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Association of Fe–Ti oxides in subalkaline dolerites of the Rai-Iz massif (Polar Urals)

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Abstract

The relevance of the research. Subalkaline dolerites, Fe–Ti oxides of which were studied in this work, occur within the largest deposits of chromium ores of the Rai-Iz massif. The study of the material composition and age of these rocks was carried out by the authors for the first time.

The purpose of the research is to reveal the patterns of changes in the chemical composition of the main accessory minerals of rocks – titanomagnetite and ilmenite, and on the basis of the obtained data to evaluate the conditions for the formation of subalkaline dolerites of the massif.

Research methodology. The chemical compositions of minerals were determined using microprobe analysis on a CAMECA SX 100 and scanning electron microscopy on a Jeol JSM-6390LV setup with an INCA Energy 450 X-Max 80 energy dispersive attachment. Raman spectra were obtained on a LabRam HR 800 Evolution spectrometer equipped with an Olimpus BX-FM microscope. The studies were carried out at the "Geoanalyst" center for the collective use of scientific equipment of the IGG, UB RAS.

Results. The typomorphism of the chemical composition of titanomagnetite and ilmenite has been established for petrographic varieties of dolerites allocated on the massif. The T–fO_2 parameters of dolerite formation were estimated and compared with metaultramafites. It is shown that titanomagnetite in amphibole dolerites undergoes maghemitization. The highest temperatures (1076–1126 °C) are recorded in pyroxene dolerites. The oxygen fugacity in these rocks is FMQ +0.6–+1 units. Hyalodolerite from the chilled margin of the pyroxene dolerite dike gives a temperature of 811–818 °C and an oxygen fugacity of 1.8 units above FMQ. The compositions of the associated ilmenite and titanomagnetite from amphibole dolerites correspond to fO_2 = –2–0 units relative to FMQ and temperature 580–720 °C. The trend of change in T–fO_2 parameters shows that the injection of the mafic melt occurred under conditions of metamorphism of ore-bearing ultramafic rocks.

Conclusions. The formation of dolerite veins occurred under conditions of ultramafic rock metamorphism. The increased fugacity of oxygen at a relatively low temperature led to the maghemitization of titanomagnetite, rather than to the redistribution of components in the magnetite-ilmenite paragenesis.

***Keywords*:** titanomagnetite, ilmenite, oxythermobarometry, subalkaline dolerites, chromitites, ultramafic rocks, Rai-Iz, Polar Urals.

Introduction

For the first time, subalkaline dolerites among the ultramafic rocks of the Rai-Iz massif were diagnosed by A. N. Zavaritsky as a vein hornblende diabase [1]. In subsequent years, during the geological study of the massif, these rocks were considered as dolerites and gabbrodolerites of the Middle-Upper Paleozoic diabase complex and did not attract the attention of researchers. We carried out detailed studies of the composition and age of these rocks [2, 3]. During the geological study of the southern part of the Rai-Iz massif, we found that dolerite dikes are localized near the main deposits of chromium ore – Tsentralnoye, Zapadnoye, no. 214. This allowed us to make an assumption about a possible genetic relationship between subalkaline dolerites and chromitites.

The purpose of this research is to reveal the patterns of changes in the chemical composition of the main accessory minerals of the rocks, titanomagnetite and ilmenite, and evaluate the conditions for the formation of subalkaline dolerites of the massif.

Research methodology

The chemical compositions of minerals were determined using microprobe analysis (CAMECA SX 100 setup, analysts I. A. Gottman, V. A. Bulatov) and scanning electron microscopy (Jeol JSM-6390LV setup with INCA Energy 450 X-Max 80 energy dispersive attachment, analyst L. V. Leonova) at the IGG UB RAS. Raman spectroscopy studies were carried out on a LabRam HR 800 Evolution spectrometer equipped

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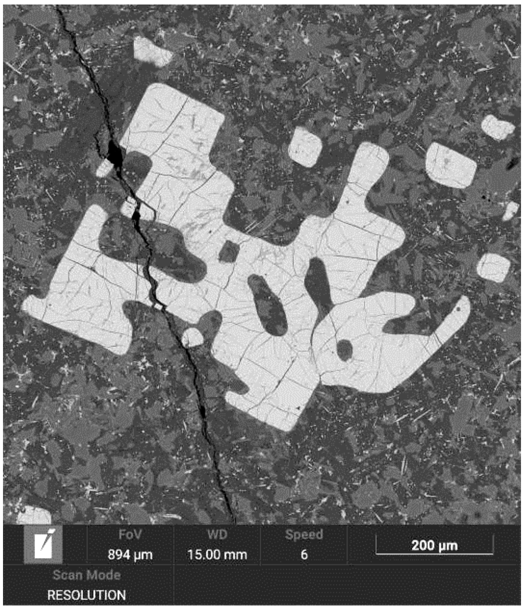

Figure 1. Titanomagnetite in pyroxene dolerite. BSE photo
Рисунок 1. Титаномагнетит в пироксеновом долерите. BSE-фото

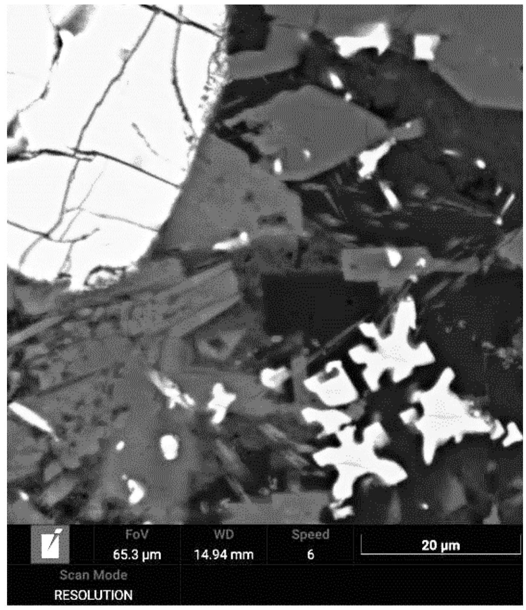

Figure 2. Ilmenite (right) and titanomagnetite (left) in pyroxene dolerite. BSE photo
Рисунок 2. Ильменит (справа) и титаномагнетит (слева) в пироксеновом долерите. BSE-фото

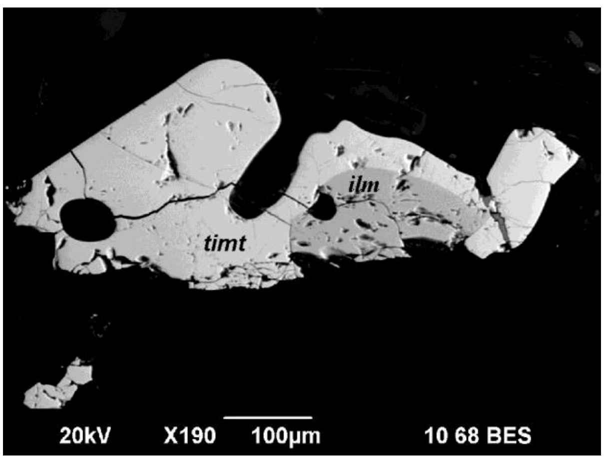

Figure 3. Titanomagnetite (*timt*) intergrown with ilmenite (*ilm*) in hyalodolerite. BSE photo
Рисунок 3. Титаномагнетит (*timt*) в срастании с ильменитом (*ilm*) в гиалодолерите. BSE-фото

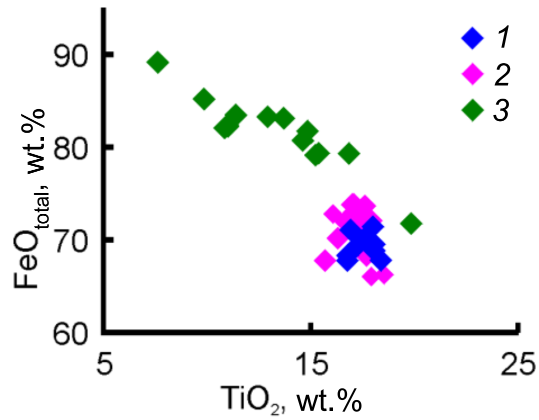

Figure 4. Ratio of TiO_2 and total FeO in titanomagnetite from dolerites of the Rai-Iz massif: *1* – hyalodolerite; *2* – pyroxene dolerite; *3* – amphibole dolerite
Рисунок 4. Соотношение TiO_2 и суммарного FeO в титаномагнетите из долеритов массива Рай-Из: *1* – гиалодолерит; *2* – пироксеновый долерит; *3* – амфиболовый долерит

with an Olimpus BX-FM microscope (IGG UB RAS, analyst E. A. Pankrushina).

Results

The investigated dolerites are divided into three petrographic varieties: hyalodolerites, pyroxene dolerites and amphibole dolerites. Hyalodolerites are developed at the contact of a dike of pyroxene dolerites with host metaultramafites [3]. Ore minerals in dolerites are represented mainly by titanomagnetite and ilmenite; pyrite, rare grains of chrome spinel and hematite are present in smaller amounts in the rocks.

Titanomagnetite is found in hyalodolerite and pyroxene dolerite, samples were taken east of the Zapadnoye deposit, as well as in amphibole dolerite, samples were taken west of deposit no. 214, upper reaches of the brook Vizuvshor. Mineral grains have a size of 100–200 microns and isometric, often octahedral shape. Edges and vertices of octahedrons are smoothed. The grains contain abundant silicate inclusions, which are either volcanic glass (in hyalodolerite) or rock-forming minerals, as well as pyrite (fig. 1–3). The amount of titanomagnetite in the rock does not exceed 1%. In reflected light with an analyzer in titanomagnetite, weak anisotropy and inhomogeneous extinction are observed.

The recalculation of the chemical analyzes of titanomagnetite was carried out according to the method of Lindsley and Spencer [4]. The content of the ulvospinel end-member (X_{usp}) and the amount of FeO and Fe_2O_3 were calculated (table 1). Each of the studied rock varieties is characterized by a specific chemical composition of titanomagnetite. The contents of the main components in titanomagnetite from hyalodolerite and pyroxene dolerite are similar (fig. 4). The highest content of

TiO_2 was found in a grain of titanomagnetite, which forms an inclusion in a plagioclase phenocrystal from pyroxene dolerite. Titanomagnetites from hyalodolerite differ from those from pyroxene dolerites by higher MgO content and lower MnO content (table 1).

Titanomagnetites from amphibole dolerites are mainly represented by individual, corroded relics of grains saturated with thin ilmenite lamellae (fig. 6, 7). In chemical composition, they differ from titanomagnetite from hyalodolerites and pyroxene dolerites by a statistically higher content of FeO = 71.1–89.9 wt. %, and low TiO_2 = 1.5–19.8 wt. % (fig. 3).

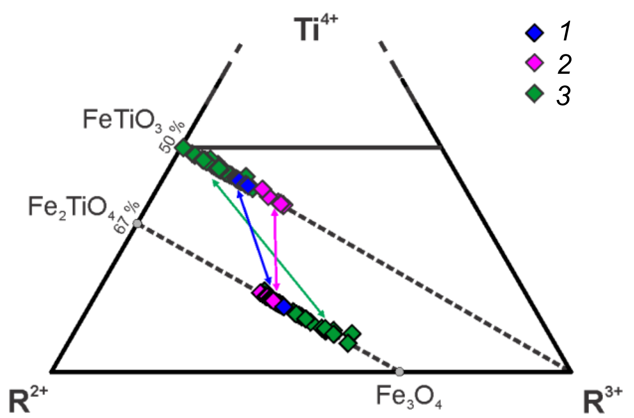

Figure 5. Diagram of compositions of titanium minerals from subalkaline dolerites of the Rai-Iz massif. The arrows show the parageneses of ilmenite and titanomagnetite from the samples; R^{2+}, R^{3+} are the sum of divalent and trivalent cations that make up the mineral

Рисунок 5. Диаграмма составов минералов титана из субщелочных долеритов массива Рай-Из. Стрелками показаны парагенезисы ильменита и титаномагнетита из образцов; R^{2+}, R^{3+} – сумма двухвалентных и трехвалентных катионов, входящих в состав минерала

The content of impurities in the mineral: V_2O_3 = 0.5–1 wt. % and MnO = 0–0.6 wt. %, the amount of MgO is below the sensitivity of the method. Microinclusions of titanomagnetite in grains of clinopyroxene from these rocks (fig. 4, lower part of the frame) correspond in composition to those from pyroxene-plagioclase dolerites.

Titanomagnetite from relic grains found in amphibole dolerites is characterized by a lower amount of ulvospinel end-member – 28–48%. Low contents of the component are observed mainly in the marginal parts of the grains, but occasionally also occur in the inner ones. The $RO–R_2O_3–TiO_2$ diagram (fig. 5) shows that individual compositions of titanomagnetites from this rock deviate from the magnetite-ulvospinel line towards an increase in the content of ferric iron. Such a trend in the change in the chemical composition indicates maghemitization of the mineral [9, 10]. The figurative points of the compositions of the other studied titanomagnetites are located along the magnetite-ulvospinel line. Raman spectroscopy revealed hematite lines in relic grains of titanomagnetite from amphibole dolerite (fig. 8).

Ilmenite is present in all studied varieties of dolerites. Its content is on average in the range of 1–3%. In hyalodolerite, a single mineral grain about 120 μm in size was found, which forms an intergrowth with a titanomagnetite crystal (fig. 3). In full-crystalline dolerites, the mineral is isolated in the form of skeletal microlites, the size of which varies in the range from 3–5 to 10–30 μm in elongation (fig. 2), which form an increased dissemination in the rock matrix. In pyroxene dolerites, ilmenite microlites form intergrowths with titanomagnetite grains. Some samples of amphibole dolerites contain relic grains of titanomagnetite with ilmenite lamellae (fig. 7), while ilmenite lattices filled with titanite are widely developed, remaining in place of replaced grains of titanomagnetite (fig. 6).

In reflected light, the mineral is distinctly anisotropic. The grains show polysynthetic twinning. The recalculation of

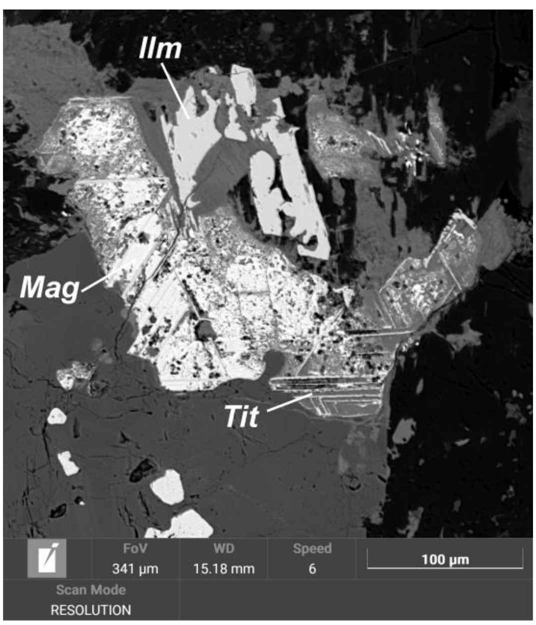

Figure 6. Ilmenite (*Ilm*), titanomagnetite (*Mag*), and titanite (*Tit*) segregation forms in amphibole dolerite. BSE photo

Рисунок 6. Формы выделения ильменита (*Ilm*), титаномагнетита (*Mag*) и титанита (*Tit*) в амфиболовом долерите. BSE-фото

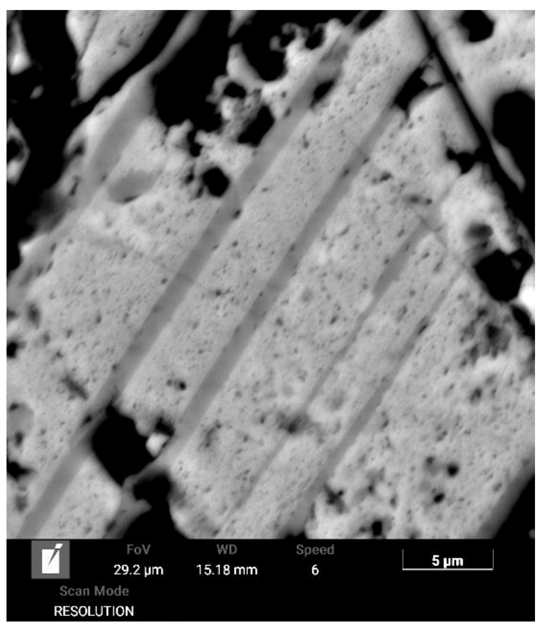

Figure 7. Fragment of a grain of titanomagnetite with ilmenite lamellae and fine microinclusions of silicates (?). BSE photo

Рисунок 7. Фрагмент зерна титаномагнетита с ламелями ильменита и тонкими микровключениями силикатов (?). BSE-фото

Table 1. Chemical composition of titanomagnetite, wt. %
Таблица 1. Химический состав титаномагнетита, мас. %

Component	Analysis number								
	1c	1ed	3	4	5	6	7	8	9
SiO_2	0,10	0,16	1,71	0,12	0,47	0,18	0,13	0,11	0,10
TiO_2	18,07	17,12	16,80	17,50	17,90	17,06	17,77	17,59	16,99
V_2O_3	0,54	0,48	0,47	0,53	0,46	0,45	0,46	0,43	0,43
Cr_2O_3	–	0,04	0,05	0,02	0,03	0,10	0,05	0,10	0,05
Al_2O_3	3,73	3,60	3,45	3,75	3,86	3,83	3,95	3,71	3,69
FeO	69,56	69,06	67,79	70,04	66,06	73,76	71,73	73,54	73,87
NiO	–	0,08	0,04	–	0,04	0,02	0,02	0,02	0,01
MnO	0,36	0,48	0,42	0,40	1,08	0,93	0,95	0,94	0,94
ZnO	–	–	0,04	0,09	0,65	0,32	0,41	0,10	0,13
MgO	4,51	4,93	5,73	4,64	0,14	0,06	0,02	0,10	0,13
CaO	0,03	0,32	0,09	0,07	0,19	0,03	0,05	0,01	0,06
Total	96,90	96,27	96,59	97,16	90,88	96,74	95,55	96,65	96,40
Formula units calculated for 3 cations									
Ti	0,487	0,463	0,458	0,470	0,535	0,477	0,504	0,493	0,476
Cr	–	0,001	0,001	0,001	0,001	0,003	0,002	0,003	0,001
V	0,016	0,014	0,014	0,015	0,015	0,013	0,014	0,013	0,013
Al	0,158	0,153	0,147	0,158	0,181	0,168	0,175	0,163	0,162
Fe	2,086	2,076	2,052	2,092	2,195	2,295	2,260	2,290	2,304
Ni	–	0,002	0,001	–	0,001	0,001	0,001	0,001	–
Mn	0,011	0,015	0,013	0,012	0,036	0,029	0,030	0,030	0,030
Zn	–	–	0,001	0,002	0,019	0,009	0,011	0,003	0,004
Mg	0,241	0,264	0,309	0,247	0,008	0,003	0,001	0,005	0,007
Ca	0,001	0,012	0,003	0,003	0,008	0,001	0,002	0,001	0,002
U_{sp},%	52,0	49,5	48,7	50,2	58,6	51,6	54,6	53,0	51,3
Fe_2O_3,%	31,53	33,47	33,83	32,93	24,28	30,44	28,00	29,53	30,70
FeO,%	41,16	38,90	37,31	40,38	43,99	46,09	46,27	46,69	45,96

Note: an. 1–4 – hyalodolerite, an. 5–9 – pyroxene dolerite; c is the center, ed is the edge of the grain.
Примечание: ан. 1–4 – гиалодолерит, ан. 5–9 – пироксеновый долерит; ц – центр, кр – край зерна.

the chemical analyzes of ilmenite was carried out according to the method [11]. Ilmenites from dolerites of each type have characteristic features of the chemical composition (table 2). The change in the ratio of the main mineral components – titanium and iron, is well illustrated by a triangular diagram (fig. 5). The highest content of the hematite component is characteristic of the mineral from pyroxene dolerite, where X_{Hem} averages 24–25%. In ilmenites from hyalodolerites, the content of the hematite end-member is lower than in the pyroxene dolerites associated with them and averages 14–17%. A characteristic feature of ilmenites from hyalodolerite is a high content of MgO = 5.85–6 wt. %, while in other varieties of dolerites the amount of the component does not exceed 0.1 wt. %. In ilmenite from amphibole dolerites, X_{Hem} is the lowest and is within 5–11%.

The amount of hematite component in the studied ilmenites is at the level characteristic of the mineral from volcanic rocks. The content of X_{Hem} in the range of 20–30% is typical for calc-alkaline basalts, and lower X_{Hem} = 0–20% is typical for tholeiite basalts [5, 12].

When comparing the compositions of ilmenite with the literature data, the MgO content attracts attention. In ilmenites from amphibole and pyroxene dolerites, its amount does not exceed 0.1 wt. %, while in ilmenite from hyalodolerite MgO is about 6 wt. %. Magnesian ilmenites are common in alkaline basalts, where the MgO content is 1–7 wt. % [5, 8]. Ilmenites with a close (about 6 wt. %) MgO content are known in olivine gabbro from the base of the Insizwa massif (South Africa). The formation of a mineral with such a composition on the massif is associated with near-liquidus (early) crystallization of ilmenite from magnesian melt [13]. This interpretation is in good agreement with the fact that the studied mineral was found in hyalodolerite from the hardening zone of a basaltoid dike, the ore phases of which, most likely, are the earliest in the rock.

Oxythermobarometry of subalkaline dolerites. The temperature and oxygen fugacity were estimated using the Andersen and Lindsley equations [14]. The calculation results are shown in the diagram (fig. 9). The highest temperatures

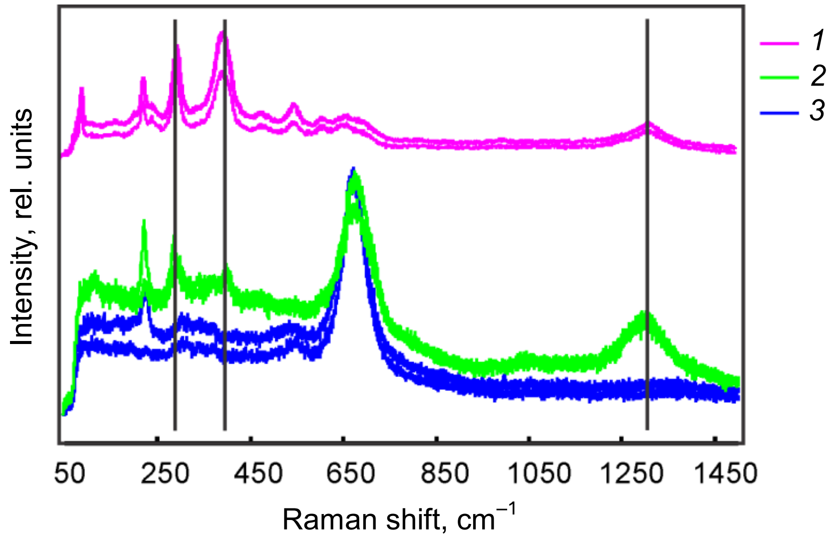

Figure 8. Raman spectra of (*1*) hematite, (*2*) maghemized titanomagnetite, and (*3*) unaltered titanomagnetite from dolerites of the Rai-Iz massif

Рисунок 8. Рамановские спектры гематита (*1*), маггемитизированного титаномагнетита (*2*) и неизмененного титаномагнетита (*3*) из долеритов массива Рай-Из

Table 2. The chemical composition of ilmenite, wt. %
Таблица 2. Химический состав ильменита, мас. %

Component	Analysis number								
	1	2	3	5	6	7	8	9	10
ZrO_2	–	–	0,08	0,02	0,07	–	–	–	–
SiO_2	0,11	0,05	0,07	0,21	0,44	0,24	0,44	0,26	0,28
TiO_2	47,56	47,06	46,06	48,70	47,49	37,70	38,18	48,00	45,93
V_2O_3	0,22	0,13	0,17	–	0,06	0,22	0,23	–	–
Cr_2O_3	–	–	–	–	–	0,02	–	–	–
Al_2O_3	0,17	0,17	0,25	0,37	0,24	0,41	0,43	0,60	0,71
FeO	49,21	49,55	48,19	45,93	47,50	54,11	53,69	44,71	45,47
NiO	0,09	–	–	0,04	–	–	0,07	–	–
CoO	–	0,12	–	0,03	0,03	0,01	–	–	–
MnO	1,98	2,01	2,62	2,34	1,98	1,56	1,45	0,43	0,36
ZnO	0,13	0,09	0,05	–	–	–	–	–	–
MgO	0,01	0,02	0,02	0,05	0,08	0,07	0,10	6,00	5,85
CaO	0,30	0,09	0,11	0,34	0,37	0,18	0,34	–	–
BaO	–	–	–	0,03	0,13	–	–	–	–
Formula units calculated for 2 cations									
Zr	–	–	0,001	–	0,001	–	–	–	–
Ti	0,900	0,895	0,890	0,940	0,915	0,747	0,755	0,865	0,838
V	0,004	0,003	0,004	–	0,001	0,005	0,005	–	–
Al	0,005	0,005	0,008	0,011	0,007	0,013	0,013	0,017	0,020
Fe	1,035	1,047	1,036	0,985	1,017	1,192	1,180	0,895	0,922
Ni	0,002	–	–	0,001	–	–	0,001	–	–
Co	–	0,002	0,000	0,001	0,001	–	–	–	–
Mg	–	0,001	0,001	0,002	0,003	0,003	0,004	0,214	0,212
Mn	0,042	0,043	0,057	0,051	0,043	0,035	0,032	0,009	0,007
Zn	0,002	0,002	0,001	–	–	–	–	–	–
Ca	0,008	0,002	0,003	0,009	0,010	0,005	0,010	–	–
Ba	–	–	–	–	0,001	–	–	–	–
Ilm,%	90,2	89,5	89,2	94,3	91,8	74,8	75,6	85,5	82,6
Hem,%	9,8	10,5	10,8	5,7	8,2	25,2	24,4	14,5	17,4

Note: an. 1–6 – amphibole dolerite; an. 7, 8 – pyroxene dolerite; an. 9, 10 – hyalodolerite.
Примечание: ан. 1–6 – амфиболовый долерит; ан. 7, 8 – пироксеновый долерит; ан. 9, 10 – гиалодолерит.

(1076–1126 °C) are recorded in pyroxene dolerites. The oxygen fugacity in these rocks is FMQ +0.6–+1 units. Hyalodolerite from the hardening zone of the pyroxene dolerite dike gives a temperature of 811–818 °C and an oxygen fugacity of 1.8 units above FMQ. The compositions of the associated ilmenite and titanomagnetite from amphibole dolerites correspond to fO_2 = –2–0 units relative to FMQ and temperature 580–720 °C.

In the amphibole-enstatite-olivine metaharzburgite rock hosting a dike of pyroxene dolerites, the temperature of 645–683 °C and fO_2 = 2.2–3.2 units above the FMQ buffer were established by olivine-spinel oxythermobarometry [15]. Such conditions are typical for ore-bearing metaultramafites of the Tsentralnoye, Zapadnoye and no. 214 deposits [16, 17].

Conclusions

The studied pyroxene dolerite dyke is relatively thin (about 0.7 m) compared to the amphibole dolerite dyke, which is 10 or more meters thick. In this regard, the change in thermodynamic conditions in the process of melt intrusion had a greater effect on the rate of rock crystallization and the chemical composition of rock-forming minerals. A decrease in temperature and an increase in oxygen fugacity from the inner part of the pyroxene dolerite dike to the chilled margin were established. The trend of changes in these parameters (arrows in fig. 9) shows that the melt injection occurred under T–fO_2 conditions of metamorphism of ore-bearing ultramafic rocks. Amphibole dolerites crystallized at temperatures close to those established for wall-rock metaultramafites. The increased oxygen fugacity at a relatively low temperature led to the maghemitization of titanomagnetite, rather than to the redistribution of components in the titanomagnetite-ilmenite paragenesis.

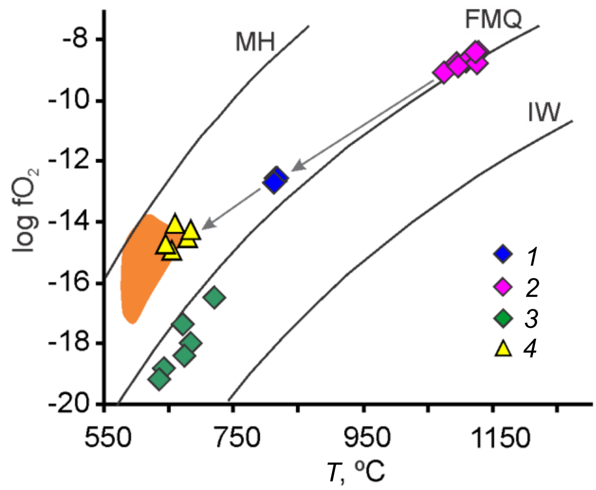

Figure 9. T–fO_2 diagram for subalkaline dolerites and ultramafic rocks of the Rai-Iz massif: *1* – hyalodolerite; *2* – pyroxene dolerite; *3* – amphibole dolerite; *4* – metaharzburgite from contact with hyalodolerite. The orange field shows T–fO_2 parameters for wall-rock ultramafic rocks of the Tsentralnoye, Zapadnoye and no. 214 deposits [14]

Рисунок 9. Диаграмма T–fO_2 для субщелочных долеритов и ультрамафитов массива Рай-Из: *1* – гиалодолерит; *2* – пироксеновый долерит; *3* – амфиболовый долерит; *4* – апогарцбургит из контакта с гиалодолеритом. Оранжевое поле – параметры образования околорудных ультрамафитов месторождений Центральное, Западное и № 214 [14]

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Ассоциация Fe–Ti оксидов в субщелочных долеритах массива Рай-Из (Полярный Урал)

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Аннотация

Актуальность исследования. Субщелочные долериты, Fe–Ti оксиды из которых исследованы в настоящей работе, встречаются в пределах наиболее крупных месторождений хромовых руд массива Рай-Из. Исследование вещественного состава и возраста этих пород произведено авторами впервые.

Цель работы – выявить закономерности изменения химического состава основных акцессорных минералов пород – титаномагнетита и ильменита – и на основе полученных данных оценить условия образования субщелочных долеритов массива.

Методы исследования. Химические составы минералов определены при помощи микрозондового анализа на установке CAMECA SX 100 и сканирующей электронной микроскопии на установке Jeol JSM-6390LV с энергодисперсионной приставкой INCA Energy 450 X-Max 80. Рамановские спектры получены на спектрометре LabRam HR 800 Evolution, оснащенном микроскопом Olimpus BX-FM. Исследования выполнены в ЦКП «Геоаналитик» ИГГ УрО РАН.

Результаты. Установлен типоморфизм химического состава титаномагнетита и ильменита для петрографических разновидностей долеритов, выделяемых на массиве. Оценены T–fO_2 параметры образования долеритов, выполнено их сопоставление с метаультрамафитами. Показано, что в амфиболовых долеритах титаномагнетит претерпевает маггемитизацию. Наиболее высокие температуры (1076–1126 °C) зафиксированы в пироксеновых долеритах. Фугитивность кислорода в этих породах составляет FMQ +0,6–+1 ед. Гиалодолерит из зоны закалки дайки пироксеновых долеритов дает температуру 811–818 °C и фугитивность кислорода 1,8 ед. выше FMQ. Составы ассоциирующих ильменита и титаномагнетита из амфиболовых долеритов отвечают fO_2 = –2–0 ед. относительно FMQ и температуре 580–720 °C. Тренд изменения T–fO_2 параметров показывает, что внедрение основного расплава происходило в условиях метаморфизма рудовмещающих ультрамафитов.

Выводы. Образование жил долеритов происходило в условиях метаморфизма ультрамафитов. Повышенная фугитивность кислорода при относительно низкой температуре привела к маггемитизации титаномагнетита, а не к перераспределению компонентов в магнетит-ильменитовом парагенезисе.

***Ключевые слова*:** титаномагнетит, ильменит, окситермобарометрия, субщелочные долериты, хромититы, ультрамафиты, Рай-Из, Полярный Урал.

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