

Phosphate mineralization in leucogranites of the Peshcherninsky stock (Reftinsky massif, Middle Urals)

Dmitriy Dmitrievich Korovin*

The Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of RAS, Ekaterinburg, Russia

Abstract

Relevance. Phosphate mineralization of Devonian intrusions in the Eastern zone of the Middle Urals is currently poorly understood, the data obtained may be important for interpreting the origin of rocks, especially in the case when standard methods of geochemical analysis of rocks do not give a clear picture. Xenotime and monazite are minerals concentrating rare earth elements, and REE distribution graphs are a very important characteristic of rocks.

Objective – study of the chemical composition of phosphates in leucogranites of the Peshcherninsky stock.

Research methodology. Determination of the chemical composition of the samples was carried out on a Cameca SX100 electron probe microanalyzer at the Common Use Center Geoanalyst, analyst V. A. Bulatov. The analysis was carried out at an accelerating voltage of 15 kV using crystal analyzers TAP, LPC0, LPET, PET, LLIF, LIF. The electron probe current was 10 nA (apatite) and 60 nA (REE, Th phosphates). The pulse accumulation time at the peak maximum was 10 s (for most elements) and 20 s (for REE, Th, U, Pb). During the analysis, on a Cameca SX100 electron probe microanalyzer, the following were used as standards: apatite (for analysis of the content of P, Ca), chlorapatite (Cl), fluorine-phlogopite (F), diopside (Mg, Si), albite (Na, Al), orthoclase (K), rhodonite (Mn), SrSO₄ (Sr), TiO₂ (Ti), Fe₂O₃ (Fe), SrSO₄ (Sr), BaSO₄ (S), Cr₂O₃ (Cr), pyromorphite (Pb) and aluminosilicate glasses doped with REE (La, Ce, Y, Sm, Pr, Nd, Th, U, Tm, Eu, Tb, Dy, Gd, Er, Yb, Lu, Ho). Due to the use of a low probe current in the analysis of apatites, the detection limits for elements were: 300–600 ppm for S, Cl, Al, Mg, Si, Ca, Na and 2000–2500 ppm for P, F, Fe, Mn, Cr. For REE phosphates, the following detection limits were achieved using an increased probe current: 100–200 ppm for Si, Ca, Cr, K, Al, Mg, Ti, Pb, 300–500 ppm for Na, S, P, Mn, Y, Th, U, 1200–1500 ppm for Sr, Nd, Ce, 1700–2000 ppm for La, Tm, Tb, 2500–2800 ppm for Yb, Dy, Lu, Pr, 3500–4700 ppm for Eu, Sm, Gd, Ho.

Results. For the first time in Russia, cheralite was found and described in a plutonic rock. The article presents the first data on the chemical composition of phosphates (apatite, monazite, xenotime, cheralite) from the leucogranites of the Peshcherninsky stock, which formed at the final stage of the formation of the polychronous and polyformational Reftinsky gabbro-granitoid massif.

Conclusion. Apatite belongs to the fluorine variety with an admixture of manganese, monazite is represented by the cerium variety, and xenotime is represented by yttrium. Cheralite has a transitional trace element composition, and depending on the zone, it can be attributed to both cerium and yttrium varieties. The admixture of manganese in apatite may indicate partial mixing of the melt with sedimentary or metasedimentary rocks.

Keywords: fluorapatite, monazite-(Ce), xenotime-(Y), cheralite, leucogranite, Reftinsky massif, Middle Urals.

Introduction

Phosphates are quite common in rocks, a striking example of this is apatite, the chemical composition of which can vary greatly depending on the conditions of formation of the rock. In particular, xenotime and monazite are minerals concentrating rare earth elements. In the chemical analysis of rocks, distribution diagrams of rare earth elements are often used to characterize rocks [1]. Therefore, the study of accessory mineralization can provide additional useful information about the genesis of rocks (in combination with other features).

The article presents the first data on the chemical composition of phosphates (apatite, monazite, xenotime, cheralite) from the leucogranites of the Peshcherninsky stock, which formed at the final stage of the formation of the polychronous and polyformational Reftinsky gabbro-granitoid massif.

Cheralite is a rare mineral from the monazite group. Cheralite was first described in a pegmatite dyke at Kuttankuli, Kerala, India [2]. In Russia, cheralite was identified as a bismuth-bearing brabantite in the rare-metal pegmatites of the Lipovsky mines in the Middle Urals [3]. In 2006, brabantite as a mineral was abolished; since then, it has been synonymous with cheralite [4]. Two more finds of cheralite were made in the Urals. It was discovered in the beresites of the Berezovsky gold deposit [5], and also described in the ores of the Mikheevsky porphyry copper deposit, Southern Urals [6].

The author discovered cheralite in the leucogranite of the Peshcherninsky stock; up to this point, no information about the finds of cheralite in plutonic rocks has been published in Russia yet. There is an assumption that, despite its rarity, the mineral is quite common, especially for rocks of granite com-

*korovin@igg.uran.ru

position. But the poor knowledge of accessory mineralization and the tiny size of crystals currently make cheralite a rather exotic mineral.

In world practice, this mineral has already been found in plutonic rocks. An example of one of these finds is the article on the Australian granites of God's Lake, in one of the largest plutons, in the western part of the Lakhan fold belt [7]. These granites are of Devonian age and belong to

S-type granites. This article compares the chemical composition of cheralite from God's Lake with cheralite from the Peshcherninsky stock.

Brief geological description. The Reftinsky gabbro-granitoid massif is one of the largest areas of magmatism on the eastern slope of the Middle Urals. It is located within the eastern margin of the Middle Ural segment of the Ural mobile belt. The Reftinsky massif is polychronous and polyformational; it

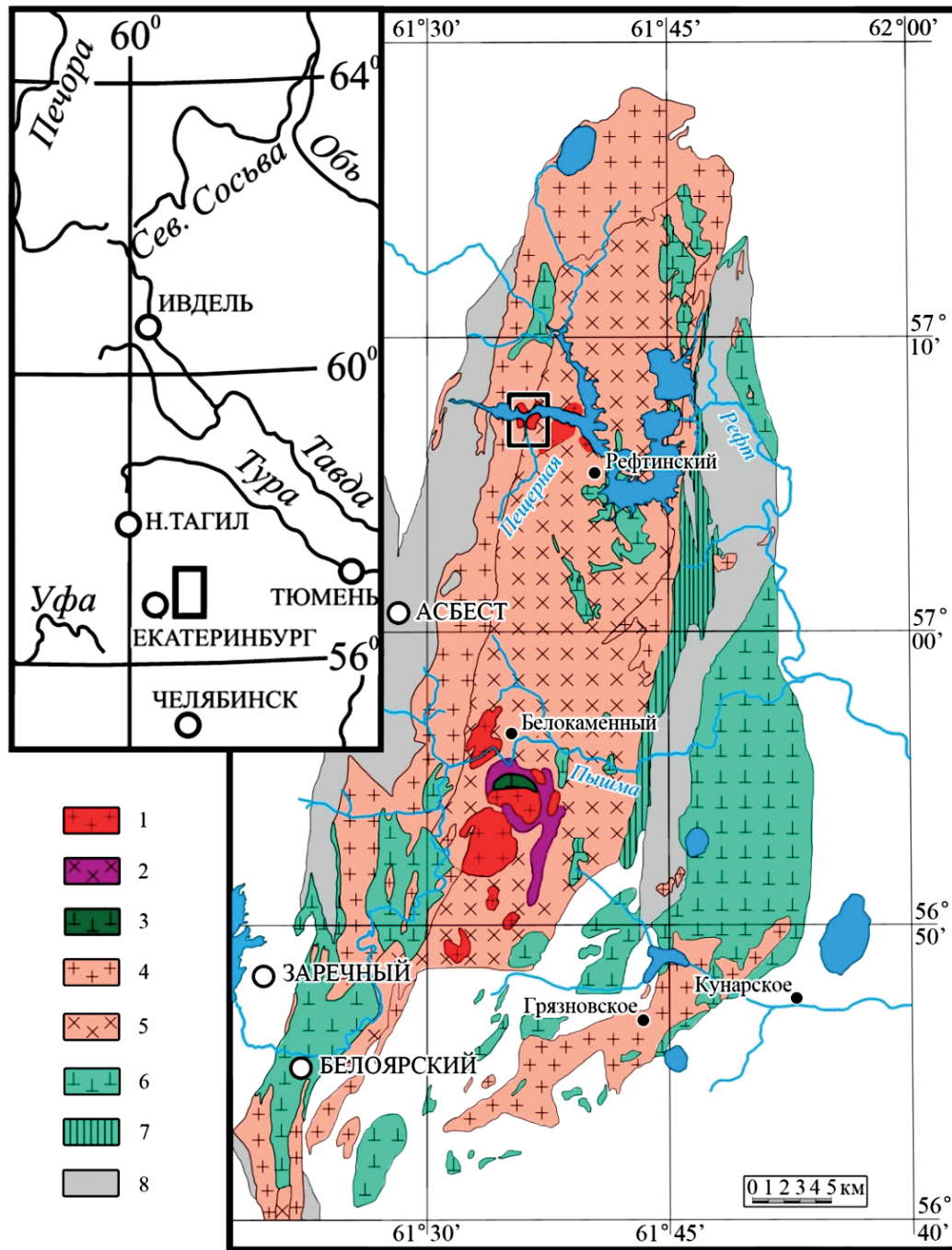


Figure 1. Geological scheme of the Reftinsky massif (compiled on the basis of the State geological map at a scale of 1 : 200,000 [15] with minor corrections by the author). The position of the Peshcherninsky stock is indicated by a rectangle; 1–3 – Devonian intrusions: 1 – granitoids (γD_2), 2 – diorites (δD_1), 3 – gabbro (νD_1); 4–7 – Reftinsky complex: 4 – plagiogranites ($\rho \gamma S_2$), 5 – quartz diorites and tonalites ($q\delta S_1$), 6 – gabbro (νS_1); 7 – complex of parallel dolerite dikes (V); 8 – rocks of ophiolite association, Alapaevsky dunite-harzburgite-gabbro complex
Рисунок 1. Геологическая схема Рефтинского массива (составлена на основе Государственной геологической карты масштаба 1 : 200 000 [15] с незначительными уточнениями автора). Положение Пещернинского штока обозначено прямоугольником; 1–3 – девонские интрузии: 1 – гранитоиды (γD_2), 2 – диориты (δD_1), 3 – габбро (νD_1); 4–7 – Рефтинский комплекс: 4 – плагиограниты ($\rho \gamma S_2$), 5 – кварцевые диориты и тоналиты ($q\delta S_1$), 6 – габбро (νS_1); 7 – комплекс параллельных долеритовых даек (V); 8 – породы офиолитовой ассоциации, Алапаевский дунит-гарцбургит-габбровый комплекс

Table 1. Chemical composition of apatite from leucogranites of the Pescherninsky stock, wt. %
Таблица 1. Химический состав апатита из лейкогранитов Пещернинского штока, мас. %

| Oxides | Analysis number | | | | | | | | | |
|----------------------------------|---|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| SO ₃ | 0,10 | 0,11 | 0,21 | 0,19 | 0,09 | – | 0,17 | 0,10 | 0,09 | 0,11 |
| P ₂ O ₅ | 40,88 | 40,60 | 41,54 | 41,43 | 41,32 | 41,31 | 41,62 | 42,59 | 42,17 | 42,57 |
| SiO ₂ | 0,26 | 0,23 | 0,22 | 0,15 | 0,12 | 0,15 | 0,12 | 0,14 | 0,13 | 0,09 |
| FeO | 0,99 | 0,77 | 1,28 | 1,25 | – | 0,17 | 0,58 | 0,20 | 0,23 | 0,28 |
| MnO | 0,97 | 1,05 | 0,93 | 0,92 | 1,27 | 1,16 | 1,34 | 1,09 | 1,31 | 1,48 |
| CaO | 54,87 | 54,33 | 54,24 | 54,31 | 54,96 | 54,78 | 53,27 | 53,60 | 53,72 | 53,14 |
| Na ₂ O | 0,27 | 0,37 | 0,29 | 0,27 | 0,17 | 0,16 | 0,28 | 0,27 | 0,22 | 0,22 |
| K ₂ O | – | – | – | – | 0,27 | 0,33 | – | – | – | – |
| F | 3,11 | 2,94 | 3,07 | 3,00 | 3,19 | 3,51 | 3,15 | 3,13 | 3,16 | 3,18 |
| Cl | 0,12 | 0,13 | 0,12 | 0,12 | 0,12 | 0,13 | 0,23 | 0,21 | 0,17 | 0,19 |
| Total | 101,57 | 100,53 | 101,90 | 101,64 | 101,50 | 101,70 | 100,76 | 101,33 | 101,20 | 101,26 |
| <i>Crystal chemical formulas</i> | | | | | | | | | | |
| 1 | (Ca _{4,93} Mn _{0,07} Fe _{0,07} Na _{0,04}) _{5,11} [(P _{2,96} Si _{0,02} S _{0,01}) _{2,99} O _{12,00}](F _{0,84} Cl _{0,02}) _{0,86} | | | | | | | | | |
| 2 | (Ca _{4,99} Mn _{0,08} Fe _{0,06} Na _{0,06}) _{5,19} [(P _{2,95} Si _{0,02} S _{0,01}) _{2,98} O _{12,00}](F _{0,80} Cl _{0,02}) _{0,82} | | | | | | | | | |
| 3 | (Ca _{4,90} Fe _{0,09} Mn _{0,07} Na _{0,05}) _{5,11} [(P _{2,97} Si _{0,02} S _{0,01}) _{3,00} O _{12,00}](F _{0,82} Cl _{0,02}) _{0,84} | | | | | | | | | |
| 4 | (Ca _{4,92} Fe _{0,09} Mn _{0,07} Na _{0,04}) _{5,12} [(P _{2,97} Si _{0,01} S _{0,01}) _{2,99} O _{12,00}](F _{0,80} Cl _{0,02}) _{0,82} | | | | | | | | | |
| 5 | (Ca _{4,98} Mn _{0,09} K _{0,03} Na _{0,03}) _{5,13} [(P _{2,96} Si _{0,01} S _{0,01}) _{2,98} O _{12,00}](F _{0,85} Cl _{0,02}) _{0,87} | | | | | | | | | |
| 6 | (Ca _{4,96} Mn _{0,08} K _{0,04} Na _{0,03} Fe _{0,01}) _{5,12} [(P _{2,96} Si _{0,01} S _{0,01}) _{2,97} O _{12,00}](F _{0,94} Cl _{0,02}) _{0,96} | | | | | | | | | |
| 7 | (Ca _{4,85} Mn _{0,10} Na _{0,05} Fe _{0,04}) _{5,04} [(P _{2,99} Si _{0,01} S _{0,01}) _{3,01} O _{12,00}](F _{0,85} Cl _{0,03}) _{0,88} | | | | | | | | | |
| 8 | (Ca _{4,83} Mn _{0,08} Na _{0,04} Fe _{0,01}) _{4,96} [(P _{3,03} Si _{0,01} S _{0,01}) _{3,05} O _{12,00}](F _{0,83} Cl _{0,03}) _{0,86} | | | | | | | | | |
| 9 | (Ca _{4,86} Mn _{0,09} Na _{0,04} Fe _{0,02}) _{5,00} [(P _{3,01} Si _{0,01} S _{0,01}) _{3,03} O _{12,00}](F _{0,84} Cl _{0,02}) _{0,86} | | | | | | | | | |
| 10 | (Ca _{4,79} Mn _{0,11} Na _{0,04} Fe _{0,02}) _{4,96} [(P _{3,03} Si _{0,01} S _{0,01}) _{3,05} O _{12,00}](F _{0,85} Cl _{0,03}) _{0,88} | | | | | | | | | |

has a complex structure [8–12]. Its western half is composed of plagioclase granitoids (quartz diorites, tonalites, trondhjemites) [13], which are intruded by small plutons composed of potassium-sodium granitoids; some bodies also contain rocks of basic and intermediate composition, it is assumed that they are of Devonian age [14]. In the eastern part of the massif, there are two blocks composed of Early Silurian hornblende gabbro of the Reftinsky complex. These blocks are separated from plagioclase granitoids by a band of rocks of the ophiolite association (gabbroids of the layered part of the section and a complex of parallel dolerite dikes), apparently of Vendian age [15].

The author studied phosphate mineralization (apatite, monazite, xenotime, cheralite) from granitoids of the Pescherninsky stock (fig. 1), which intrude quartz diorites and tonalites of the Reftinsky complex. The Pescherninsky stock is composed of fairly homogeneous leucogranites, which contain aplite veins. For research, samples of leucogranite were taken on the right bank of the Peshchernaya River, at its mouth. The coordinates of the sampling point on the GPS receiver are 57°07.069' north latitude, 61°36.286' east longitude.

The leucogranites of the Pescherninsky stock are fine-medium-grained, quartz-feldspar rocks with biotite, have a hypidiomorphic-grained structure and a massive texture. Accessory phosphate mineralization in granitoids occurs as euhedral grains, as well as in intergrowths.

Chemical analysis of phosphates. According to its chemical composition, apatite corresponds to fluorapatite, because it contains from 2.94 to 3.51 wt. % fluorine, and chlorine varies (0.12–0.23 wt. %). The content of the main elements of the

formula varies – CaO (53.14–54.96 wt. %), P₂O₅ (40.60–42.59 wt. %). In addition to the main elements included in the crystal chemical formula of apatite, impurity elements were found that are included in the position of calcium - these are such as: MnO (0.92–1.48 wt. %), FeO (0.17–1.28 wt. %), Na₂O (0.16–0.37 wt. %), in a separate case, an impurity of K₂O appears (0.27–0.33 wt. %). In the position of phosphorus, there is an insignificant admixture of SiO₂ (0.09–0.26 wt. %) and SO₃ from 0.09 to 0.21 wt. % (table 1).

It is assumed that variations in the chemical composition of apatite depend on the stage of the onset of crystallization of the mineral and the matrix in which it was enclosed. On fig. 2, a, apatite composes euhedral grains captured by magnetite, up to 100 microns in size. In the crystal chemical formula of apatites, elevated iron contents are observed, points 1–4 (table 1). Fig. 2, b shows a transverse hexagonal section of an apatite crystal, up to 20 microns in size, which is located in potassium feldspar, points 5, 6 (a perthite plagioclase ingrowth is observed to the left of the grain). If you look at the crystal chemical formula of apatite in Fig. 2b, you can notice its distinctive feature – the presence of potassium, which is not found in other crystals in the analyzed section. Intergrowths of apatite with monazite are observed in the rock (fig. 3, a), in the figure we see two apatite grains, one of them is located on the left side of the figure in the biotite matrix in close proximity to monazite. The second grain is located on the right side of the presented image, has an intergrowth with a grain of ilmenite, monazite, and biotite, being in a plagioclase matrix (fig. 3, a). Data on the crystal chemical composition are presented in table 1.

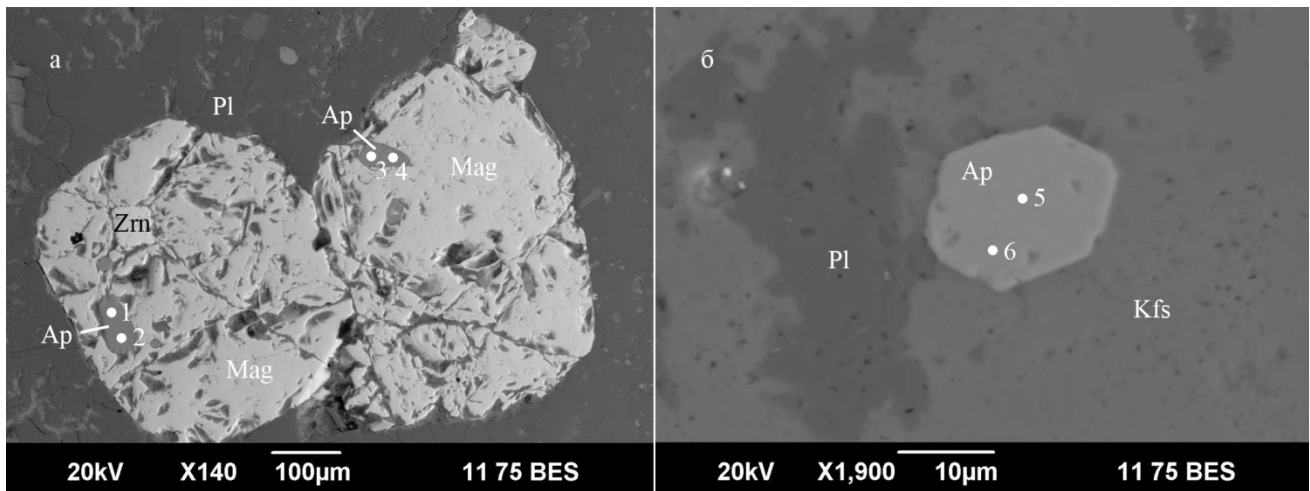


Figure 2. Apatite from leucogranites of the Pescherninsky stock: *a* – apatite and zircon inclusions in magnetite; *b* – apatite grains in potassium feldspar; the numbers indicate the points corresponding to the chemical analysis numbers in table 1; symbols (hereinafter): Ap – apatite, Mag – magnetite, Zrn – zircon, Pl – plagioclase, Kfs – potassium feldspar; photo in reflected electrons, CAMECA SX 100

Рисунок 2. Апатит из лейкогранитов Пещернинского штока: *a* – включения апатита и циркона в магнетите; *b* – зерно апатита в калиевом полевоом шпате; цифрами обозначены точки, соответствующие номерам химического анализа в табл. 1; условные обозначения (здесь и далее): Ap – апатит, Mag – магнетит, Zrn – циркон, Pl – плагиоклаз, Kfs – калиевый полевой шпат; фото в отраженных электронах, CAMECA SX 100

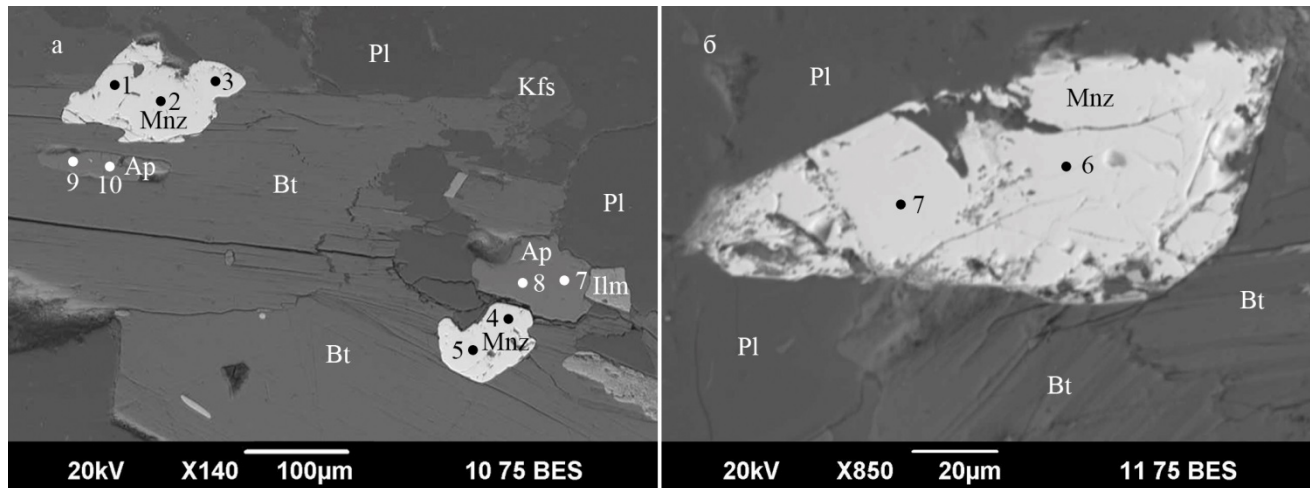


Figure 3. Monazite from leucogranites of the Peshcherninsky stock: *a* – monazite in association with apatite and ilmenite in a biotite matrix; *b* – monazite in a biotite and plagioclase matrix; the numbers indicate the points corresponding to the numbers of chemical analysis in tables 1, 2; symbols (hereinafter): Mnz – monazite, Bt – biotite, Ilm – ilmenite; photo in reflected electrons, CAMECA SX 100

Рисунок 3. Монацит из лейкогранитов Пещернинского штока: *a* – монацит в ассоциации с апатитом и ильменитом в матрице биотита; *b* – монацит в матрице биотита и плагиоклаза; цифрами обозначены точки, соответствующие номерам химического анализа в табл. 1, 2; условные обозначения (здесь и далее): Mnz – монацит, Bt – биотит, Ilm – ильменит; фото в отраженных электронах, CAMECA SX 100

Monazite, in the leucogranites of the Pescherninsky stock, forms elongated and rounded individuals up to 180 µm in size. Some crystals have intergrowths with apatite. According to the chemical composition, monazite belongs to the cerium variety, the content of the main rare earth elements varies, according to Ce₂O₃ from 25.58 to 29.05 wt. %, La₂O₃ (10.71–15.21 wt. %), Nd₂O₃ (9.83–11.84 wt. %). There is also a small proportion of impurities of the following elements: UO₂ (0.04–0.51 wt. %), ThO₂ (5.14–7.06 wt. %), Yb₂O₃ (0.04–0.25 wt. %), Tm₂O₃ (0.01–0.12 wt. %), Dy₂O₃ (0.11–0.88 wt. %), Gd₂O₃ (0.96–1.99 wt. %), Eu₂O₃ (0.04–0.26 wt. %), Sm₂O₃ (1.13–2.36 wt. %), Pr₂O₃ (2.99–3.79 wt. %), Y₂O₃ (1.14–3.47 wt. %), PbO (0.09–0.15 wt. %), SrO (0.20–0.25 wt. %), MnO (0.56–0.70 wt. %), CaO (0.63–1.11 wt. %). The content of phosphorus oxide has slight variations from 28.14 to 29.88 wt. %, as well as the admix-

ture of SiO₂ (0.53–1.17 wt. %) in position P. Monazite crystals located within one biotite lath (fig. 3, *a*), do not have any special differences in their crystal chemical composition, as well as a fine cross section of a monazite grain in fig. 4, *a* (table 2). If we compare the composition from monazite grains at points (1–5, 8) with analyzes from points (6, 7) in the crystal in fig. 3, *b*, then there are small differences, because at points (6, 7), the content of Ce and La decreases. Monazite from the biotite matrix (fig. 3, *a*) has the highest contents of Ce and La (table 2, an. 5).

Xenotime is rather rare in leucogranites of the Pescherninsky stock, mainly in intergrowths with zircon (fig. 4, *b*). According to chemical analysis, xenotime belongs to the yttrium variety, the content of Y₂O₃ is about 45.82–48.30 wt. %, and there are also impurities of such lanthanides as: Gd₂O₃ (3.84–4.95 wt. %), Dy₂O₃ (3.89–4.42 wt. %), Yb₂O₃ (4.00–4.38

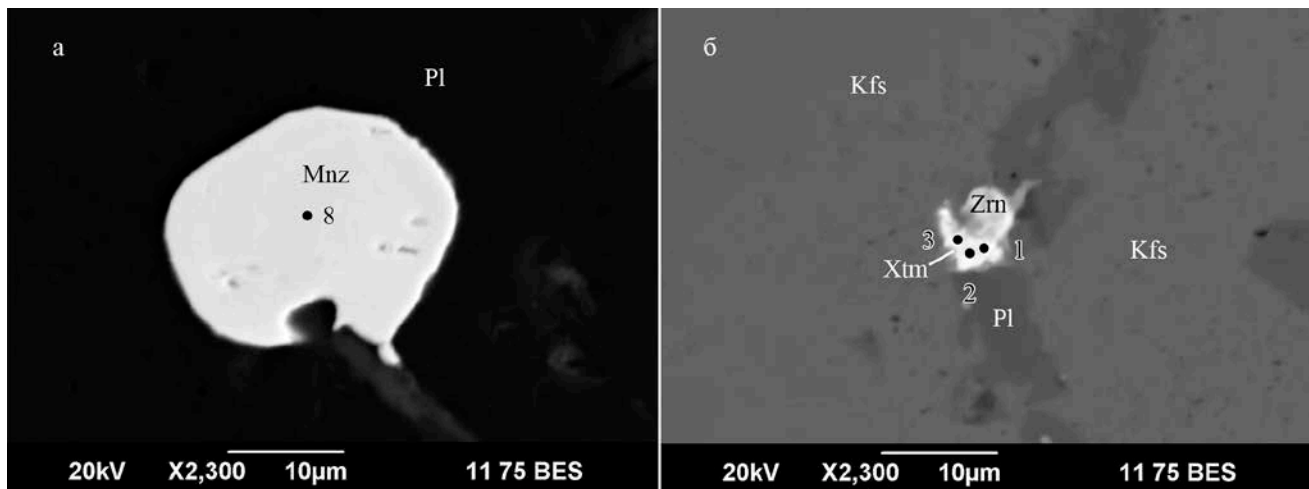


Figure 4. Monazite and xenotime from leucogranites of the Peshcherninsky stock: *a* – monazite in a plagioclase matrix; *b* – intergrowth of zircon and xenotime in a K-feldspar matrix at the boundary with a perthite plagioclase ingrowth; the number 8 indicates the point that corresponds to the analysis in table 2; the numbers 1, 2, 3 indicate the points corresponding to the chemical analysis numbers in table 3; symbols: Xtm – xenotime; photo in reflected electrons, CAMECA SX 100

Рисунок 4. Монацит и ксенотим из лейкогранитов Пещернинского штока: *a* – монацит в матрице плагиоклаза; *b* – сросток циркона и ксенотима в матрице калишпата на границе с пертитовым вростком плагиоклаза; цифрой 8 обозначена точка, которая соответствует анализу в табл. 2; цифрами 1, 2, 3 обозначены точки, соответствующие номерам химического анализа в табл. 3; условные обозначения: Xtm – ксенотим; фото в отраженных электронах, CAMECA SX 100

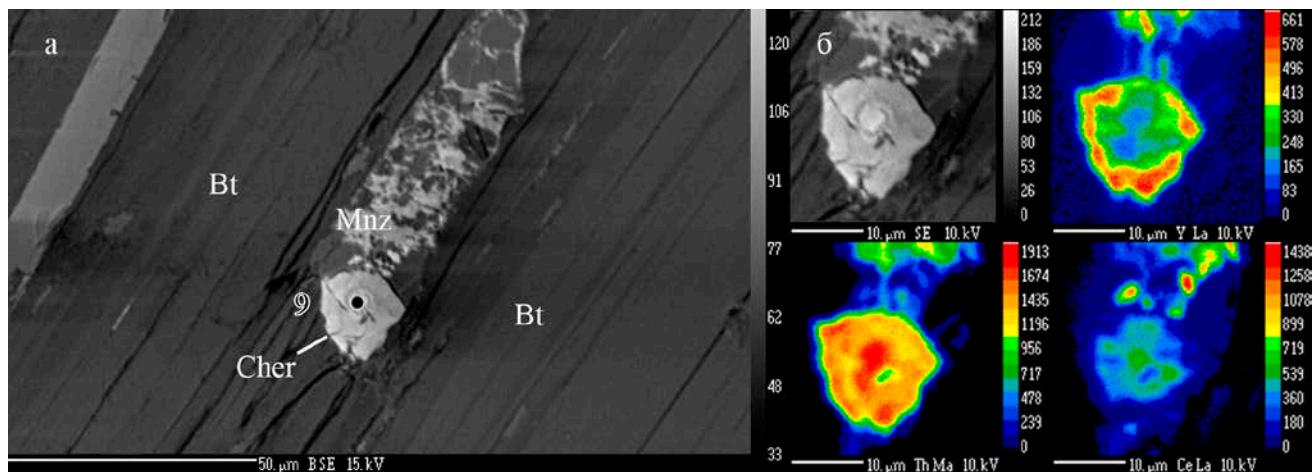


Figure 5. Cheralite with monazite in biotite from leucogranites of the Peshcherninsky stock: *a* – cheralite in a biotite matrix; *b* – distribution map of the elements Y, Th, and Ce and their content in cheralite; number 9 indicates a point that corresponds to the analysis in Table 2; symbols: Cher – cheralite; photo in reflected electrons, CAMECA SX 100

Рисунок 5. Чералит с монацитом в биотите из лейкогранитов Пещернинского штока: *a* – чералит в матрице биотита; *b* – карта распределения элементов Y, Th, Ce и их содержание в чералите; цифрой 9 обозначена точка, которая соответствует анализу в табл. 2; условные обозначения: Cher – чералит; фото в отраженных электронах, CAMECA SX 100

wt. %), Er_2O_3 (3.47–3.56 wt. %), Tm_2O_3 (0.58–0.97 wt. %), (3.89–0.01 wt. %). The content of phosphorus oxide has slight variations from 31.85 to 33.22 wt. %, as well as the SiO_2 impurity (0.52–0.82 wt. %) in position P. UO_2 (0.16–0.61 wt. %) ThO_2 (0.09–0.35 wt. %), CaO (0.13–0.22 wt. %).

A tiny cross section of cheralite grains up to 15 microns in size associated with monazite was found in the biotite grain matrix (fig. 5, *a*). This mineral is a rare calcium-thorium phosphate from the monazite group. According to the chemical composition, it mainly belongs to the cerium variety, the analysis data are given in table 2, under number 9. Cheralite from the leucogranites of the Peshcherninsky stock in comparison with cheralite from the granites of God's Lake (Australia), where it was also found in the biotite matrix, has, according to a chemical composition, two times lower content of rare earth

elements. However, the content of thorium oxide is twice that of cheralite from God's Lake [7]. In the photographs after mapping chemical elements, we observe the zoning of the mineral, cerium tends to the central part of the cheralite grain, and yttrium is concentrated in its marginal parts, and as a result, it passes from the cerium variety to the yttrium one as it crystallizes from the melt. Thorium also has a slightly higher content in the center of the grain, then it is evenly distributed (fig. 5, *b*). The presence of rare earth elements in its composition speaks in favor of the magmatic origin of this mineral.

Discussion of the obtained data

In the leucogranites of the Peshcherninsky stock, apatite is represented by a fluorine variety, the main impurity element of which is manganese. In the 2018 article by A. Shushkevich et al. [16], the authors talk about the genesis of manganese-rich

Table 2. Chemical composition of monazite from leucogranites of the Peshcherninsky stock, wt. %
Таблица 2. Химический состав монацита из лейкогранитов Пещернинского штока, мас. %

| Oxides | Analysis number | | | | | | | | |
|--------------------------------|-----------------|--------|-------|-------|-------|--------|--------|--------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| P ₂ O ₅ | 29,14 | 28,90 | 28,23 | 28,45 | 28,14 | 28,89 | 28,89 | 29,88 | 28,51 |
| UO ₂ | 0,42 | 0,51 | 0,39 | 0,06 | 0,04 | 0,06 | 0,08 | 0,20 | – |
| ThO ₂ | 7,03 | 5,41 | 6,49 | 5,79 | 5,14 | 7,05 | 7,06 | 5,60 | 41,38 |
| SiO ₂ | 0,72 | 0,54 | 0,76 | 0,68 | 0,87 | 0,95 | 1,17 | 0,53 | 1,4 |
| Yb ₂ O ₃ | 0,13 | 0,21 | 0,10 | 0,05 | 0,16 | 0,25 | 0,08 | 0,04 | 0,31 |
| Tm ₂ O ₃ | 0,05 | 0,01 | 0,03 | 0,05 | 0,07 | 0,02 | 0,12 | 0,11 | 0,24 |
| Dy ₂ O ₃ | 0,82 | 0,88 | 0,65 | 0,63 | 0,11 | 0,83 | 0,83 | 0,51 | 0,47 |
| Gd ₂ O ₃ | 1,49 | 1,11 | 0,98 | 1,07 | 0,96 | 1,99 | 1,56 | 1,04 | 0,57 |
| Eu ₂ O ₃ | 0,13 | 0,08 | 0,10 | 0,17 | 0,15 | 0,08 | 0,31 | 0,54 | – |
| Sm ₂ O ₃ | 3,50 | 3,19 | 2,96 | 3,71 | 2,37 | 4,55 | 4,95 | 3,52 | 1,76 |
| Nd ₂ O ₃ | 10,12 | 10,23 | 9,83 | 11,03 | 10,62 | 11,84 | 11,81 | 10,12 | 3,11 |
| Pr ₂ O ₃ | 3,20 | 3,54 | 2,99 | 3,34 | 3,35 | 3,79 | 3,43 | 3,10 | 0,85 |
| Ce ₂ O ₃ | 25,95 | 26,98 | 27,40 | 27,80 | 29,05 | 25,58 | 25,85 | 27,32 | 6,96 |
| La ₂ O ₃ | 13,19 | 14,05 | 14,62 | 12,60 | 15,21 | 10,71 | 11,09 | 14,31 | 3,73 |
| Y ₂ O ₃ | 3,05 | 3,05 | 2,58 | 2,32 | 1,14 | 3,47 | 2,92 | 2,26 | 1,56 |
| PbO | 0,15 | 0,13 | 0,13 | 0,09 | 0,11 | 0,13 | 0,11 | 0,13 | 0,14 |
| SrO | 0,22 | 0,21 | 0,20 | – | 0,25 | – | 0,20 | 0,22 | 0,41 |
| MnO | 0,58 | 0,56 | 0,61 | 0,61 | 0,62 | 0,70 | 0,69 | 0,61 | 0,15 |
| CaO | 1,07 | 0,90 | 0,72 | 0,82 | 0,63 | 0,79 | 1,06 | 1,11 | 8,22 |
| Total | 100,96 | 100,49 | 99,77 | 99,27 | 98,99 | 101,68 | 102,21 | 101,15 | 99,77 |

Crystal chemical formulas

| | |
|---|---|
| 1 | (Ce _{0,39} La _{0,20} Nd _{0,15} Y _{0,07} Pr _{0,05} Sm _{0,03} Th _{0,03} Ca _{0,02} Gd _{0,02} Dy _{0,01} Mn _{0,01}) _{0,98} [(P _{1,01} Si _{0,01}) _{1,02} O _{4,00}] |
| 2 | (Ce _{0,40} La _{0,21} Nd _{0,15} Y _{0,07} Pr _{0,05} Th _{0,03} Sm _{0,02} Ca _{0,02} Gd _{0,02} Dy _{0,01} Mn _{0,01}) _{0,99} [(P _{1,00} Si _{0,01}) _{1,01} O _{4,00}] |
| 3 | (Ce _{0,41} La _{0,22} Nd _{0,15} Y _{0,06} Pr _{0,05} Th _{0,03} Sm _{0,03} Ca _{0,02} Gd _{0,01} Dy _{0,01} Mn _{0,01}) _{0,99} [(P _{0,99} Si _{0,02}) _{1,01} O _{4,00}] |
| 4 | (Ce _{0,40} La _{0,21} Nd _{0,15} Y _{0,05} Pr _{0,05} Sm _{0,03} Th _{0,03} Ca _{0,02} Gd _{0,01} Dy _{0,01} Mn _{0,01}) _{0,97} [(P _{1,02} Si _{0,01}) _{1,03} O _{4,00}] |
| 5 | (Ce _{0,42} La _{0,19} Nd _{0,16} Y _{0,05} Pr _{0,05} Sm _{0,03} Th _{0,03} Ca _{0,02} Gd _{0,01} Dy _{0,01} Mn _{0,01}) _{0,98} [(P _{1,00} Si _{0,01}) _{1,01} O _{4,00}] |
| 6 | (Ce _{0,38} Nd _{0,17} La _{0,16} Y _{0,08} Pr _{0,06} Sm _{0,03} Th _{0,03} Gd _{0,03} Ca _{0,02} Dy _{0,01} Mn _{0,01}) _{0,98} [(P _{1,00} Si _{0,02}) _{1,02} O _{4,00}] |
| 7 | (Ce _{0,38} Nd _{0,17} La _{0,17} Y _{0,06} Pr _{0,05} Sm _{0,04} Th _{0,03} Gd _{0,02} Ca _{0,02} Dy _{0,01} Mn _{0,01}) _{0,96} [(P _{1,00} Si _{0,02}) _{1,02} O _{4,00}] |
| 8 | (Ce _{0,44} La _{0,23} Nd _{0,16} Y _{0,03} Pr _{0,05} Sm _{0,02} Th _{0,02} Ca _{0,01} Gd _{0,01} Mn _{0,01}) _{0,98} [(P _{0,99} Si _{0,02}) _{1,01} O _{4,00}] |
| 9 | (Th _{0,22} Ca _{0,20} Ce _{0,12} La _{0,06} Nd _{0,05} Y _{0,04} Dy _{0,01} Gd _{0,01} Sm _{0,01} Pr _{0,01} Sr _{0,01}) _{0,73} [(P _{1,12} Si _{0,03}) _{1,15} O _{4,00}] |

Table 3. Chemical composition of xenotime from leucogranites of the Peshcherninsky stock, wt. %
Таблица 3. Химический состав ксенотима из лейкогранитов Пещернинского штока, мас. %

| Oxides | Analysis number | | |
|--------------------------------|-----------------|-------|-------|
| | 1 | 2 | 3 |
| P ₂ O ₅ | 33,22 | 31,90 | 31,85 |
| UO ₂ | 0,16 | 0,61 | 0,59 |
| ThO ₂ | 0,71 | 0,78 | 0,66 |
| TiO ₂ | 0,35 | 0,09 | 0,15 |
| SiO ₂ | 0,52 | 0,54 | 0,82 |
| Yb ₂ O ₃ | 4,07 | 4,38 | 4,00 |
| Tm ₂ O ₃ | 0,64 | 0,97 | 0,58 |
| Er ₂ O ₃ | 3,51 | 3,56 | 3,47 |
| Dy ₂ O ₃ | 3,89 | 4,42 | 4,10 |
| Gd ₂ O ₃ | 4,15 | 4,95 | 3,84 |
| Y ₂ O ₃ | 48,30 | 46,62 | 45,82 |
| CaO | 0,22 | 0,17 | 0,13 |
| Total | 99,74 | 98,99 | 96,01 |

Crystal chemical formulas

| | |
|---|--|
| 1 | (Y _{0,87} Gd _{0,05} Dy _{0,04} Yb _{0,04} Er _{0,04} Tm _{0,01}) _{1,05} [(P _{0,95} Si _{0,01}) _{0,96} O _{4,00}] |
| 2 | (Y _{0,86} Gd _{0,06} Dy _{0,05} Yb _{0,05} Er _{0,04} Tm _{0,01}) _{1,07} [(P _{0,94} Si _{0,01}) _{0,95} O _{4,00}] |
| 3 | (Y _{0,86} Dy _{0,05} Gd _{0,04} Yb _{0,04} Er _{0,04} Tm _{0,01}) _{1,04} [(P _{0,95} Si _{0,01}) _{0,96} O _{4,00}] |

apatites in pegmatites. They describe the specific geotectonic position of this pegmatite, which is located at the boundary of crustal and oceanic rocks in the central part of the Sudetensky accretionary complex, which is a decisive factor involved in creating a favorable environment for the melting of metasedimentary rocks, which became the source of melt for these pegmatites [16]. In other words, the presence of manganese is a characteristic feature for sedimentary and metasedimentary rocks. The presence of an admixture of manganese in the apatites of the Peshcherninsky stock may indicate that during intrusion there was a partial mixing of the initial melt with the crustal substance and its assimilation.

Intergrowths of xenotime with zircon are observed in the rock, it is assumed that these minerals are among the first to crystallize from the melt, controlling heavy rare earth elements, followed by crystallization of monazite group minerals,

taking light rare earth elements. Apatite can crystallize at different stages of mineral formation; it occurs in rocks as inclusions in magnetite, biotite, plagioclase, and potassium feldspar.

Thus, for the first time in Russia, cheralite was found and described in a plutonic rock. In the leucogranites of the Peshcherninsky stock, apatite, monazite, and xenotime have been identified and studied. Data on the chemical composition of minerals were obtained: apatite belongs to the fluorine variety and contains an admixture of manganese, monazite is assigned to the cerium (Ce) variety, and xenotime is assigned to the yttrium (Y) variety. Cheralite has a transitional composition of the main impurity elements, from Ce to Y. The order of crystallization of phosphates in leucogranite of the Peshcherninsky stock, as well as mineral associations: xenotime with zircon, cheralite with monazite, has been established.

The studies were carried out within the framework of the State Assignment of the IGG UB of the Russian Academy of Sciences, on the state budget topic "Tectonics, geodynamics, evolution and minerageny of structural-material complexes that arose during the formation of the continental crust (using the example of the Paleozoic Ural-Mongolian mobile belt and the West Siberian plate)" using equipment of the Common Use Center Geoanalyst of the IGG UB of the Russian Academy of Sciences. The retrofitting and comprehensive development of the Common Use Center Geoanalyst of the IGG UB of the Russian Academy of Sciences is carried out with the financial support of a grant from the Ministry of Science and Higher Education of the Russian Federation, Agreement no. 075-15-2021-680.

REFERENCES

1. Sun S. S., McDonough W. F. 1989, Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geological Society, London, Special Publications*, vol. 42, no. 1, pp. 313–345. <https://doi.org/10.1144/GSL.SP.1989.042.01.19>
2. Bowie S. H. U. Horne J. E. T. 1953, Cheralite, a new mineral of the monazite group. *Mineralogical Magazine*, vol. 30, issue 221, pp. 93–99. <https://doi.org/10.1180/minmag.1953.030.221.02>
3. Pekov I. V. 2002, Bismuth-bearing brabantite from rare-metal pegmatites of Lipovka, Middle Urals. *Ural'skiy geologicheskii zhurnal* [Ural Geological Journal], no. 5 (29), pp. 119–128. (In Russ.)
4. Linthout K. 2007, Tripartite division of the system $2\text{REEPO}_4\text{--CaTh}(\text{PO}_4)_2\text{--}2\text{ThSiO}_4$, discreditation of brabantite, and recognition of cheralite as the name for members dominated by $\text{CaTh}(\text{PO}_4)_2$. *The Canadian Mineralogist*, vol. 45(3), pp. 503–508. <http://dx.doi.org/10.2113/gscanmin.45.3.503>
5. Shagalov E. S., Stepanov S. Yu., Veretennikova T. Yu. 2018, On the mineralogy of the Berezovsky gold deposit (Middle Urals): sulfides and minerals of thorium and uranium. *Ural'skaya mineralogicheskaya shkola* [Ural Mineralogical School], no. 24, pp. 252–259. (In Russ.)
6. Azovskova O. B., Rovnushkin M. Yu., Bairamgalina L. N., Gemel V. A. 2019, Uranium and thorium mineralization in the ores of the Mikheevsky porphyry copper deposit, Southern Urals. *Metallogeniya drevnikh i sovremennykh okeanov* [Metallogeny of ancient and modern oceans], no. 1, pp. 114–117. (In Russ.)
7. Mills S. J., Birch W. D., Maas R., Plimer I. R. 2008, Lake Boga Granite, northwestern Victoria: mineralogy, geochemistry and geochronology. *Australian Journal of Earth Sciences: An International Geoscience Journal of the Geological Society of Australia*, vol. 55, issue 3, pp. 281–299. <https://doi.org/10.1080/08120090701769449>
8. State geological map of the Russian Federation. Scale 1:1 000 000 (new series). Sheet O-40, (41). Ekaterinburg, 1997, 252 p. (In Russ.)
9. Smirnov V. N. 1981, Gabbro-granitoid series of the Eastern zone of the Urals. *Doklady AN SSSR* [Reports of the Academy of Sciences of the USSR], vol. 259, no. 6, pp. 1453–1457. (In Russ.)
10. 1984, Eugeosynclinal gabbro-granitoid series. G. B. Fershtater [et al.]. Moscow, 264 p. (In Russ.)
11. Lobova E. V. 2013, Silurian intrusive magmatism in the Eastern zone of the Middle Urals, PhD thesis. Saint Petersburg, 20 p. (In Russ.)
12. Smirnov V. N., Ivanov K. S., Ronkin Yu. L., Serov P. A., Gerdes A. 2018, Sr, Nd, and Hf isotope composition of rocks of the Reft gabbro-diorite-tonalite complex (Eastern slope of the Middle Urals): petrological and geological implications. *Geokhimiya* [Geochemistry], no. 6, pp. 499–513. (In Russ.)
13. Smirnov V. N., Nastavko E. V., Ivanov K. S., Bayanova T. B., Rodionov N. V., Serov P. A. 2014, Results of isotopic dating of rocks of the Reft gabbro-diorite-tonalite complex. *Litosfera* [Lithosphere], no. 5, pp. 3–18. (In Russ.)
14. Fershtater G. B., Krasnobaev A. A., Bea F., Montero P., Borodina N. S., Kholodnov V. V., Zinkova E. A., Shardakova G. Yu., Pribavkin S. V. 2007, Stages of the Paleozoic intrusive magmatism of the Ural orogen and their geodynamic interpretation. Geodynamics, magmatism, metamorphism and ore formation. Collection of scientific papers. Ekaterinburg, pp. 89–120. (In Russ.)
15. Kazakov I. I., Storozhenko E. V., Kharitonov I. N., Stefanovsky V. V., Koshevoy Yu. N., Kozmin S. V., Martynov S. E., Fadeicheva I. F., Ronkin Yu. L., Lukin V. G. 2017, State Geological Map of the Russian Federation, scale 1:200 000 (second edition). Series Middle Ural. Sheet O-41-XXVI. Explanatory letter. Saint Petersburg, 284 p. (In Russ.)
16. Szuszkiewicz A., Pieczka A., Gołębiewska B., Dumańska-Słowik M., Marszałek M., Szełęg E. 2018, Chemical Composition of Mn- and Cl-Rich Apatites from the Szklary Pegmatite, Central Sudetes, SW Poland: Taxonomic and Genetic Implications. *Minerals*, vol. 8 (8), pp. 1–21. <https://doi.org/10.3390/min8080350>

The article was received on January 20, 2023

Фосфатная минерализация в лейкогранитах Пещернинского штока (Рефтинский массив, Средний Урал)

Дмитрий Дмитриевич КОРОВИН*

Институт геологии и геохимии им. акад. А. Н. Заварицкого УрО РАН, Екатеринбург, Россия

Аннотация

Актуальность. Фосфатная минерализация девонских интрузий Восточной зоны Среднего Урала в настоящее время слабо изучена, полученные данные могут иметь значение для интерпретации происхождения горных пород, особенно в том случае, когда стандартные методы геохимического анализа горных пород не дают ясной картины. Ксенотим и монацит являются минералами-концентраторами редкоземельных элементов, а графики распределения РЗЭ являются весьма важной характеристикой горных пород.

Цель работы – изучение химического состава фосфатов в лейкогранитах Пещернинского штока.

Методология исследования. Определение химического состава образцов выполнено на электронно-зондовом микроанализаторе Cameca SX100 в ЦКП «Геоаналитик», аналитик В. А. Булатов. Анализ проводился при ускоряющем напряжении 15 кВ с использованием кристаллов-анализаторов TAP, LPCO, LPET, PET, LLIF, LIF. Ток электронного зонда – 10 нА (апатит) и 60 нА (РЗЭ, Th фосфаты). Время накопления импульсов в максимуме пика составило 10 с (для большинства элементов) и 20 с (для РЗЭ, Th, U, Pb). При проведении анализа на электронно-зондовом микроанализаторе Cameca SX100 в качестве стандартов использовались: апатит (для анализа содержания P, Ca), хлорапатит (Cl), фтор-флогопит (F), диопсид (Mg, Si), альбит (Na, Al), ортоклаз (K), родонит (Mn), SrSO₄ (Sr), TiO₂ (Ti), Fe₂O₃ (Fe), SrSO₄ (Sr), BaSO₄ (S), Cr₂O₃ (Cr), пироморфит (Pb) и алюмосиликатные стекла, легированные РЗЭ (La, Ce, Y, Sm, Pr, Nd, Th, U, Tm, Eu, Tb, Dy, Gd, Er, Yb, Lu, Ho). Из-за использования низкого тока зонда при анализе апатитов пределы обнаружения элементов составили: 300–600 ppm для S, Cl, Al, Mg, Si, Ca, Na и 2000–2500 ppm для P, F, Fe, Mn, Cr. Для РЗЭ фосфатов при помощи повышенного тока зонда были достигнуты следующие пределы обнаружения: 100–200 ppm для Si, Ca, Cr, K, Al, Mg, Ti, Pb, 300–500 ppm для Na, S, P, Mn, Y, Th, U, 1200–1500 ppm для Sr, Nd, Ce, 1700–2000 ppm для La, Tm, Tb, 2500–2800 ppm для Yb, Dy, Lu, Pr, 3500–4700 ppm для Eu, Sm, Gd, Ho.

Результаты. Впервые в России найден и описан чералит в плутонической горной породе. В статье приведены первые данные по химическому составу фосфатов (апатит, монацит, ксенотим, чералит) из лейкогранитов Пещернинского штока, образовавшегося на завершающем этапе формирования полихронного и полиформационного Рефтинского габбро-гранитоидного массива.

Заключение. Апатит относится к фтористой разновидности с примесью марганца, монацит представлен цериевой разновидностью, а ксенотим – иттриевой. Чералит обладает переходным микроэлементным составом, и в зависимости от зоны его можно относить как к цериевой, так и к иттриевой разновидности. Примесь марганца в апатите может свидетельствовать о частичном смешении расплава с осадочными или метаосадочными породами.

Ключевые слова: фторапатит, монацит-(Ce), ксенотим-(Y), чералит, лейкограниты, Рефтинский массив, Средний Урал.

Исследования выполнены в рамках Государственного задания ИГГ УрО РАН по госбюджетной теме «Тектоника, геодинамика, эволюция и минералогия структурно-вещественных комплексов, возникших при формировании континентальной земной коры (на примере палеозойского Урало-Монгольского подвижного пояса и Западно-Сибирской плиты)» с использованием оборудования ЦКП «Геоаналитик» ИГГ УрО РАН. Дооснащение и комплексное развитие ЦКП «Геоаналитик» ИГГ УрО РАН осуществляется при финансовой поддержке гранта Министерства науки и высшего образования Российской Федерации, Соглашение № 075-15-2021-680.

ЛИТЕРАТУРА

1. Sun S. S., McDonough W. F. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes // Geological Society, London, Special Publications. 1989. Vol. 42. № 1. P. 313–345. <https://doi.org/10.1144/GSL.SP.1989.042.01.19>
2. Bowie S.H.U., Horne J.E.T. Cheralite, a new mineral of the monazite group // Mineralogical Magazine. 1953. Vol. 30. Issue 221. P. 93–99. <https://doi.org/10.1180/minmag.1953.030.221.02>
3. Пеков И. В. Висмутосодержащий брабантит из редкометалльных пегматитов Липовки, Средний Урал // Уральский геологический журнал. 2002. № 5 (29). С. 119–128.

*korovin@igg.uran.ru

4. Linthout K. Tripartite division of the system $2\text{REEPO}_4\text{-CaTh}(\text{PO}_4)_2\text{-2ThSiO}_4$, discreditation of brabantite, and recognition of cheralite as the name for members dominated by $\text{CaTh}(\text{PO}_4)_2$ // *The Canadian Mineralogist*. 2007. Vol. 45(3). P. 503–508. <http://dx.doi.org/10.2113/gscanmin.45.3.503>
5. Шагалов Е. С., Степанов С. Ю., Веретенникова Т. Ю. К минералогии Берёзовского золоторудного месторождения (Средний Урал): сульфиды и минералы тория и урана // *Уральская минералогическая школа*. 2018. № 24. С. 252–259.
6. Азовскова О. Б., Ровнушкин М. Ю., Байрамгалина Л. Н., Гемель В. А. Урановая и ториевая минерализация в рудах Михеевского медно-порфирирового месторождения, Южный Урал // *Металлогения древних и современных океанов*. 2019. № 1. С. 114–117.
7. Mills S. J., Birch W. D., Maas R., Phillips D., Plimer I. R. Lake Boga Granite, northwestern Victoria: mineralogy, geochemistry and geochronology // *Australian Journal of Earth Sciences: An International Geoscience Journal of the Geological Society of Australia*. 2008. Vol. 55. Issue 3. P. 281–299. <https://doi.org/10.1080/08120090701769449>
8. Государственная геологическая карта Российской Федерации. Масштаб 1:1 000 000 (новая серия). Лист О-40, (41): объяснит. записка. Екатеринбург: Уралгеолком, УГСЭ, 1997. 252 с.
9. Смирнов В. Н. Габбро-гранитоидные серии Восточной зоны Урала // *Докл. АН СССР*. 1981. Т. 259. № 6. С. 1453–1457.
10. Эвгеосинклинальные габбро-гранитоидные серии / Г. Б. Ферштатер [и др.]. М.: Наука, 1984. 264 с.
11. Лобова Е. В. Силурийский интрузивный магматизм Восточной зоны Среднего Урала: автореф. дис. ... канд. геол.-минерал. наук. СПб: НМСУ «Горный», 2013. 20 с.
12. Смирнов В. Н., Иванов К. С., Ронкин Ю. Л., Серов П. А., Гердес А. Изотопный состав Sr, Nd и Hf в породах Рефтинского габбро-диорит-тоналитового комплекса (Восточный склон Среднего Урала): петрологические и геологические следствия // *Геохимия*. 2018. № 6. С. 499–513.
13. Смирнов В. Н., Наставко Е. В., Иванов К. С., Баянова Т. Б., Родионов Н. В., Серов П. А. Результаты изотопного датирования пород Рефтинского габбро-диорит-тоналитового комплекса, Восточная зона Среднего Урала // *Литосфера*. 2014. № 5. С. 3–18.
14. Ферштатер Г. Б., Краснобаев А. А., Беа Ф., Монтеро П., Бородин Н. С., Холоднов В. В., Зинькова Е. А., Шардакова Г. Ю., Прибавкин С. В. Этапы палеозойского интрузивного магматизма Уральского орогена и их геодинамическая интерпретация // *Геодинамика, магматизм, метаморфизм и рудообразование: сборник науч. трудов*. Екатеринбург: ИГГ УрО РАН, 2007. С. 89–120.
15. Казаков И. И., Стороженко Е. В., Харитонов И. Н., Стефановский В. В., Кошевой Ю. Н., Козьмин С. В., Мартынов С. Э., Фадеечева И. Ф., Ронкин Ю. Л., Лукин В. Г. Государственная геологическая карта Российской Федерации масштаба 1:200 000 (изд. 2-е). Сер. Средне-Уральская. Лист О-41-XXVI (Асбест): объяснит. записка. СПб: Картограф. фабрика ВСЕГЕИ, 2017. 284 с.
16. Szuszkiewicz A., Pieczka A., Gołębiewska B., Dumańska-Słowik M., Marszałek M., Szełęg E. Chemical Composition of Mn- and Cl-Rich Apatites from the Szklary Pegmatite, Central Sudetes, SW Poland: Taxonomic and Genetic Implications // *Minerals*. 2018. Vol. 8(8). P. 1–21. <https://doi.org/10.3390/min8080350>

Статья поступила в редакцию 20 января 2023 года