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The redox state of chromitites from the Yambotyvissky area (Voikar-Syninsky massif, Polar Urals)

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The relevance of the work is due to insufficient knowledge of the redox state of chromitites of the Voikar-Syninsky massif.
The aim of the work is to establish how did redox conditions change during the formation of Al-rich chemical type chromitites within the Yambotyvissky area.
Research methodology: study of the composition of ore-forming chrome-spinels and olivines from chromitites of the Yambotyvissky area; evaluation of the temperature of olivine-spinel equilibrium and oxygen fugacity in chromitite samples; study of variation in the composition of minerals and T – fO_2 parameters within the whole area and within individual ore bodies.
Results of the work. The composition features of ore-forming chrome-spinels and redox state of the chromitites of the Voikar-Syninsky massif of the Yambotyvissky area are studied. It was shown that ore-forming spinels of ore bodies occurring in dunites have lower Cr-number compared to chrome spinels of ores localised in harzburgites. It was found that Fe/(Fe+Mg) of olivines and spinels, which compose the chromitite of the area, were directly proportional. It indicates the rock – ore equilibrium existence in the system. The change in the chemical composition of ore-forming chrome spinels, the temperature of olivine-spinel equilibrium and oxygen fugacity within individual ore bodies were studied. The oxygen fugacity increases from the inner parts of chromitite bodies towards their endocontacts. It was shown that in Al-rich chromitites an increase in oxygen fugacity is followed by an enrichment of chrome spinel quantity in the ore. Chromitites occurring both in the dunite bodies and harzburgites, have been formed under close redox conditions. The data obtained were compared with the results of mineral composition and redox state of the chrome ores of the Ray-Is massif from previous studies.

Keywords: redox state, chromitites, ultramafites, Voikar-Syninsky massif, metamorphism, ore formation.

Introduction

The geological and petrological studies of the Voikar-Syninsky massif significantly contributed to the development of ideas on the conditions of formation and evolution of ophiolite complexes. Despite the remoteness and inaccessibility of the object, compared with the Ray-Iz massif located to the north, the quantity of scientific research is very high. Issues concerning the geological structure of the massif, the metamorphism of mafic and ultramafic rocks, their petrostructural features and chromite content are highlighted in A. A. Savelyev, G. N. Savelyeva, N. L. Dobretsov, Yu. E. Moldavantsev, V. N. Puchkov, S. A. Shcherbakov A. B. Makeev, E. P. Tsaritsyn, I. S. Chashchukhin, A. A. Efimov and many others.

The oxythermobarometry study of the Voikar-Syninsky massif chromitites was performed [1–4]. I. S. Chashchukhin and co-authors [1] have studied several samples of chromium ores from different parts of the massif. For the sample of aluminous chromitite (the Cr_2O_3 content in the ore-forming spinel is less than 40 wt.%), the lowest values of fO_2 (0.8 logarithmic units above FMQ buffer) were obtained, and the highest values (1.8–2.7 logarithmic units above FMQ buffer) were for high-chromium chromitites. This data is presented in the table of results, and the relationship between the chemical type of spinel and oxygen fugacity is not discussed. The results of I. S. Chashchukhin are used in the article [2].

In our works [3, 4], it was found that the Al-rich chromitites of the northern part of the Voikar-Syninsky massif are less oxidised (–0.5 ... + 1.5 logarithmic units regarding the FMQ buffer) than chromium ones (+ 1.8 ... + 3, 5 logarithmic units in relation to FMQ buffer) [3]. In the ore body section of high-chromium chromitites of the Arkashorsky ore occurrence, fO_2 (FMQ) varies within + 1.8 ... + 2.8 logarithmic units. A decrease in fO_2 is observed where the body comes into contact with the host rocks and inside the deformation zone dividing it into two blocks [4].

The purpose of this work is to establish how did redox conditions change during the formation of Al-rich chromitites within the Yambotyvissky area.

Geological structure of the Yambotyvissky area

The ultramafic Voykaro-Syninsky, Ray-Iz and Syum-Keu massifs constitute most of the main watershed range of the Polar Urals. Ophiolites are integrated into the system of allochtons, overriding westward to the Paleozoic sequences of the Central Ural uplift [5, 6]. According to modern concepts [6, 7] they are large fragments of the oceanic-type crust and lithosphere formed in the back-arc and inter-arc marginal basins, including in the sub-subduction conditions in the Early and Middle Paleozoic.

Ultramafites of the Voikar-Syninsky massif are represented by rocks of the reticular and banded dunite-harzburgite complex, which are fringed with gabbroids both from the north and from the south. There can be traced metamorphic zoning in rocks: from west to east, the high-temperature apoharzburgite mineral parageneses are replaced by low-temperature ones [8].

The Yambotyvissky area is located at the Yambotyvis stream watershed and the Left Payera River (Fig. 1). In the southeast the tectonic contact of ultramafites and gabbroids takes place; therefore, in ultramafites of the southern part of the area, rocks of the vein dunite-wehrlite-clinopyroxenite (Kershorsky) complex occured.

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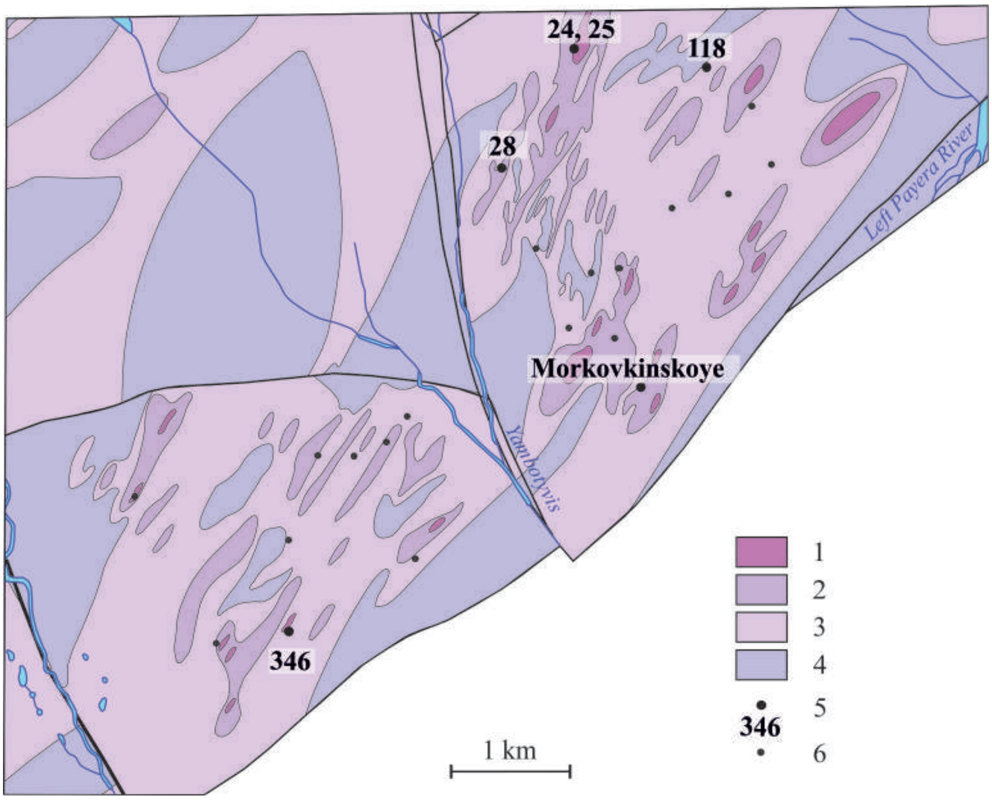

Figure 1. The geological structure of the Yambotyvissky area. 1–4 – rocks of the dunite-harzburgite complex: 1 – dunites. 2–4 – the content of the dunite component in harzburgite: 2 – more than 30%, 3 – 10-30%, 4 – less than 10%; 5 – ore occurrences studied in this work and their numbers; 6 – other ore occurrences.

Рисунок 1. Геологическое строение Ямботывисской площади. 1–4 – породы дунит-гарцбургитового комплекса: 1 – дуниты; 2–4 – содержание дунитовой составляющей в гарцбургитах: 2 – более 30 %, 3 – 10–30 %, 4 – менее 10 %; 5 – рудопроявления, изученные в настоящей работе, и их номера; 6 – прочие рудопроявления.

The amount of dunite component in the dunite-harzburgite complex rocks of the Yambotyvissky area varies from 10-70%, with a background content of 15–20%. Dunites appeared both in the form of veins in harzburgites, whch thickness varies from the first centimetres to tens of centimetres, and as a dunite bodies with a width of up to 100–150 m. The form of dunite bodies is predominantly lenticular, less often close to isometric. Dunite bodies and areas with a high dunite content have a northeast extintion (Fig. 1).

Apoharzburgite metamorphic associations are formed under the influence of equilibrium and non-equilibrium metamorphism [8]. Non-equilibrium metamorphism (amphibolisation) is manifested in the development of talc-amphibole aggregate pseudomorphose on enstatite. Equilibrium metamorphic rocks are represented by amphibole-olivine, amphibole-olivine-antigorite and olivine-antigorite (voikarite) rocks.

The apoharzburgite metamorphic rocks of the northern part of the area are represented by voikarites; to the south they are replaced by amphibole-olivine-antigorite rocks and after amphibole-olivine rocks; further to the south, amphibolised and serpentinisated harzburgites dominate.

In the present work, the chromitites of the largest chromite occurrences No. 24, 25, 28, 118, 346, Morkovkinskoye (Fig. 1) were studied. They differ both in structural and textural features and in the petrographic composition of the ore-bearing rock section.

Chromitites of the occurrences 24 and 25 occur in the body of dunites. In ore manifestation 24, impregnated-banded chromitites of a poorly-rarely impregnated structure prevail and occurrence 25 has medium-densely disseminated with thick schlieren.

The mineralization of ore occurrences 28, 118, 346 and Morkovkinskoye is localised in apoharzburgites. The ore bodies are surrounded by a dunite envelope, which thickness varies from 10–15 cm to 1–2 metres. The chromitites of chromite occurrence 28 are medium-grained, varying from medium to densely disseminated. At the occurrence 118 densely disseminated chromitites of massive structure are developed. For chromitites of the occurrence 346, schlieren texture is typical – among the fine-grained medium-disseminated matrix there are isolated lenticular and irregular shapes composed of densely disseminated medium-grained chromitite. Nodular chromitites are typical of the Morkovkinsky ore occurrence. The nodules have the shape of distorted octahedra with rounded edges and an average diameter of approximately 1.5 cm.

The chemical composition of ore-forming chrome spinel

The chemical composition of minerals is determined using microprobe analysis (Cameca SX-100 installation, the analysts are N. N. Kononkova, V. I. Vernadsky (Institute of Geochemistry and Analytical Chemistry of RAS, Moscow). The ore-forming chromic spinels of the Yambotyvissky area chromitites are of the Al-rich magnesia chemical type (Fig. 2) and contain 37–44 wt.% Cr_2O_3 with an Al_2O_3 content of 24–30 wt.%. Spinels from chromite ores of ccurrences 24 and 25 have the lowest chromium content and the highest one from occurrence 28. The compositions of the chrome spinels of the Morkovkinskoye ore manifestations

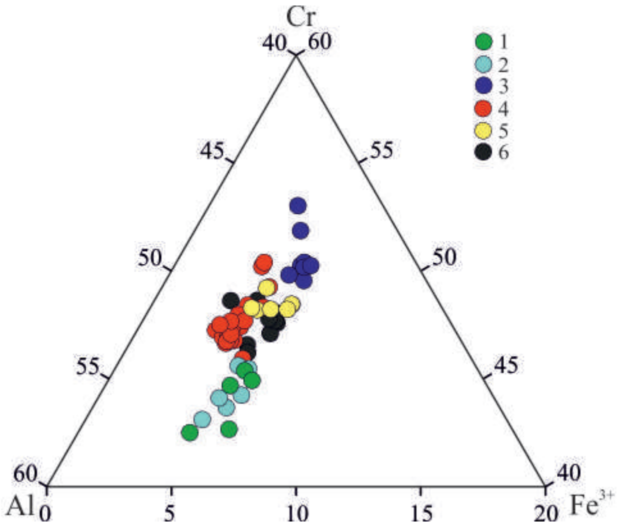

Figure 2. Compositions of ore forming chrome spinels from Yambotyvissky area. Ore occurrences: 1–24, 2–25, 3–28, 4–118, 5–346, 6 – Morkovkinskoye.

Рисунок 2. Диаграмма составов рудообразующих хромовых шпинелей Ямботывисской площади. Рудопроявления. 1 – 24, 2 – 25, 3 – 28, 4 –118, 5 – 346, 6 – Морковкинское.

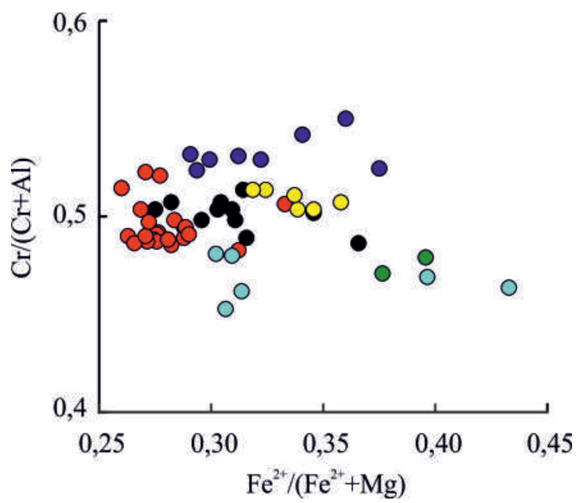

Figure 3. Cr/(Cr+Al) vs $Fe^{2+}/(Fe^{2+}+Mg)$ diagram of the ore-forming chromic spinels of the Yambotyvissky area. The legend keys are shown in Figure 2.

Рисунок 3. Диаграмма железистость–хромистость рудообразующих хромовых шпинелей Ямботывисской площади. Условные обозначения см. на рисунке 2.

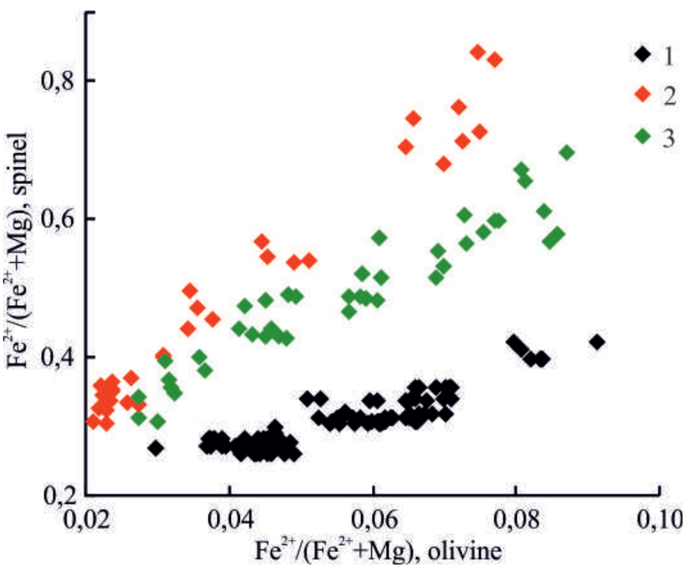

Figure 4. Ferruginosity of olivine – ferruginosity of spinel diagram. 1 – chromitites of the Yambotyvissky area, 2 – chromitites and wall-rock ultramafites fromTsentralnoye deposit, 3 – chromitites and wall-rock ultramafites from Engayskoye ore within the Ray-Iz massif.

Рисунок 4. Диаграмма железистость оливина–железистость шпинели. 1 – хромититы Ямботывисской площади, 2 – хромититы и ультрамафиты месторождения Центральное, 3 – хромититы и ультрамафиты Енгайского рудопроявления массива Рай-Из.

118, 118a and 346 are close to each other. In terms of the ratio of Cr and Al cations they occupy an intermediate position between the spinels of the ore occurrences 24, 25 and 28.

Iron oxidation state (Fe # = $Fe^{3+} / (Fe^{3+} + Fe^{2+})$) in spinel for all the studied ore occurrences is in the range of 15–27%. Spinels of 118 occurrence contain the least amount of trivalent iron; they also have the lowest ferruginosity ($f = Fe^{2+} / (Fe^{2+} + Mg)$). It is noteworthy (Fig. 3) that there is no correlation between the contents of divalent and trivalent cations, which is typical of the ore-forming chrome spinels of the Ray-Iz massif [9].

There is a direct proportionality of $Fe^{2+}/(Fe^{2+}+Mg)$ between of olivine and spinel (Fig. 4). The ratio of olivine *Fa*/ferruginosity of spinel for Yambotyvissky area chromitites is two times higher than for the Tsentralnoye deposit of the Ray-Iz massif and one and a half times higher than those of Engayskoe occurence [9]. For the Ray-Iz massif trends in the composition of olivine and spinel for each of the objects are common to chromitites and the equilibrium meta-ultramafites enclosing them (Fig. 4). This indicates the metamorphic genesis of the chromitites. The studied chromitites of the Yambotyvissky area occur in non-equilibrium metamorphites (amphibolised harzburgites), however, the compositions of olivine and chrome spinels fall on a single trend line. This confirms that the change in the trend line slope reflects the change in the parameters of ore formation and metamorphism, but not the different Cr content of spinel [10, 11].

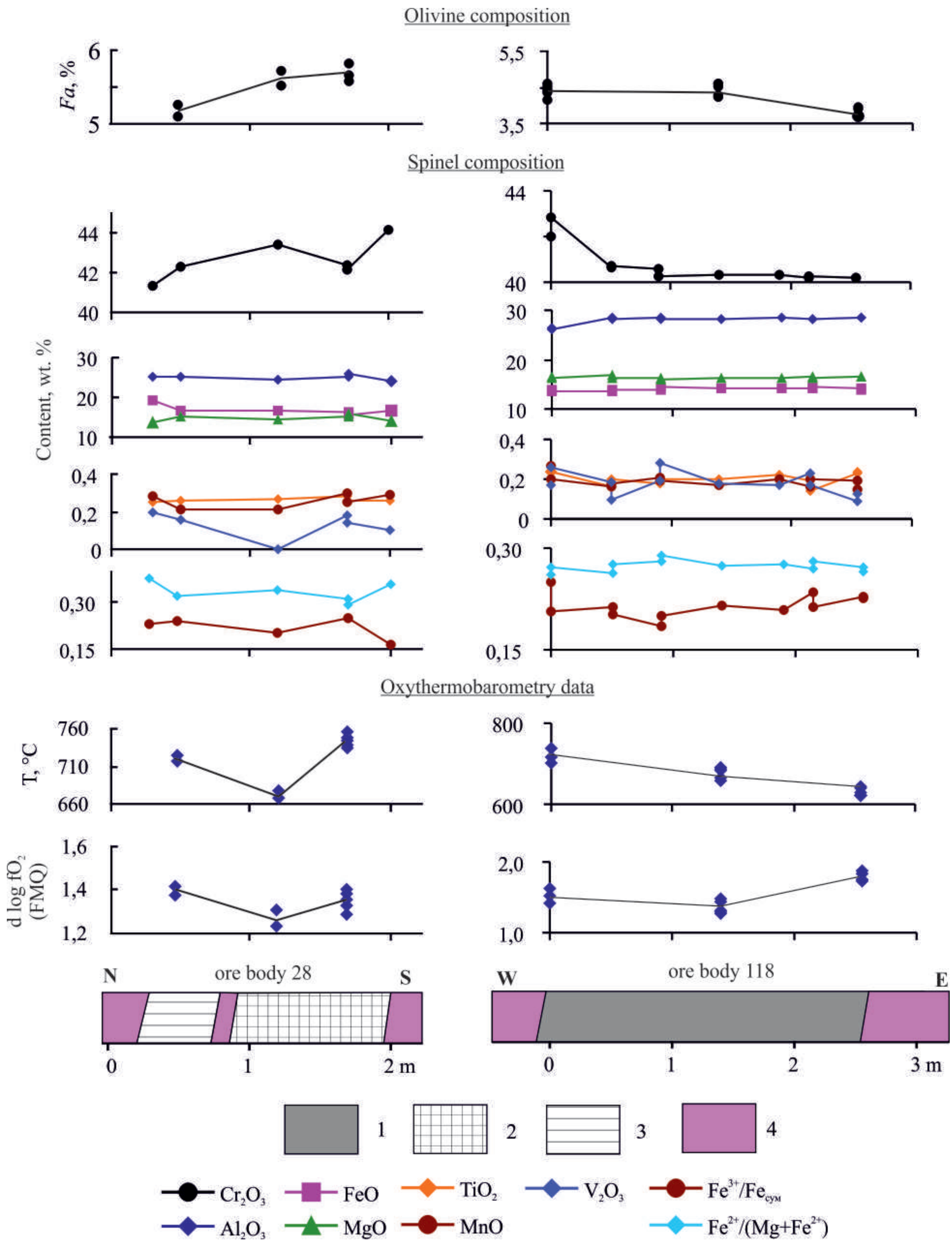

Figure 5. Chemical composition of the ore-forming spinel, the temperature of the olivine-spinel equilibrium and the oxygen fugacity within the chromitite bodies 28 and 118 in the Yambotyvissky area. 1-3 is chromitite structure in terms of the content of ore-forming spinel: 1 – solid; 2 – densely disseminated; 3 – medium disseminated; 4 – dunites.

Рисунок 5. Изменение химического состава рудообразующей шпинели, температуры оливин-шпинелевого равновесия и фугитивности кислорода внутри тел хромититов 28 и 118 Ямботывисской площади. 1–3 – структура хромититов по содержанию рудообразующей шпинели: 1 – сплошные, 2 – густовкрапленные; 3 – средневкрапленные; 4 – дуниты.

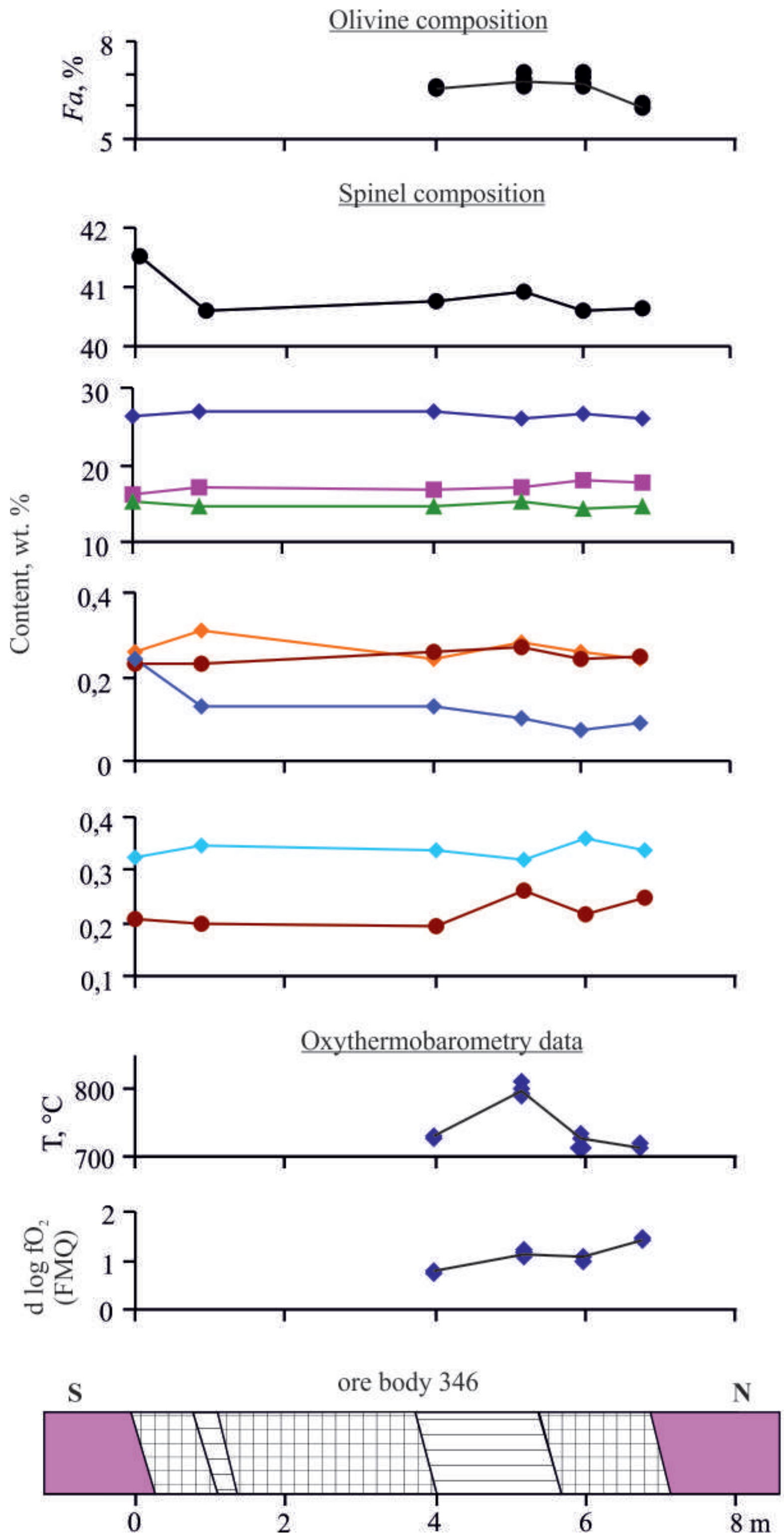

Figure 6. Chemical composition of the ore-forming spinel, the temperature of the olivine-spinel equilibrium and the oxygen fugacity within the chromitite body 346 of the Yambotyvissky area. The legend keys are shown in Figure 5.

Рисунок 6. Изменение химического состава рудообразующей шпинели, температуры оливин-шпинелевого равновесия и фугитивности кислорода внутри тела хромититов 346 Ямботывисской площади. Условные обозначения см. на рисунке 5.

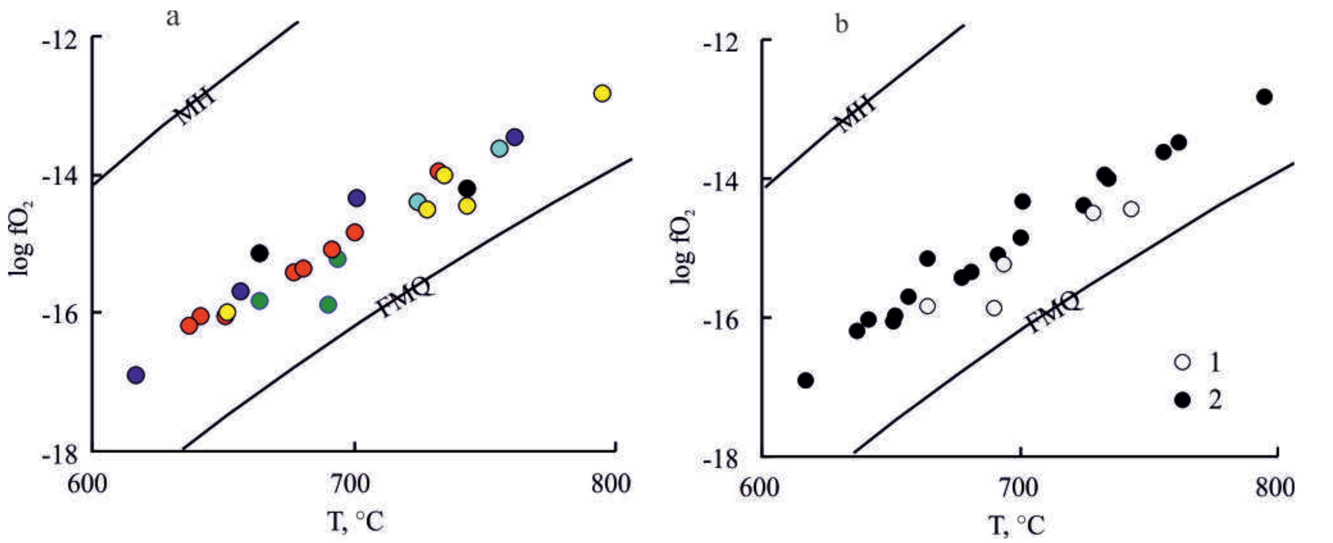

Figure 7. T–fO_2 diagrams for chromitites of the Yambotyvissky area. a – for chromitites of ore occurrences studied (for symbols, see figure 2). b – different impregnations: 1 – poorly and rarely disseminated; 2 – from moderately disseminated to massive.

Рисунок 7. Диаграммы T–fO_2 для хромититов Ямботывисской площади. а – для хромититов изученных рудопроявлений (условные обозначения см. на рисунке 2); б – различной вкрапленности: 1 – убого- и редковкрапленные; 2 – от средневкрапленных до сплошных.

Within the range of ore occurrences 28, 118 and 346, there was an increase in the content of Cr_2O_3 to one of the contacts (Fig. 5, 6) by 1 wt.% (occurence 346) and about 3 wt.% (occurrences 118 and 28). All these were accompanied by a decrease in the content of Al_2O_3 and Fe#. According to the content of divalent cations the most pronounced zonality is observed at the ore occurrence 28 where ferruginosity of spinel to its contacts increases. On the contrary, in the chromitite bodies of ore occurrences 118 and 346 the most ferruginous spinels are localizes in the inner parts of the ore deposits.

Ferruginosity (*Fa* = Fe / (Fe + Mg)) of olivine within the studied chromitite bodies varies slightly (within 0.7%) and increases to one of the contacts simultaneously with the amount of Cr_2O_3 in the spinel. The content of the fayalite molecule within one sample varies by 0.5%, that may be due to the existence of the chemical zonality of the mineral.

Oxythermobarometry of chromitites of the Yambotyvissky area

The oxygen fugacity and temperature of the olivine-spinel equilibrium were calculated using a Ballhaus-Berry-Green geothermometer and oxybarometer [12, 13] (Ballhaus et al., 1990, 1991). The calculated temperatures vary in the range of 600–795 °C within separate ore deposits.

In general, the lowest fO_2 values in the Yambotyvissky area are estimated (Fig. 7, a) in chromitites of 346 and 24 occurences (0.6–1.5 units above the FMQ buffer). The highest oxygen fugacity is determined in chromitites of 28, 118 and 118a occurrences (FMQ + 1.5. + 1.9 units). Poorly and rarely disseminated chromitites are more reduced than the moderately disseminated, densely disseminated and massive ones (Fig. 7, *b*). This illustrates the increase in chrome spinel amount in chromitite with an increase in fO_2 in the ore body of 346 occurrence (Fig. 6).

Chromitites of the internal parts of the ore bodies are less oxidised compared with the end-contact parts (Fig. 5, 6). From the centre of the ore body to the host rocks fO_2 increases by 0.2–0.6 units. The temperature of the olivine-spinel equilibrium, determined near the contacts of the ore bodies, is higher than in the internal parts.

In the ore body 346, an increase in amount of chrome spinel impregnation from the centre to the northern end contact is observed. The structure of chromitite varies from rarely disseminated and moderately disseminated to densely disseminated. At the same time, the value of fO_2 rises from 0.8–1.4 logarithmic units above FMQ buffer.

Conclusion

The Yambotyvissky area chromitites are localised both in the rocks of the dunite-harzburgite complex and in the dunite bodies. Chromitites occurring in large dunite bodies (occurrences 24 and 25) are distinguished by lower Cr content in spinel. They are characterised by a somewhat lower Fe# in spinel. The difference in Fe# spinel from chromitites of the dunite-harzburgite complex and dunite bodies is insignificant and corresponds to the difference in oxygen fugacity of 0.1–0.2 logarithmic units. This value is within the error of the method (0.4 logarithmic units [13]) and the change in fO_2 within the area does not depend on the petrographic composition of the host rocks. There is another regularity: with the oxygen fugacity rising, the spinel amount in chromitite increases. This is clearly manifested in chromitite body 346. Another example is the studied chromitite occurrences of 24 and 25, which occur in the same dunite body and consist of chrome spinels of a similar composition. They differ in structure: rarely disseminated in occurrence 24 and densely disseminated to massive in occurrence 25. The oxygen fugacity determined for chromitites of occurrence 25 is statistically higher than for the occurrence of chromium ore 24. The highest values of fO_2 are noted for occurrence 118, composed with massive and densely disseminated to massive chromitites. These facts indicate the existence of a relationship between the amount of the ore-forming mineral in chromitite with the change in oxygen fugacity during ore formation. We found a similar pattern in the high-chromium chromitites of the Ray-Iz massif [3, 9]. In this massif the greatest oxygen fugacity is found in densely disseminated chromitites of the Tsentralnoye, Zapadnoye and other deposits, and the smallest one in disseminated-banded and rarely disseminated chrome ores of the Engayskoye, Yugo-Zapadnoye-2 and Yugo-Zapadnoye-3 ore occurrences.

Oxygen fugacity in all the investigated ore occurrences in the Yambotyvissky area increases to ore bodies contacts (by 0.2–0.6 logarithmic units). In this case, the rising in fO_2 occurs independently of the change in the ore-forming mineral content in the ore and is apparently associated with retrograde metamorphism (similar with the formation of chrome spinel grain rims, for example [14, 15]).

The direct proportionality between ferruginosity of the coexisting olivines and chromite spinels of the studied Yambotyvissky area ore occurrences indicates the existence of equilibrium in the rock/ore system.

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Окислительно-восстановительное состояние хромититов Ямботывисской площади Войкаро-Сыньинского массива (Полярный Урал)

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Актуальность работы обусловлена слабой изученностью окислительно-восстановительного состояния хромититов Войкаро-Сыньинского массива.
Цель работы состоит в том, чтобы установить закономерности изменения окислительно-восстановительных условий в процессе образования хромититов глиноземистого химического типа, развитых в пределах Ямботывисской площади.
Методология исследования: изучение составов рудообразующих хромовых шпинелей и оливинов из хромититов Ямботывисской площади; оценка температуры оливин-шпинелевого равновесия и фугитивности кислорода в образцах хромититов; изучение изменения составов минералов и T–fO_2 параметров в пределах площади в целом и внутри отдельных рудных тел.
Результаты работы. Изучены особенности состава рудообразующих хромовых шпинелей и окислительно-восстановительное состояние хромититов Ямботывисской площади Войкаро-Сыньинского массива. Показано, что рудообразующие шпинели рудопроявлений, залегающих в дунитах, менее хромисты по сравнению с хромовыми шпинелями руд, локализованных в гарцбургитах. Установлено, что железистости оливинов и шпинелей, слагающих хромититы площади, прямо пропорциональны, что указывает на существование равновесия в системе порода/руда. Изучено изменение химического состава рудообразующих хромовых шпинелей, температуры оливин-шпинелевого равновесия и фугитивности кислорода в пределах отдельных рудных тел. Фугитивность кислорода возрастает от внутренних частей тел хромититов по направлению к их эндоконтактам. Показано, что в глиноземистых хромититах повышение фугитивности кислорода коррелирует с увеличением густоты вкрапленности хромовой шпинели в руде. Хромититы, залегающие в телах дунитов и в гарцбургитах, образовались при близких окислительно-восстановительных условиях. Проведено сравнение полученных данных с результатами исследования состава минералов и окислительно-восстановительного состояния хромовых руд массива Рай-Из.

Ключевые слова: редокс-состояние, хромититы, ультрамафиты, Войкаро-Сыньинский массив, метаморфизм, рудообразование

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