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Distribution of lanthanides in amphibole and plagioclase from plagioclasites of the Ray-Iz massif (Polar Urals)

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Relevance. This work shows the results of mineralogical, petrographic, and geochemical studies of plagioclasites localized among chromite-bearing ultramafic rocks of the Ray-Iz massif (Polar Urals). The spatial confinement of plagioclasites to the Tsentralnoye chrome ore deposit (corundum-bearing plagioclasites) and the Yugo-Zapadnoye IV ore occurrence (plagioclasites without corundum) determine the need for a detailed study of the rocks of the vein series of chromite-bearing sections.
The purpose of the work. The study of mineralogical and petrographic characteristics, as well as the geochemistry of lanthanides in plagioclase and amphibole from plagioclasites of the Ray-Iz massif (Polar Urals).
Results. In view of the results of microprobe analysis, it was found that the compositions of amphibole in plagioclasites vary considerably in accordance with the modern classification of calcium amphiboles, pargasite, edenite, magnesiohornblende and actinolite. Two types of zoning are determined in amphibole. Amphibole grains with zoning of the first type are characterized by an increase in the contents of Al_2O_3, TiO_2, FeO, Na_2O from the center toward the periphery of the grains; when zoning of the second type, on the contrary, there is a decrease in these components. The chemical composition of plagioclase corresponds to oligoclase $An_{10–30.1}$. The decrease in the content of the anorthite molecule from the center to the edge of the grain was noted. The study of nature of the distribution of REE in rock-forming minerals made it possible to determine that amphibole is the main mineral concentrator of lanthanides in plagioclasites: the total REE content in the mineral is 250–450 ppm, while 16–18 ppm of lanthanides are concentrated in the plagioclase. It was established that the reason for the existence of two types of distribution spectra of lanthanides identified earlier is the ratio of the total amount of amphibole and plagioclase in the rock. The distribution of rare-earth elements in calcic amphiboles from plagioclasites is compared with the distribution of REEs in the amphiboles of the Nyurundukansky mafic complex in the North-Western Baikal region, the studies of which were carried out by S. G. Skublov. Using the amphibole-plagioclase geothermometer by T. Holland, J. Blundy and geobarometer by M. W. Schmidt parameters of amphibole plagioclasites formation were determined.
Conclusion. The nature of the distribution of lanthanides in the main rock-forming minerals – plagioclase and amphibole – is found. The comparison of parameters and compositional characteristics of amphiboles allowed us to conclude that there is a direct relationship between temperature, the sum of REE and TiO_2 in the mineral.

Keywords: amphibole, plagioclase, plagioclasite, REE, Ray-Iz, Polar Urals.

Introduction

The Ray-Iz ultramafic massif is one of the largest in the Urals and is located at the base of the crust-mantle section of the Voykarskaya Paleozoic paleo-island arc zone overriding the main Ural deep fault to the edge of the Eastern European continent [1].

Plagioclasite bodies are found among chromite-bearing ultramafites of the massif – plagioclasites without corundum and corundum-bearing ones [1–3]. Both types of plagioclasites form a vein series in the rocks of the dunite-harzburgite complex.

A brief history of the study of plagioclasites

Corundum-bearing plagioclasites are known in the southwestern part of the chrome ore deposit called Tsentral'noye. They compose the well-known occurrence of corundum mineralization called Rubinovy Log, and have been attracted the attention of researchers due to the unique ruby mineralization. Corundums and host rocks were first described by V. P. Sorokin and B. V. Perevozchikov in 1973 [4]. Single microprobe analyses of rock-forming minerals of phlogopite plagioclasites from the Rubinovy Log occurrence were first published by N. I. Bryanchaninova and A. B. Makeev with co-authors [5]. Zoning in the structure of rocks with ruby mineralization was described by S. V. Shcherbakova. She has investigated the composition of minerals, and concluded about the genetic relationship of plagioclase rocks and their host ultramafites [6, 7].

The study of the composition and age of plagioclasites, both corundum-bearing and corundum-free in recent years [1–3] allowed to establish the existence of two types of distribution spectra of rare earth elements in them. At the same time, the question of the content of rare earths in amphiboles and plagioclases, the main rock-forming minerals of plagioclasites, remained open. In this paper, we studied the chemical composition of minerals and the nature of the distribution of lanthanides in plagioclase and amphibole; it is concluded that there are two REE distribution spectra in plagioclasites.

Chemical composition and zoning of rock-forming minerals

Microprobe analysis of minerals was performed in the laboratory of physical and chemical research methods at the Institute of Geology and Geochemistry, Ural Branch of the Russian Academy of Sciences (Ekaterinburg, the analyst is V. V. Khiller) using the electronic probe microanalyzer CAMECA SX 100.

In view of the results of microprobe analysis, it was found that the compositions of amphibole vary considerably in accordance with the modern classification of calcic amphiboles [8, 9], pargasite, edenite, magnesiohornblende and actinolite.

Amphibole grains exhibit chemical zoning. Central parts in amphibole are from plagioclasite without corundum (sample Y-12/1) of the Yugo-Zapadnoe IV ore occurrence of chrome ores. As a rule, they are represented by hornblendite and edenite, and the peripheral ones are represented by a low-alumina, actinolite – a kind of alkalies – poor amphibole. Its Na_2O content is 1.63–2.97 wt.%, and the amount of alumina is in the range of 4.17–9.59 wt.% (Table 1). In addition, there are minor impurities of MnO 0.11–0.26

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wt.%, Cr_2O_3 0.01–0.21 wt.% and TiO_2 0.38–0.76 wt.% in the mineral. Amphibole iron content $f = Fe^{2+} \times 100\% / (Fe^{2+} + Mg)$ varies from 25.33 to 31.67%. Ferruginosity and the content of Al_2O_3, TiO_2, FeO, Na_2O decrease from the center toward the periphery of the grains (analysis points are shown in Fig. 1; Table 1). The chemical composition of plagioclase corresponds to oligoclase $An_{10–24.9}$. The amount of anorthite molecule decreases from the center to the edge of the grain (the analysis points are shown in Fig. 1; Table 2).

In amphibole from amphibole plagioclase without corundum (sample Y-200/1), the inverse zoning is shown. The central parts of the grains are actinolite, and the peripheral parts are hornblendite and edenite. The Na_2O content in the mineral is 1.28–2.66 wt.%, and the amount of alumina varies between 3.46–10.51 wt.%. The mineral contains significant impurities of FeO (6.01–8.35 wt.%), as well as small impurities of TiO_2 (0.2–0.54 wt.%) and Cr_2O_3 (0–0.04 wt.%, that is almost at the detection limit of the device). Ferruginosity of amphibole varies from 15.11 to 23.29%. Ferruginosity and the content of Al_2O_3, TiO_2, FeO, Na_2O increase from the center toward the periphery of the grain. The chemical composition of plagioclase corresponds to oligoclase $An_{14.8–17.7}$.

In amphibolic plagioclase (sample Y-292/2) from the occurrence of corundum mineralization called Rubinovy Log (Tsentralnoye chromium ore deposit), amphibole is in intergrowth with plagioclase (Fig. 2). The central parts of amphibole grains correspond to edenite, and the edge ones correspond to pargasite; some individual actinolite grains are also present. The alumina content in amphibole varies from 3.54 to 15.45 wt.%; Na_2O – from 0.79 to 3.48 wt.%; FeO – 4.73–5.36 wt.%; the amount of Cr_2O_3 is not large and amounts to 0.06–0.18 wt.%. The mineral contains impurities of TiO_2 (0.11-0.15 wt.%). Amphibole ferruginosity in the most aluminiferous varieties (edenite, pargasite) varies from 13.44 to 15.02% and from 11.46 to 12.13% in actinolite. Ferruginosity and Al_2O_3 content, TiO_2, FeO, Na_2O increase toward the periphery. Pargasite is characterized by the highest content of Na_2O and Al_2O_3. The chemical composition of plagioclase corresponds to oligoclase $An_{13.6–30.1}$.

Plagioclase contains BaO impurities in an amount of from 0 to 0.11 wt.%; K_2O (0.02–0.40 wt.%) and SrO, the amount of which in amphibole plagioclasites without corundum (sample Y-12/1, sample Y-200/1) varies from 0 to 0.11 wt.%, and in corundum-bearing amphibole plagioclase (sample Y-292/2) – from 0.98 to 1.26 wt.% (Table 2). Among the regularities in the distribution of chemical elements in plagioclase, it is worth noting an increase in the amount of Na_2O from the central parts of the grains toward the peripheral ones in all the samples studied. The edge parts of the grains are more acidic.

Features of the trace element composition of rock-forming minerals. Geothermobarometry

The study of the trace element composition of the main rock-forming minerals of plagioclase and amphibole in rocks made it possible to establish that amphibole is the main lanthanide-concentrating mineral: the total REE content in the mineral is 250–450 ppm, while 16–18 ppm of lanthanides are concentrated in the plagioclase.

According to the results of the ICP-MS analysis, chondrite (C1) normalization was performed [10] and the behavior of REEs

Table 1. The chemical composition of amphibole from amphibole plagioclasites, wt.%.
Таблица 1. Химический состав амфибола из амфиболовых плагиоклазитов, мас.%.

Sample number	Sample Y-12/1						Sample Y-200/1		Sample Y-292/2	
	1_37 e	1_38 c	2_39 c	2_40 e	3_41 c	3_42 e	5_3 e	5_4 c	13_3 c	13_3 e
SiO_2	50.86	48.54	52.04	51.98	51.25	52.09	50.92	53.53	47.96	46.12
TiO_2	0.59	0.59	0.46	0.60	0.67	0.50	0.43	0.30	0.15	0.12
Al_2O_3	7.98	7.93	5.08	5.25	5.41	4.79	6.44	4.89	13.1	15.45
Cr_2O_3	0.04	0.09	0.04	0.02	0.21	0.01	0.01	0.00	0.09	0.06
FeO	9.92	10.30	10.43	10.35	10.73	10.41	7.53	6.50	4.97	5.36
MgO	14.84	15.62	16.47	16.39	16.11	16.49	16.88	18.08	17.96	17.01
MnO	0.19	0.23	0.18	0.28	0.26	0.22	0.16	0.17	0.11	0.11
CaO	10.46	10.44	10.47	10.76	10.62	10.26	11.72	12.51	11.26	11.51
Na_2O	2.97	2.38	1.77	1.75	1.76	1.71	2.23	1.57	3.11	3.48
K_2O	0.08	0.12	0.06	0.07	0.07	0.07	0.07	0.08	0.16	0.19
Total	97.93	96.24	97.00	97.45	97.09	96.55	96.39	97.63	98.87	99.41
Formula coefficients (rate per 23 oxygen atoms)										
Si	7.24	7.08	7.47	7.44	7.38	7.51	7.31	7.52	6.66	6.41
Ti	0.06	0.07	0.05	0.07	0.07	0.05	0.05	0.03	0.02	0.01
Al	1.34	1.36	0.86	0.89	0.92	0.81	1.09	0.81	2.14	2.53
Al^{IV}	0.76	0.92	0.53	0.56	0.62	0.49	0.69	0.48	1.34	1.59
Al^{VI}	0.58	0.44	0.33	0.32	0.30	0.32	0.40	0.33	0.81	0.94
Cr	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.01	0.01
Fe	1.18	1.26	1.25	1.24	1.29	1.26	0.90	0.76	0.58	0.62
Mg	3.15	3.40	3.53	3.50	3.46	3.54	3.61	3.79	3.72	3.52
Mn	0.02	0.03	0.02	0.03	0.03	0.03	0.02	0.02	0.01	0.01
Ca	1.60	1.63	1.61	1.65	1.64	1.58	1.80	1.88	1.68	1.71
Na	0.82	0.67	0.49	0.49	0.49	0.48	0.62	0.43	0.84	0.94
K	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.03

Notes: e – grain edge; c – grain centre.

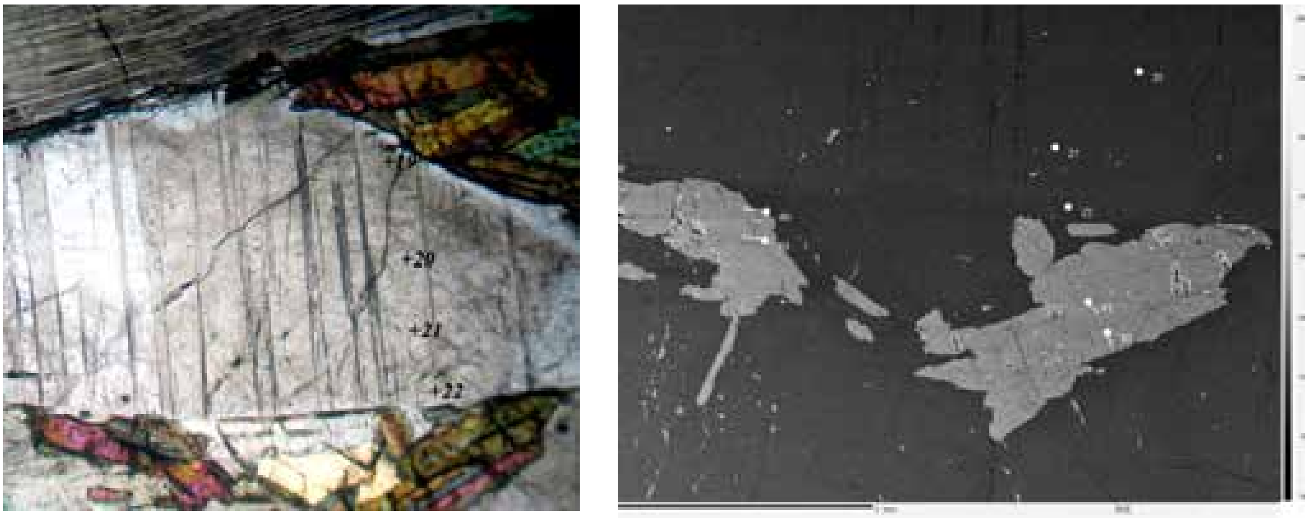

Figure 1. Plagioclase in the intergrowths with amphibole. Sample. Y-12/1. The photo of a thin section with an analyzer is on the left. BSE image is on the right. Analysis points – see Table 1, 2.
Рисунок 1. Плагиоклаз в срастании с амфиболом. Обр. Y-12/1. Слева – фото шлифа с анализатором. Справа – BSE-изображение. Точки анализов – см. табл. 1, 2.

in monomineralic fractions of amphibole and plagioclase from plagioclasites was analyzed. The REE content in amphibole, plagioclase, and in the rock as a whole was determined by ICP-MS analysis at the Institute of Geology, Ural Branch of the Russian Academy of Sciences (Ekaterinburg) and Institute of Minerology of the Ural Branch of the Russian Academy of Sciences (Miass).

Amphiboles and plagioclases of corundum-bearing amphibole plagioclasites (sample Y-292/2) with a distribution spectrum of lanthanides of the first type (Fig. 3, a) are characterized by enrichment with light lanthanides and depletion by heavy ones – the curve has a negative slope for both the main minerals and the rock as a whole.

Amphibole plagioclasites without corundum of the Yugo-Zapadnoye IV ore occurrence of chromite (Fig. 3, b, c) with the distribution spectra of REEs of the second type are characterized by a slight depletion of light lanthanides – the distribution curve for the rock has a sub-horizontal position. If plagioclase, which constitutes more than 90% of the rock thickness, is characterized by enrichment with light lanthanides, then for amphibole contained in plagioclase in an amount of 3 to 10%, the type of REE distribution spectrum is different. In amphibole from plagioclasites without corundum, a significantly lower content of light REEs is observed compared to heavy ones, and a negative europium anomaly is also determined [15] (Fig. 3, b, c).

The analysis of REE distribution in amphiboles depending on the faces of metamorphism was in [11]. When comparing the results of this work with those obtained by S. G. Skublov, a similarity of the REE distribution spectra in the amphiboles of corundum-bearing amphibole plagioclasites is observed (sample Y-292/2), as well as REE spectra of amphiboles formed under granulite facies of metamorphism. Amphiboles from amphibole plagioclasites without corundum are close to the mineral from the rocks of the upper amphibolite facies.

Figure 2. Intergrowth of plagioclase and amphibole (pargasite). Sample. Y-292/2. The photo of a thin section without an analyzer. 100x magnification (1 mm in vertical frame dimension). Am – amphibole, Pl – plagioclase**.**
Рисунок 2. Срастание плагиоклаза и амфибола (паргасита). Обр. Y-292/2. Фото шлифа без анализатора. Увеличение 100х (1 мм по высоте кадра). Am – амфибол, Pl – плагиоклаз.

Table 2. The chemical composition of plagioclase from amphibole plagioclasites, wt.%.
Таблица 2. Химический состав плагиоклаза из амфиболовых плагиоклазитов, мас. %.

Sample number	Sample Y-12/1					Sample. Y-200/1				
	19 e	20 c	21 c	22 e	1_1 c	1_2 e	2_15 e	2_16 e	2_17 c	2_18 c
SiO_2	66.47	61.53	62.31	64.28	64.33	65.01	64.27	64.49	64.50	64.21
TiO_2	0.00	0.00	0.01	0.00	0.03	0.02	0.00	0.00	0.01	0.03
Cr_2O_3	0.03	0.48	0.01	0.04	0.01	0.03	0.05	0.01	0.01	0.00
Al_2O_3	20.86	22.97	23.02	22.47	22.34	22.10	21.95	21.99	21.98	22.32
FeO	0.09	0.03	0.07	0.01	0.00	0.04	0.02	0.05	0.05	0.04
CaO	2.09	5.13	4.97	3.87	3.51	3.18	3.44	3.43	3.57	3.69
Na_2O	10.64	8.44	8.84	9.47	9.60	9.61	9.80	9.68	9.54	9.43
K_2O	0.05	0.07	0.07	0.06	0.05	0.40	0.03	0.04	0.05	0.06
SrO	0.06	0.07	0.07	0.00	0.09	0.04	0.04	0.11	0.08	0.09
BaO	0.00	0.00	0.00	0.03	0.00	0.00	0.03	0.00	0.01	0.00
Total	100.34	98.75	99.42	100.26	100.00	100.44	99.63	99.82	99.80	99.88
Formula coefficients (per 5 cations)										
Si	2.91	2.77	2.78	2.83	2.84	2.86	2.84	2.85	2.86	2.84
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	1.08	1.22	1.21	1.17	1.16	1.15	1.15	1.15	1.15	1.16
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.10	0.25	0.24	0.18	0.17	0.15	0.16	0.16	0.17	0.18
Na	0.90	0.74	0.76	0.81	0.82	0.82	0.84	0.83	0.82	0.81
K	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
An., %	10.0	24.9	23.9	18.3	16.8	15.1	16.5	16.5	17.2	17.7

Notes: e – grain edge; c – grain centre.

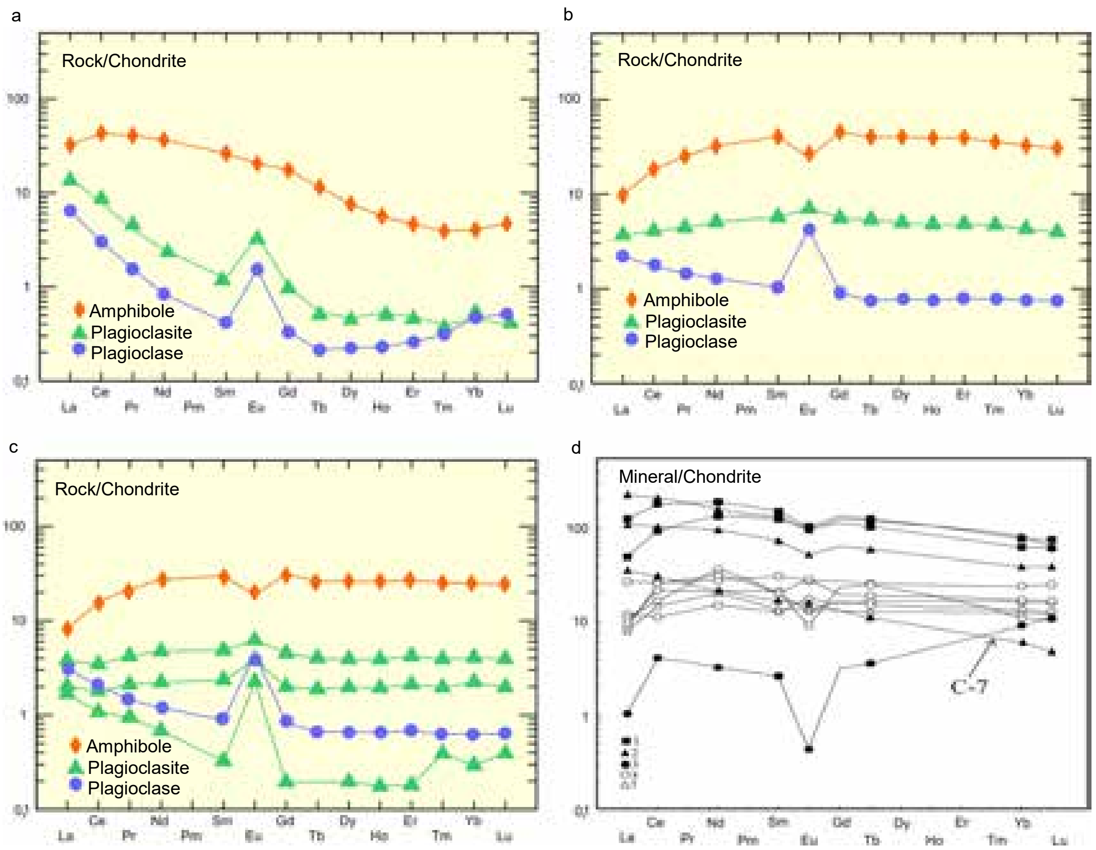

Figure 3. REE distribution spectra in plagioclasites and main rock-forming minerals. a – sample Y-292/2 – amphibole plagioclasite (Tsentralnoye deposit); b – sample Y-12/1– amphibole plagioclasite (Yugo-Zapadnoe IV); c – sample Y-200/1– amphibole plagioclasite (Yugo-Zapadnoe IV); d – mafic complex of the northwestern Baikal region [11]. Amphibole compositions are shown. 1 – kaersutites, 2 – amphibole granulite facies (C-7 is close to the amphibolite facies of metamorphism), 3 – metasomatic amphiboles, 4 – high-temperature amphibolite facies, 5 – low-temperature amphibolite facies.
Рисунок 3. Спектры распределения РЗЭ в плагиоклазитах и главных породообразующих минералах. а – Y-292/2 – афибоповый плагиоклазит (месторождение Центральное); б – Y-12/1 – амфиболовый плагиоклазит (рудопроявление Юго-Западное IV); в – Y-200/1– амфиболовый плагиоклазит (рудопроявление Юго-Западное IV); г – мафический комплекс Северо-Западного Прибайкалья [11]. Показаны составы амфиболов. 1 – керсутитов, 2 – амфиболов гранулитовой фации (С-7 близок к амфиболитовой фации метаморфизма), 3 – метасоматических амфиболов, 4 – высокотемпературной амфиболитовой фации, 5 – низкотемпературной амфиболитовой фации.

Table 3. P–T parameters of plagioclasite formation and amphibole compositional features.
Таблица 3. Р–Т-параметры образования плагиоклазитов и особенности состава амфибола.

Sample number	*T*, °C	*P*, kbar	Amount of REE in amphibole, ppm	TiO_2, wt. %
Y-12/1	622–674	3,3–4,2	453,90	0,38–0,76
Y-200/1	591–625	2,2–4,1	330,40	0,20–0,54
Y-292/2	591–612	7,2–9,0	255,62	0,11–0,15

In amphiboles, a direct proportional dependence of TiO_2 and the sum of REEs was determined. The highest amount of REE is 454 ppm, with a TiO_2 content of 0.38–0.76 wt.% is observed in amphibole from plagioclasite without corundum (sample Y-12/1); in the amphibole from the sample Y-200/1, the REE amount is 330 ppm and the TiO_2 content is 0.2–0.54 wt.%. The smallest amount of REE among the studied amphiboles (256 ppm) and TiO_2 content of 0.11–0.15 wt.% is observed in amphibole from corundum-bearing plagioclasite (sample Y-292/2).

The temperature of formation of amphibole plagioclasites was determined by Holland and Blundy amphibole-plagioclase geothermometer [12], and the pressure by Schmidt amphibole geobarometer [13]. For amphibole plagioclasite (sample Y-12/1), the calculated pressure was 3.3–4.2 kbar, temperature – 622–674 °C. The pressure for the amphibole plagioclasite Y-200/1 is 2.2–4.1 kbar, the temperature is 591-625 °C. For corundum-bearing amphibole plagioclasite (sample Y-292/2) from the Tsentralnoye deposit, the parameters are the following: T = 591–612 °C, P = 7,2–9,0 kbar (Table 3) [14].

Conclusion

The comparison of parameters and compositional characteristics of amphiboles allow us to assume a direct relationship between temperature, the sum of REE and TiO_2, as well as the inverse correlation between pressure and total REE content. According to S. G. Skublov, with an increase in the temperature of metamorphism, the total REE concentration in amphiboles increases [11], which is also reflected in our research results.

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Распределение лантаноидов в амфиболе и плагиоклазе из плагиоклазитов массива Рай-Из (Полярный Урал)

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Актуальность. В настоящей работе приведены результаты минералого-петрографических и геохимических исследований плагиоклазитов, локализованных среди хромитоносных ультрамафитов массива Рай-Из (Полярный Урал). Пространственная приуроченность плагиоклазитов к месторождению хромовых руд Центральному (корундсодержащие плагиоклазиты) и рудопроявлению Юго-Западному IV (бескорундовые плагиоклазиты) определяет необходимость детального исследования пород жильной серии хромитоносных разрезов.
Цель работы. Исследование минералого-петрографических характеристик, а также геохимии лантаноидов в плагиоклазе и амфиболе из плагиоклазитов массива Рай-Из (Полярный Урал).
Результаты. По результатам микрозондового анализа было установлено, что составы амфибола в плагиоклазитах заметно варьируют, соответствуя по современной классификации кальциевых амфиболов паргаситу, эдениту, магнезиогорнблендиту и актинолиту. В амфиболе установлена зональность двух типов. Зерна амфибола с зональностью первого типа характеризуются увеличением содержаний Al_2O_3, TiO_2, FeO, Na_2O от центра к периферии зерен, с зональностью второго типа – напротив, снижением этих компонентов. Плагиоклаз по химическому составу соответствует олигоклазу $An_{10-30,1}$. Отмечено снижение содержания анортитовой молекулы от центра к краю зерна. Изучение характера распределения РЗЭ в породообразующих минералах позволило установить, что главным минералом-концентратором лантаноидов в плагиоклазитах является амфибол: суммарное содержание РЗЭ в минерале составляет 250–450 г/т, тогда как в плагиоклазе концентрируется 16–18 г/т лантаноидов. Установлено, что причиной существования двух типов спектров распределения лантаноидов, выявленных ранее, является соотношение суммарного количества амфибола и плагиоклаза в породе. Проведено сравнение распределения редкоземельных элементов в кальциевых амфиболах из плагиоклазитов с распределением РЗЭ в амфиболах нюрундуканского мафического комплекса в Северо-Западном Прибайкалье, исследования которых выполнены С. Г. Скубловым. С помощью амфибол-плагиоклазового геотермометра (T. Holland, J. Blundy) и геобарометра (M. W. Schmidt) были определены параметры образования амфиболовых плагиоклазитов.
Выводы. Выявлен характер распределения лантаноидов в главных породообразующих минералах – плагиоклазе и амфиболе. Сравнение параметров и особенностей состава амфиболов позволило сделать вывод о прямой зависимости между температурой, суммой РЗЭ и TiO_2 в минерале.

Ключевые слова: амфибол, плагиоклаз, плагиоклазит, геохимия РЗЭ, Рай-Из, Полярный Урал.

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