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Monazite from lithium-bearing pegmatites of the Lipovskoye vein field, Middle Urals (composition and chemical dating)

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Abstract

The relevance of the research is due to the need to improve the method of chemical dating as applied to high-thorium accessory minerals, which are difficult to study by isotope research methods.
Purpose of the research is to study the chemical composition of monazite from lithium-bearing granite pegmatites of the Lipovskoye vein field and to determine their age.
Research methodology. The quantitative analysis of the chemical composition of monazite was performed on a CAMECA SX 100 electron probe microanalyzer (IGG UB RAS, Ekaterinburg). Measurement conditions: accelerating voltage 15 kV, current strength 250 nA, electron beam diameter 2 µm. The pressure in the sample chamber is $2 \cdot 10^{-4}$ Pa. The spectra were obtained on tilted wave spectrometers, the intensity was measured using analytical lines: Th *Ma*, U *Mb*, Pb *Ma*, Y *La*, Si *Ka*, Ca *Ka*, P *Ka*, Ce *La*, La *La*, Pr *Lb*, Nd *La*, Sm *Lb*, Dy *La*, Gd *Lb*. Standard samples: ThO_2, UO_2, $Pb_2P_2O_7$, diopside, synthetic rare-earth phosphates. The intensity measurement time at the peak for Th is 180 s, U is 100 s, and Pb is 500 s (240 s on one and simultaneously 260 s on another spectrometer), for Y and Si 20 s each, for the other elements 10 s; on the background – two times less. The detection limits for Th, U, and Pb in monazite are 290, 350, and 64 ppm, respectively. The oxygen content was determined under the assumption of the stoichiometry of the composition.
Results. It has been established that monazite belongs to the cerium variety and is characterized by high contents of thorium (ThO_2 up to 23.6 wt. %) and uranium (UO_2 up to 2.5 wt. %). At the same time, cheralite-type isomorphism is realized in phosphate. In a closed Th–U–Pb-system (β = 0.92–0.97), according to the results of chemical dating (according to 20 analyses), monazite-(Ce) shows a weighted average age of 243 ± 7 Ma. When plotting the dependence ($ThO_2 + UO_2^{eq}$) – PbO, the points fall on one isochrone. Calculation of the age from the slope of the isochron gave a dating of 242 ± 17 Ma, MSWD = 0.21, probability = 1.00.
Conclusion. It has been established that accessory monazite from lithium-bearing granitic pegmatites of the Lipovskoye vein field (Middle Urals) is of Triassic age. Apparently, this dating shows the time of the secondary transformation of lithium-bearing granitic pegmatites, which are often tectonized, and in some places even boudinaged.

Keywords**:** monazite-(Ce), lithium-bearing granitic pegmatites, chemical dating, Lipovskoye vein field, Middle Urals.

Introduction

Granite pegmatites of the Lipovskoe vein field are located on the eastern slope of the Middle Urals (70 km northeast of Ekaterinburg and 5 km west of the village of Lipovskoye). The world-famous and already developed manifestation of pink tourmalines (rubellites) is associated with them. Pegmatites are confined to a gently sloping synclinal structure sandwiched between three large granite massifs – Murzinsky (from the northwest), Aduisky (from the southwest) and Sokolovsky (from the east). The syncline itself is composed of metamorphic rocks of the Proterozoic age, which is dominated by various gneisses, shales, and amphibolites [1, 2]. Separate bodies of serpentinites and marbles are also noted here, which are usually tectonically interspersed with each other in the melange zone. The well-known and also depleted Lipovskoye deposit of silicate-nickel ores is associated with karst marbles and weathering crusts of serpentinites. Granite vein bodies are widespread within the Lipovskoye pegmatite field and are usually represented by intragranite, lithium-bearing and plagioclasite (desilitic) types. Moreover, the latter develop and replace intragranitic pegmatites, which cut through blocks of serpentinites. Despite the abundance of lithium-bearing veins in this area and their relatively good mineralogical state of knowledge [2–6], it turned out that no age dating was given for them.

Structure and zoning of lithium-bearing pegmatites of Lipovskoye

Lithium-bearing pegmatites within the Lipovskoye vein field occur exclusively in serpentinites. The dip angle of different veins of this type, as a rule, varies from 40° to 90°, and their thickness varies from 0.3 to 1.5 m, and these bodies are often subject to tectonic influences. In the described

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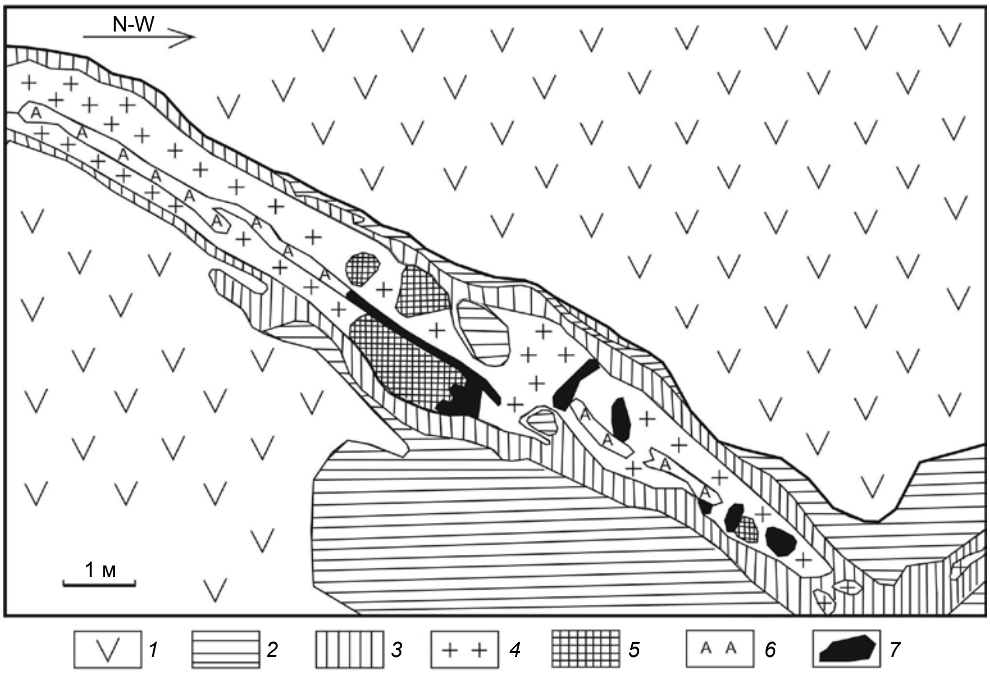

Figure 1. Structure of the Toporkov pegmatite vein (according to [7] with our additions): *1* – serpentinite; 2 – disintegrated serpentinite; *3* – zone of quartz-muscovite-montmorillonite aggregate; *4* – fine- and medium-pegmatoidal pegmatite (with individuals up to 10 cm); *5* – block microcline; *6* – quartz-muscovite-albite aggregate; *7* – lepidolite-albite aggregate

Рисунок 1. Строение пегматитовой жилы Топоркова (по [7] с нашими дополнениями): *1* – серпентинит; *2* – дезинтегрированный серпентинит; *3* – зона кварц-мусковит-монтмориллонитового агрегата; *4* – пегматит мелко- и среднепегматоидный (с индивидами до 10 см); *5* – блоковый микроклин; *6* – кварц-мусковит-альбитовый агрегат; *7* – лепидолит-альбитовый агрегат

lithium-bearing veins, the following zones are distinguished (from the periphery to the center): 1. Fine pegmatoid microcline-albite with individuals up to 5 cm; 2. Medium pegmatoid microcline-albite with individuals up to 10 cm; 3. Small-block microcline (microcline-perthite); 4. Lepidolite-albite; 5. Granular albite; 6. Small block quartz. The selected zones are very unevenly distributed along the veins. If the first zone can be traced along the strike of the veins quite constantly, then the rest of the zones are distinguished in separate joints of the veins, which have a large thickness. The shape of these zones is nests and lenses. Another fifth zone, usually located in the center of the vein, can be traced more or less often.

Below is a detailed description of two veins of this type of pegmatite.

The Toporkov vein occupies the western part of the Sherlovaya Kop manifestation, which has been mined since the discovery of rubellites at Lipovskoye. This is the only vein described more or less in detail in the literature [2]. Pegmatite has a lenticular structure with the development of an aplitoid microcline–albite aggregate at the edges, and block zones of quartz, microcline, and a lepidolite–albite aggregate with disseminated elbaite are noted in the center (fig. 1).

The described vein was complicated by late tectonic movements, as a result of which a lenticular structure arose. The general strike of the vein is meridional with a bend of its northern end to the northwest, and the southern end to the south-southeast. The total length of the vein, counting with the pinch sections, is 42 m. The western dip is 43–50°. The maximum thickness of the vein is 1.5 m, the average is 1.0 m. The wedging out of the vein along the strike is gradual and, at the same time, it branches into several apophyses, traced in the form of lenses and nests in the near-contact quartz-muscovite-montmorillonite rock. The vein is wedged out in the fall and in the uprising. Its contacts with host rocks are sharp and tectonic. Here, relics of host rocks of various shapes are often wedged into the body of the vein.

The Sibiryachka vein was discovered in 2005 in the western part of the northern quarry (no. 6 according to the numbering of the former Lipovskoye mine). It is represented by a pegmatite vein, having a plate-like shape, the thickness of the body does not exceed 30–40 cm, with a northeast strike and a dip at an angle of 60° to the northwest (fig. 2).

Several cavities with pink tourmalines and blue topazes were unearthed in the vein. The pegmatite has a rather distinct albeit asymmetric zoning (fig. 3). Three zones were distinguished in it from the edge to the center: pegmatoid (with a crystal size of 5–10 cm), block (with significant albitization of potassium feldspar), and central with lepidolite-albite aggregate. The central zone was characterized by the development of cavities with semiprecious mineralization. But, as in the Toporkov vein, the identified zones are very unevenly and fragmentarily distributed within the entire vein body.

At the moment, within the Lipovskoye ore field, only three lithium-bearing pegmatites are available for study, two veins have spoil heaps of a nickel mine, and about a dozen veins, uncovered in the sides of quarries, went under water when the workings were flooded. Thus, in the Lipovskoye vein field, in a relatively small area of several km^2, there is a significant accumulation of lithium-bearing pegmatites, the potential ore content of which has yet to be assessed.

Figure 2. Appearance of the Sibiryachka pegmatite vein at the time of development. Quarry no. 6, Lipovskoye vein field. Photo by M. P. Popov, 2005

Рисунок 2. Внешний вид пегматитовой жилы Сибирячка в момент разработки. Карьер № 6, Липовское жильное поле. Фото М. П. Попова, 2005 г.

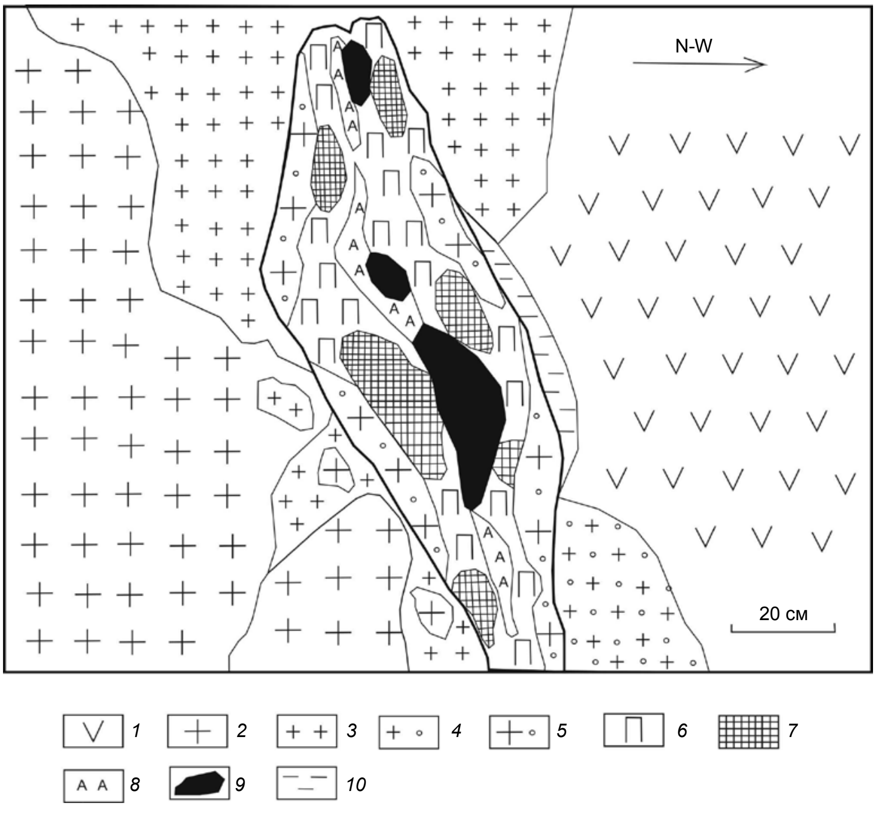

Figure 3. Scheme of the structure of the pegmatite vein Sibiryachka (according to the oral description of S. Z. Smirnov provided in the Rezhevsky reserve) with simplifications of the authors: *1* – serpentinite; *2* – medium to coarse-grained pegmatite; *3* – fine-grained two-mica gneissic leucogranite; *4* – granite-aplite with garnet, tourmaline and muscovite; *5* – fine pegmatoidal pegmatite (with individuals up to 5 cm) with schorl, muscovite, garnet and blue beryl; *6* – medium pegmatoidal pegmatite (with individuals up to 10 cm), mineral composition is the same as in the previous zone, but lepidolite and verdelite occur and in some places with albitization of potassium feldspar; *7* – block pegmatite (mineral composition, as in the previous zone, but with more significant albitization of potassium feldspar); *8* – quartz-mica-albite complex; *9* – quartz-lepidolite-albite complex with miarols (the latter include topaz, albite, colored tourmaline, quartz, potassium feldspar, lepidolite); *10* – chlorite-phlogopite rock

Рисунок 3. Схема строения пегматитовой жилы Сибирячка (по устному описанию С. З. Смирнова, предоставленному в Режевской заказник) с упрощениями авторов: *1* – серпентинит; *2* – пегматит от средне- до крупнозернистого; *3* – мелкозернистый двуслюдяной гнейсовидный лейкогранит; *4* – гранит-аплит с гранатом, турмалином и мусковитом; *5* – пегматит мелкопегматоидный (с индивидами до 5 см) с шерлом, мусковитом, гранатом и голубым бериллом; *6* – пегматит среднепегматоидный (с индивидами до 10 см), минеральный состав, как и в предыдущей зоне, но встречаются лепидолит и верделит и местами с альбитизацией КПШ; *7* – блоковый пегматит (минеральный состав, как и в предыдущей зоне, но с более существенной альбитизацией КПШ); *8* – кварц-слюдисто-альбитовый комплекс; *9* – кварц-лепидолит-альбитовый комплекс с миаролами (в состав последних входят топаз, альбит, цветной турмалин, кварц, КПШ, лепидолит); *10* – хлорит-флогопитовая порода

Research methodology

Quantitative analysis of the chemical composition of monazite was carried out on a CAMECA SX 100 electron probe microanalyzer (IGG UB RAS, Ekaterinburg). Polished sections were made from pieces of rock, then sprayed with a thin layer of carbon. Measurement conditions: accelerating voltage 15 kV, current strength 250 nA, electron beam diameter 2 μm. The pressure in the sample chamber is $2 \cdot 10^{-4}$ Pa. The spectra were obtained on tilted wave spectrometers, the intensity was measured using analytical lines: Th *Ma*, U *Mb*, Pb *Ma*, Y *La*, Si *Ka*, Ca *Ka*, P *Ka*, Ce *La*, La *La*, Pr *Lb*, Nd *La*, Sm *Lb*, Dy *La*, Gd *Lb*. Standard samples: ThO_2, UO_2, $Pb_2P_2O_7$, diopside, synthetic rare-earth phosphates. The intensity measurement time at the peak for Th is 180 s, U is 100 s, and Pb is 500 s (240 s on one and simultaneously 260 s on another spectrometer), for Y and Si 20 s each, for the other elements 10 s; on the background - two times less. The detection limits for Th, U, and Pb in monazite are 290, 350, and 64 ppm, respectively. The oxygen content was determined under the assumption of the stoichiometry of the composition. The theoretical and practical substantiation of the chemical dating method using X-ray microprobe analysis is given in numerous publications on this topic [8, 9], including one of the authors [10, 11]. The main condition of this method is that the mineral did not lose radiogenic lead during evolution (i. e., the Th–U–Pb system was closed), all lead in the mineral was formed due to the decay of thorium and uranium.

Results and discussion

Accessory monazite is often found in lithium-bearing granitic pegmatites of the Lipovskoye vein field. Rare earth phosphate forms euhedral crystals, about 100 μm in length, often having radioactive yards in the form of a cheralite rim, and is located in the interstices of tourmaline (elbaite) grains in a lepidolite "boiler" (fig. 4). According to the chemical composition, rare earth phosphate belongs to the cerium variety (table 1) and is characterized by high contents of thorium (ThO_2 up to 23.6 wt. %) and uranium (UO_2 up to 2.5 wt. %). It is known that for thorium and uranium impurities in monazite, the huttonite ($Th^{4+}(U^{4+}) + Si^{4+} \rightarrow REE^{3+} + P^{5+}$) and (or) cheralite ($Th^{4+}(U^{4+}) + Ca^{2+}(Sr^{2+}, Ba^{2+}, Pb^{2+}) \rightarrow 2REE^{3+}$) type of isomorphism is realized. From the available analyzes of the chemical composition of monazite, it can be argued that the cheralite type of isomorphism is realized in phosphate.

Table 1. Chemical composition of monazite from Li-bearing veins of Lipovskoye wt. %
Таблица 1. Химический состав монацита из литиеносных жил Липовки, мас. %

Oxides	Analysis number									
	1	2	3	4	5	6	7	8	9	10
P_2O_5	30,37	30,37	30,23	30,20	29,85	30,08	29,90	29,86	29,90	30,09
ThO_2	22,20	21,06	19,75	20,92	21,04	20,12	20,16	19,79	20,54	19,86
UO_2	2,37	2,39	2,54	2,15	2,07	2,48	1,91	1,90	2,45	2,52
SiO_2	0,33	0,36	0,38	0,43	0,40	0,40	0,39	0,36	0,41	0,40
Ce_2O_3	15,68	15,95	16,06	16,81	17,08	15,73	17,52	18,14	15,67	16,03
La_2O_3	6,23	6,13	6,15	6,88	7,06	6,24	7,29	7,30	6,21	6,22
Nd_2O_3	7,15	7,34	7,52	7,39	7,31	7,47	7,53	7,44	7,44	7,48
Pr_2O_3	1,88	2,10	2,13	2,09	2,12	2,15	2,21	2,21	2,09	2,01
Sm_2O_3	3,84	4,07	4,27	3,69	3,66	4,10	3,69	3,79	3,89	3,97
Gd_2O_3	2,53	2,61	2,76	2,30	2,07	2,65	2,24	2,16	2,66	2,91
Dy_2O_3	0,73	0,90	1,01	0,73	0,70	0,92	0,72	0,69	0,89	0,97
Y_2O_3	2,38	2,60	2,89	1,99	1,97	2,90	1,90	1,90	2,80	2,93
PbO	0,31	0,30	0,29	0,28	0,28	0,28	0,27	0,27	0,29	0,29
CaO	4,67	4,28	4,14	4,35	4,35	4,25	4,19	4,13	4,21	4,17
Total	100,67	100,47	100,11	100,21	99,93	99,77	99,91	99,92	99,44	99,85
Oxides	Analysis number									
	11	12	13	14	15	16	17	18	19	20
P_2O_5	30,22	30,05	29,91	30,02	29,74	29,55	29,47	29,78	29,62	30,09
ThO_2	22,43	22,36	21,97	22,32	22,45	21,97	19,99	21,31	23,60	19,71
UO_2	2,40	2,37	2,34	2,38	2,27	2,29	1,95	1,95	2,19	2,53
SiO_2	0,35	0,35	0,36	0,35	0,50	0,36	0,38	0,44	0,52	0,39
Ce_2O_3	15,55	15,48	15,69	15,30	15,40	15,88	17,82	16,70	14,89	16,11
La_2O_3	5,85	6,18	6,15	6,07	6,00	6,32	7,23	7,13	6,07	6,30
Nd_2O_3	7,03	6,92	7,09	7,14	7,15	7,15	7,53	7,32	6,94	7,59
Pr_2O_3	1,92	2,04	1,94	1,86	1,98	2,00	2,04	1,88	1,99	2,00
Sm_2O_3	3,69	3,85	3,68	3,58	3,88	3,52	3,91	3,56	3,69	4,03
Gd_2O_3	2,39	2,50	2,37	2,36	2,65	2,33	2,18	2,32	2,37	2,94
Dy_2O_3	0,83	0,77	0,72	0,80	0,82	0,83	0,77	0,70	0,73	0,91
Y_2O_3	2,37	2,40	2,30	2,35	2,55	2,26	1,94	1,98	2,20	2,92
PbO	0,31	0,32	0,30	0,30	0,31	0,30	0,26	0,28	0,31	0,29
CaO	4,66	4,63	4,59	4,64	4,45	4,59	4,14	4,45	4,73	4,18
Total	100,01	100,20	99,43	99,47	100,16	99,36	99,62	99,80	99,85	100,00

Note: IGG UB RAS, CAMECA SX 100 microanalyzer, analyst V. V. Khiller.

In the well-known work [12], the parameter $\beta = (Si + Ca)/(Th + U + Pb)$, which characterizes the degree of charge compensation of $Th^{4+}(U^{4+})$ impurities, was considered as an indicator of the closedness of the Th–U–Pb system of monazite: when it is close to unity, the system is considered closed. For monazite from lithium-bearing veins, the parameter $\beta = 0.92–0.97$, which indicates the closed nature of the system and means the possibility of a correct assessment of the age of the mineral.

According to the results of chemical dating (according to 20 analyses), monazite-(Ce) shows a weighted average age of 243 ± 7 Ma, MSWD = 0.09, probability = 1.00 (fig. 5, *a*). When plotting the dependence ThO_2^*–PbO, the points fall on one isochrone. Here $ThO_2^* = (ThO_2 + UO_2^{eq})$, where UO_2^{eq} is the uranium content recalculated to the equivalent thorium content capable of producing the same amount of lead during the lifetime of the system if the U–Pb and Th–Pb age values are equal. Calculation of the age from the slope of the isochron gives a dating of 242 ± 17 Ma, MSWD = 0.21, probability = 1.00 (fig. 5, *b*).

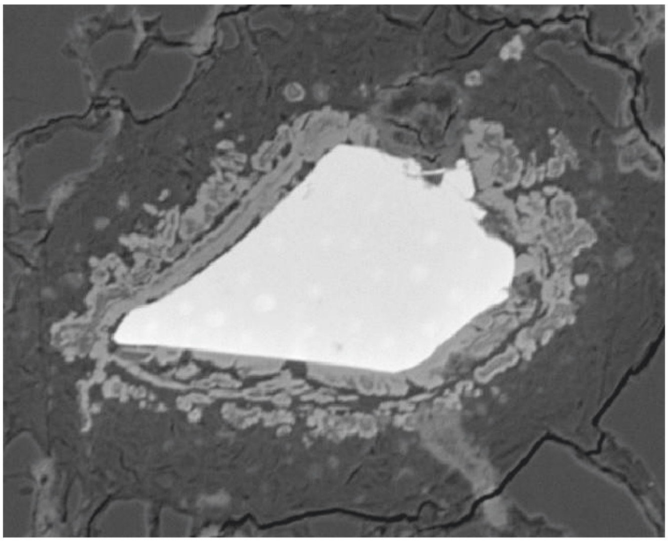

Figure 4. An individual of monazite-(Ce), up to 200 μm in size, with a rim composed of a cheralite aggregate. BSE photo, CAMECA SX 100
Рисунок 4. Индивид монацита-(Се) размером до 200 мкм с оторочкой, сложенной агрегатом чералита. BSE-фото, CAMECA SX 100

As mentioned above, no dating of the Lipovskoye lithium-bearing pegmatites has been carried out so far. In most cases, the issue of age was not even discussed in publications [2], and in some works it was casually indicated that pegmatites are related to the surrounding Upper or Late Paleozoic granites [5]. Relatively recently, we obtained the age of formation of the most common classical granite pegmatites in the Lipovskoye vein field. A three-mineral (by monazite, uraninite, and coffinite) isochrone of 266.4 ± 2.6 Ma was constructed for them using the chemical dating method [11]. At the same time, it is obvious that the lithium-bearing pegmatites of the Lipovskoye vein field were formed somewhat later than the classical granitic pegmatites, the formation of which took place in the Middle Permian. This follows not only from the obtained geochronological data, but also from visual geological observations, where it is clear that vertically lying lithium-bearing pegmatites often “rest” against screening gently sloping classical pegmatites.

Our dating of accessory monazite (243 ± 7 Ma) is somewhat surprising, since it is believed that magmatism did not exist in this area later than 255–250 Ma [13]. In addition, recently, we presented the first data on argon-argon dating of the same Li-bearing pegmatites of Lipovskoye, which showed an age of 254 Ma [14]. Apparently, the Triassic dating of monazite shows the time of the secondary transformation of lithium-bearing granitic pegmatites, which are often tectonized, and in some places even boudinaged. Within the Murzinsko-Aduisky complex, pegmatites often contain not only Permian dates, but also Triassic ages [15, 16]. It is likely that they arose as a result of tectonic-magmatic activation, the influence of which was widely manifested due to the large Susansky tectonic fault, framing most of the eastern contact of the Aduisky and Murzinsky granite massifs. In any case, the Triassic ages of

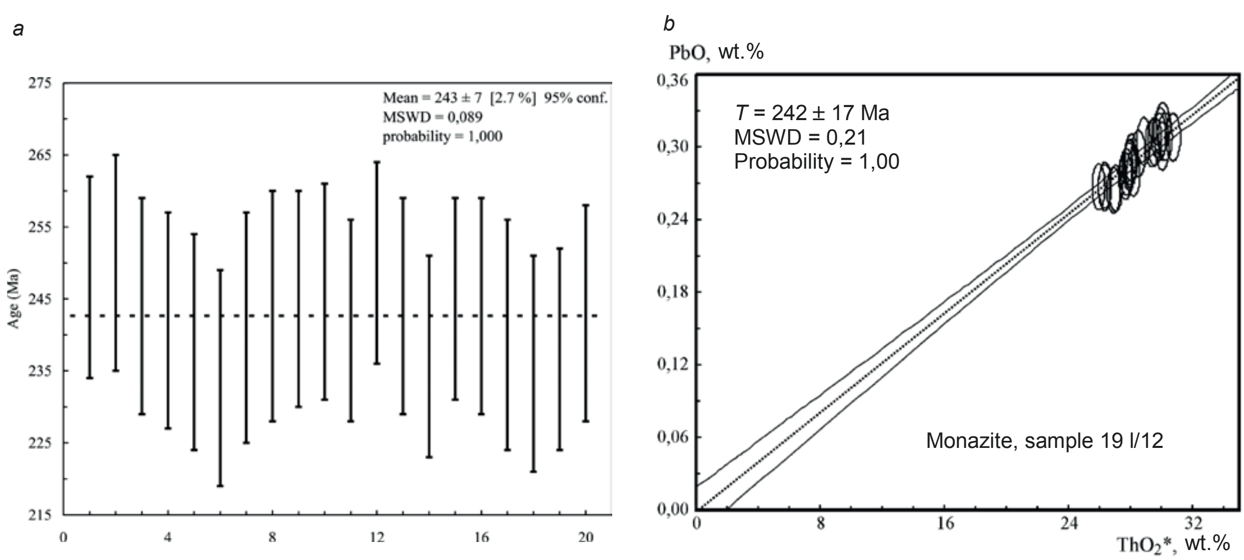

Figure 5. Weighted average age (*a*) and isochrone (*b*) for monazite
Рисунок 5. Средневзвешенный возраст (*а*) и изохрона (*б*) по монациту

rocks or minerals for a given study area were often mentioned in various publications [16–18].

Conclusions

Thus, we have studied in detail accessory monazite from lithium-bearing granitic pegmatites of the Lipovskoye vein field (Middle Urals). According to the chemical composition, the mineral belongs to monazite-(Ce). Using chemical dating, point U–Th–Pb ages of monazite were obtained, which together give a weighted average age of 243 ± 7 Ma (MSWD = 0.09) and an isochrone of 242 ± 17 Ma (MSWD = 0.21). Apparently, this Triassic date indicates the time of the secondary transformation of lithium-bearing granitic pegmatites, which are often tectonized, and in some places even boudinaged.

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Монацит из литиеносных пегматитов Липовского жильного поля, Средний Урал (состав и химическое датирование)

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Аннотация

Актуальность работы обусловлена необходимостью совершенствования метода химического датирования в применении к высокоториевым акцессорным минералам, которые сложно изучать изотопными методами исследования.

Цель работы – исследование химического состава монацита из литиеносных гранитных пегматитов Липовского жильного поля и определение их возраста.

Методология исследования. Количественный анализ химического состава монацита выполнен на электронно-зондовом микроанализаторе CAMECA SX 100 (ИГГ УрО РАН, г. Екатеринбург). Условия измерения: ускоряющее напряжение 15 кВ, сила тока 250 нА, диаметр пучка электронов 2 мкм. Давление в камере образцов $2 \cdot 10^{-4}$ Па. Спектры получены на наклонных волновых спектрометрах, измерение интенсивности проводились по аналитическим линиям: Th *Ma*, U *Mb*, Pb *Ma*, Y *La*, Si *Ka*, Ca *Ka*, P *Ka*, Ce *La*, La *La*, Pr *Lb*, Nd *La*, Sm *Lb*, Dy *La*, Gd *Lb*. Стандартные образцы: ThO_2, UO_2, $Pb_2P_2O_7$, диопсид, синтетические фосфаты РЗЭ. Время измерения интенсивности на пике для Th – 180 с, U – 100 с и Pb – 500 с (240 с на одном и одновременно 260 с на другом спектрометре), для Y и Si по 20 с, для остальных элементов 10 с; на фоне – в два раза меньше. Пределы обнаружения Th, U и Pb в монаците 290, 350 и 64 г/т соответственно. Содержание кислорода определялось в предположении о стехиометрии состава.

Результаты. Установлено, что монацит относится к цериевой разновидности и характеризуется высокими содержаниями тория (ThO_2 до 23,6 мас. %) и урана (UO_2 до 2,5 мас. %). При этом в фосфате реализуется чералитовый типа изоморфизма. В замкнутой Th–U–Pb-системе (β = 0,92–0,97) по результатам химического датирования (по данным 20 анализов) монацит-(Ce) показывает средневзвешенный возраст 243 ± 7 млн лет. При построении зависимости ($ThO_2 + UO_2^{экв}$)–PbO точки ложатся на одну изохрону. Расчет возраста по углу наклона изохроны дал датировку 242 ± 17 млн лет, СКВО = 0,21, вероятность равна 1,00.

Выводы. Установлено, что акцессорный монацит из литиеносных гранитных пегматитов Липовского жильного поля (Средний Урал) имеет триасовый возраст. По всей видимости, эта датировка показывает время вторичного преобразования литиеносных гранитных пегматитов, которые часто тектонизированы, а местами даже разлинзованы.

***Ключевые слова*:** монацит-(Ce), литиеносные гранитные пегматиты, химическое датирование, Липовское жильное поле, Средний Урал.

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