace elements in the rock-forming pegmatite minerals of the Kolmozero lithium deposit has not been studied enough.



This project is aimed at studying the rare elements distribution in spodumene, plagioclase, microcline and muscovite from rare-metal pegmatites of the Kolmozero deposit. The results of research in the content of trace elements in minerals have been obtained on the basis of modern research methods.

## 2. Research methods

The sample (K1-GH-11) from the central part of vein No. 1-2 of rare-metal pegmatites from the Kolmozero lithium deposit was taken for researches. The following monofractions of minerals were extracted from this sample: spodumene, microcline, plagioclase and muscovite. The purification of mineral samples from solid-phase mineral inclusions was not performed. The content of rare elements in the minerals was determined using inductively coupled plasma mass spectroscopy (ICP-MS) in the ICAP Qc mass spectrometer (Thermo Fisher Scientific, Germany). The studies were performed at Kazan Federal University.

The research procedure includes the following stages. A sample (100 mg) is weighed in a teflon autoclave on an analytical balance with an accuracy of 0.1 mg. Concentrated hydrochloric acid (2 ml, 38% HCl, OFS), 1 ml of hydrofluoric acid (38% HF) and 1 ml of concentrated nitric acid (68% of HNO<sub>3</sub>) are added to the autoclave with dispensers. The acids undergo additional purification. To account for the background, a mixture of the acids without the sample is prepared. The hermetically closed Teflon autoclaves are placed in the Mars 6 microwave oven (CEM Corporation, USA), in which the samples are heated to 210° C for 30 minutes and kept at this temperature for 30 minutes. After that, 10 ml of the 4.5% solution of boric acid is added to form complexes and transfer fluoride rare-earth elements that are insoluble in water to the solution. The autoclaves are heated to 170°C for 30 minutes and kept at this temperature for 30 minutes. After the autoclaves cooling, the obtained solution is quantitatively transferred into a test tube and brought to 50 ml with deionised water. An aliquot of 500 µl of the prepared solution is taken and diluted with the deionised water to 10 ml with the addition of an internal standard In with the final concentration of 5 ppb and the addition of hydrochloric acid. The final content of all acids in the solution is equal to 2%. The resulting solution is analyzed in the mass spectrometer, pre-calibrated using multi-element standards with the concentration of each element in the range from 1 to 100 ppb. The obtained concentration values are recalculated to the initial concentration, with regard for the empty sample, weighed sample and dilution of the solution.

The studies of the rock petrographic composition were carried out with the Axioplan-2 optical microscope.

## 3. Main part

The content of rare elements (minor elements, elements-impurities) in the mineral composition can vary over a wide range. Therefore, the distribution regularities of impurity elements in crystalline phases are used to solve various petrological problems. Rare elements in minerals are indicators of PT-conditions for mineral formation or late superimposed processes. Rare elements that do not form their own phases, but are completely dispersed as an isomorphic impurity in the grids of rock-forming minerals, serve as reliable indicators of the development of mineral formation processes. For the pegmatite process, such microelements are: Rb, Cs, Ba, Sr, Pb and Tl. The presence of extreme rare element contents in minerals indicates the physical-chemical conditions of the system development. These contents are noteworthy.

The rare-metal (albite-spodumene) pegmatites of the Kolmozero deposit are leucocratic rocks with a heterogeneous structure, regularly changing from fine-grained in the marginal zone to pegmatoid and block structure in the central part. The main rock-forming pegmatite minerals are represented by quartz (30–35 %), plagioclase (30–35 %), microcline (10–25 %), spodumene (~ 20 %) and muscovite (5–7 %). Ore minerals are spodumene, columbite, tantalite and beryl. The most common are auxiliary and accessory minerals - apatite, spessartine, sphalerite and others. Secondary minerals are phosphates and zeolites [12, 13].

A characteristic feature of lithium-type pegmatites is the presence of several generations of the same mineral, which crystallization occurs at different stages of the pegmatite process. Several generations of rock-forming minerals have also been found in the pegmatites of the Kolmozero lithium deposit [12, 14]. According to petrographic studies, a large prismatic spodumene, large table albite, block microcline and large-tabular muscovite are observed in the KI-GH-11 sample.

In the central part of the pegmatite veins, spodumene is mainly represented by well-formed crystals of flattened prismatic habit with varying degrees of elongation – from short- to elongate- prismatic or their clusters. The sizes of individuals can reach 1.5 m in length. The mineral is greyish-green to green, opaque, rarely translucent. Among the solid-phase mineral inclusions in spodumene, the most common albite, quartz and muscovite, minerals of the columbite group, apatite, garnet and cassiterite have been diagnosed. Quartz inclusions usually are rounded, drop-shaped or irregular shaped and are found in the form of isolated crystals or their clusters, mainly along cleavage fractures in the central parts of spodumene individuals. Albite inclusions of isometric form are concentrated along cleavage cracks, as well as in the marginal parts of spodumene. Lamellar muscovite together with quartz is confined to the central regions, but scurvy muscovite with fine-grained albite occurs in the marginal parts of spodumene crystals. Here in the marginal areas of spodumene, there are also inclusions of fluorapatite and spessartine. Based on morphology of the inclusions and their location in the host spodumene, one can assume the proto- and syngenetic nature of most mineral inclusions. The inclusions of quartz, muscovite and albite healing the fissures in spodumene crystals, can be considered as epigenetic [14].

Lithium is the main element of spodumene. It is included in the spodumene crystal lattice. The lithium content in the studied spodumene was investigated by two methods: chemical analysis [14] and ICP-MS. The lithium content in spodumene, determined by the ICP-MS method, amounted to 36068.53 ppm (Figure 1), which in terms of  $\text{Li}_2\text{O}$  is 7.77 wt. %

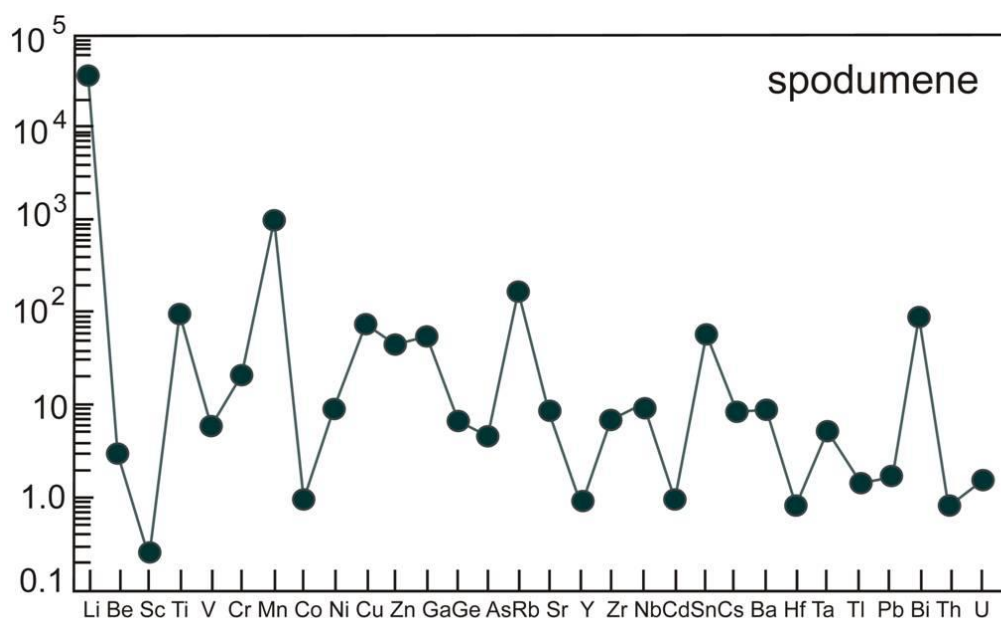


Figure 1. Rare elements distribution in spodumene of rare-metal pegmatites from the Kolmozero lithium deposit

The content of  $\text{Li}_2\text{O}$ , determined by the chemical analysis in the same spodumene, varies from 7.11 to 8.08 wt. %. Thus, comparable lithium contents in the studied spodumene were obtained by various methods. The calculations showed that spodumene takes 96% of the lithium total content in the studied minerals, plagioclase – 0.85%, potassium feldspar – 0.26% and muscovite – 1.88%.

The analysis of rare elements distribution showed that in spodumene, the following elements are noted as impurity elements: Be, Ta, Nb, Cs, Rb, Mn, Ti, Hf, Sr, Ba, Tl, Pb, Th, U, Y, Zr, Zn, Sc, V, Cr, Co, Ni, Cu, Ga, Ge, As, Cd, Sn and Bi. The distinctive feature of the spodumene composition is a high content of Mn (993.20 ppm), Rb (1673.58 ppm), Ti (95.20 ppm), Bi (85.76 ppm) and Sn (55.18 ppm). The content of Sc, Co, Y and Th is less than 1 ppm. The presence of numerous impurity elements in the spodumene composition, in most cases, is due to numerous mineral inclusions (see above).

Plagioclase in the central part of the veins of rare-metal pegmatites of the Kolmozero deposit is represented by albite of large-tabular habit up to 2–3 cm in length. Microscopic studies have established a fine polysynthetic twinning of mineral individuals. Solid-phase inclusions in plagioclase are apatite, muscovite, zircon, and quartz.

In plagioclase, the content of rare elements varies from 318 (Li) to 0.19 ppm (Cd) (Figure 2). High contents are noted for Li (317.78 ppm), Mn (130.60 ppm), Ti (48.08 ppm), Rb (41.15 ppm) and Cr (26.03 ppm). The contents of V, Ni, Cu, Zn, Ga, Ge, Sr, Zr, Nb, Sn, Cs, Ba, Hf, Bi, Pb and U are lower. Less than 1 ppm is the content of Be, Co, Y, Cd, Tl and Th. Rare elements – Sc, As, and Ta identified in spodumene are absent in albite.

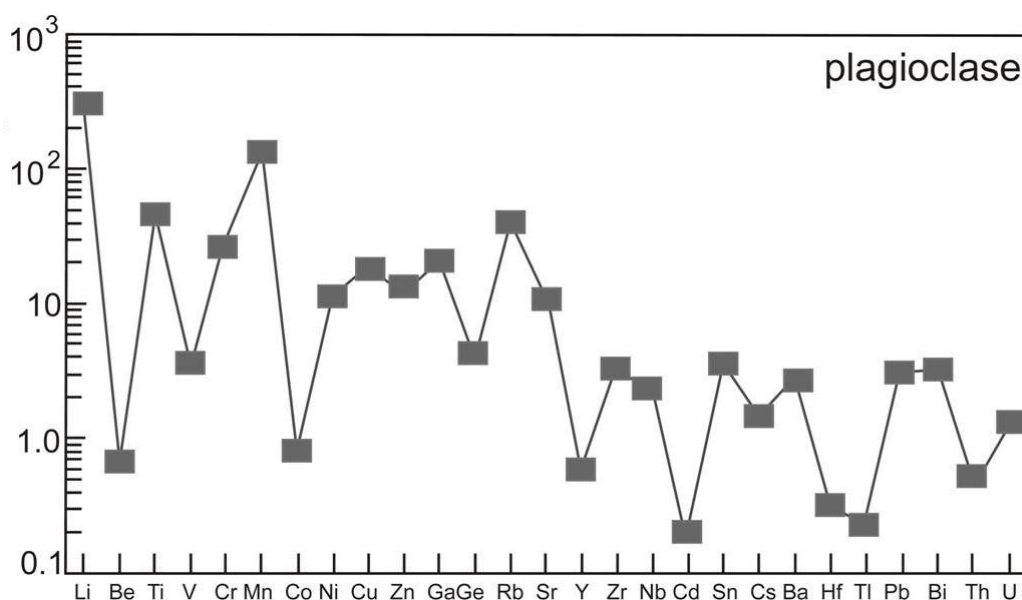


Figure 2. Rare elements distribution in albite of rare-metal pegmatites from the Kolmozero lithium deposit

Pink-red potassium feldspar of rare-metal pegmatites from the Kolmozero deposit in the central parts of the veins is represented by a block microcline. The sizes of individuals reach 40–60 cm in diameter. Microcline contains an insignificant amount of micropertite ingrowths of plagioclase. The research results showed that the composition of microcline is characterized by great variability in the content of rare elements (Figure 3). This is due to the isomorphic replacement of potassium in the microcline structure by such minor elements as Rb, Cs, Ba, Sr, Tl and Pb [15]. In the pegmatite process, these impurity elements play an important part. Variations in the content of individual rare elements may be partly due to the presence of solid-phase mineral inclusions in microcline.

The content of impurity elements – Rb, Cs, Li, Mn, Tl and Pb in the composition of the microcline is higher than the content of Ti, Ba, Sr, Ga, Zr, Nb and Ge. The rubidium content is 5638.69 ppm. The caesium content (154.61 ppm) is 36.5 times less than that of rubidium. The contents of Li (98.85 ppm) and Mn (80.99 ppm) are comparable with each other and the content of Tl (42.19 ppm), Pb (29.17 ppm), Ti (20.31 ppm), Ga (13.64 ppm), Ba (10.57 ppm) and Sr (16.28 ppm) is lower. The content of

Sc, Cr, Co, Ni, Y, Cd, Bi, Th and U is less than 1 ppm. According to the set of rare elements, microcline and plagioclase are comparable with each other. However, the rare elements V, Cr and Hf defined in plagioclase are absent in microcline. In microcline, as in spodumene, Sc is present in insignificant amounts (0.24 ppm).

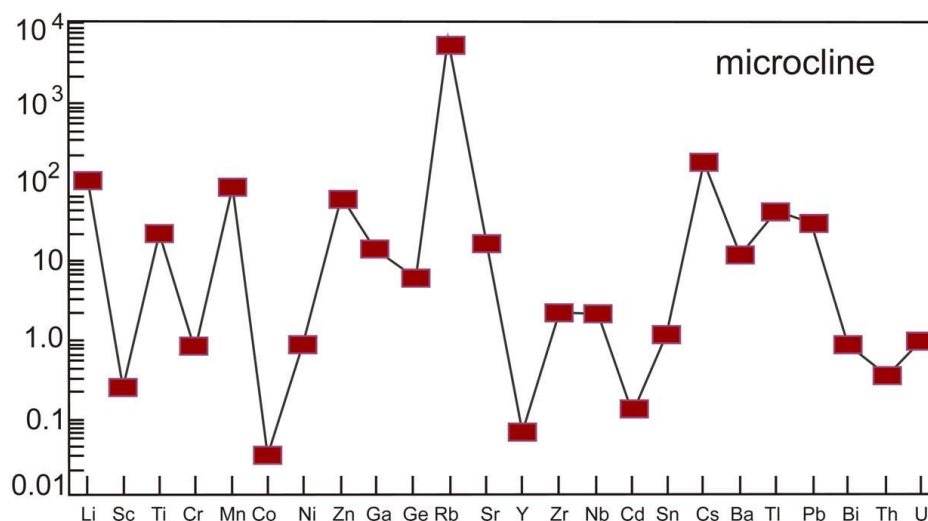


Figure 3. Rare elements distribution in microcline of rare-metal pegmatites from the Kolmozero lithium deposit

Colourless muscovite with a greenish tinge, from the central parts of the veins of rare-metal pegmatites from the Kolmozero deposit is represented by tabular crystals up to 1.5 cm in length. Muscovite is evenly distributed in the rock or forms clusters. Muscovite clusters can reach 15 cm in diameter. The composition of muscovite is characterized by significant variations in the content of rare elements (Figure 4).

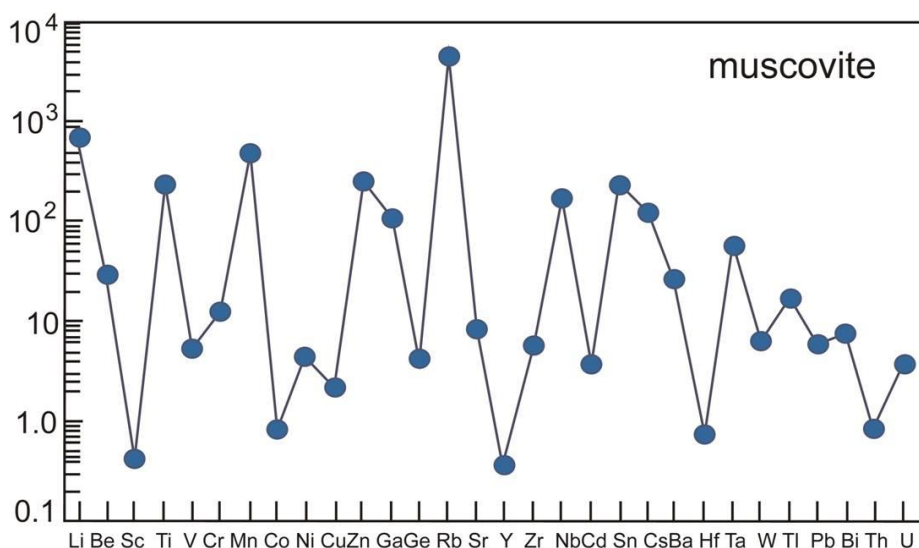


Figure 4. Rare elements distribution in muscovite of rare-metal pegmatites from the Kolmozero lithium deposit

In comparison with plagioclase and microcline, muscovite is characterized by higher contents of Li (705.14 ppm), Ta (58.09 ppm), Mn (493.78 ppm), Ti (230.16 ppm), Be (29.19 ppm), Zn (244.56 ppm), Ga (115.05 ppm), Sn (231.36 ppm), Ba (28.13 ppm) and Tl (16.55 ppm).

#### 4. Conclusion

The content of rare elements: Li, Be, Ta, Nb, Cs, Rb, Mn, Ti, Hf, Sr, Ba, Tl, Pb, Th, U, Y, Zr, Zn, Sc, V, Cr, Co, Ni, Cu, Ga, Ge, As, Cd, Sn, Bi and W was determined in spodumene, plagioclase, microcline and muscovite from rare metal pegmatites of the Kolmozero lithium deposit by the mass spectroscopy method with inductively coupled plasma (ICP-MS).

The presence of a large number of rare elements in the composition of spodumene, plagioclase, microcline and muscovite may be due to isomorphism processes and the presence of mineral inclusions.

High contents of Li, Be, Nb, Ta, Cs, Ti, Mn, Zn and Rb in the studied minerals indicate the enrichment of the pegmatite melt with these elements in the process of pegmatite formation.

#### Acknowledgements

The current research has been conducted in the framework of the State order on the topic of scientific research 0226-2019-0053 of Geological Institute of the Kola Science Centre of the Russian Academy of Sciences

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