Chemical zoning of chrome-spinel nodules and oxythermobarometry of nodular chromitites of the Engayskoe-3 occurrence in the Rai-Iz massif (Polar Urals)

Pavel Borisovich SHIRYAEV1, 2, *, Nadezhda Vladimirovna VAKHRUSHEVA1, 2, **

1Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of RAS, Ekaterinburg, Russia
2Ural State Mining University, Ekaterinburg, Russia

Relevance of the work. Chromitites of nodular texture are found in all chromite-bearing alpine type ultramafite massifs of the world. The question of the geological and thermodynamic conditions of their formation still remains debated. The geology, mineralogy and petrography of the nodular chromitites of the ophiolitic massifs of the Polar Urals, the results of studies of which are presented in this work, are slightly highlighted in Russian and foreign literature.

Purpose of the work. To study the chemical zoning of chrome-spinel nodules from the chromitite of the Engayskoe-3 occurrence of the Rai-Iz massif (Polar Urals), to establish the patterns of changes in the content of chemical elements in the core and rims of the nodules, to determine the T–fO2 parameters for the formation of the studied chromitites.

Results. The nodules of chromitites of the Engayskoe-3 occurrence consist of the core composed of interspersed chromite, which is surrounded by a solid rim of chromite. The change in the ratio of trivalent cations in the spinels of a nodule rim (from its inner part towards the edge and core) occurs mainly by replacing Al3+ ↔ Fe3+, as indicated by the inverse proportionality of the number of these cations in the unit cell of the mineral. Similarly, the composition of spinel grains changes forming an impregnation in the space between the nodules. For chrome spinels from the nodule core, the change in the composition of the mineral grain from the center to the edge is due to the isomorphic replacement of Al3+ ↔ Cr3+. The central parts of the spinel grains from the nodule core have the oxygen fugacity values to 0.7 logarithmic units above the FMQ buffer, on average, about FMQ +2 logarithmic units. The edge parts of the grains are much more oxidized: oxygen fugacity (determined for them) is FMQ + 3.1...+ 3.3 logarithmic units. The inner part of the nodule rim is recomposed (fO2 (FMQ) = +1.2...+1.7 logarithmic units) compared to the marginal (fO2 (FMQ) = +3.3...+3.6 logarithmic units above FMQ buffer). The temperature of olivine-spinel equilibrium is at the level of 550–600 °C.

Conclusion. It was assumed that the core of the studied nodules are fragments of earlier disseminated chromitites. The formation of nodules rims is associated with a stage of metamorphism, in which the paragenesis of chlorite, amphibole, and talc was formed in the silicate part of chromitites; and olivine retained its plasticity.

Keywords: nodular chromitites, chemical zoning, the Polar Urals, ophiolites, oxythermobarometry.

Introduction

Nodular chromitites structure are common in chromite-bearing ophiolite massifs around the world. Despite the fact that chromitites of this type have been studied for more than a century and having a variety of their models [1–8, etc.], their genesis remains debated. One of the first models was proposed by A. P. Karpinsky [1], a well-known Russian geologist, who considered nodular chromitites as pebbles formed during the mechanical movement of ore material at high temperature and in a short period of time. In the 1950s–1960s, most scientists (including a major researcher of chromitites of the Kempiraysky massif N. V. Pavlov [2]) adhered to the point of view, according to which nodules are formed as a result of the segregation of ore-silicate melt. Nowadays, several possible ways for the formation of nodular chromitites are being considered.

The first of them was proposed by K. Ballhaus [4]. From the point of view of the author, the formation of nodular chromitites occurs by mixing of melts with different SiO2 content and, as a result, viscosity. More basic and less viscous melt forms droplets in a more acidic and more viscous melt. Chrome spinel crystallizes within these droplets. The mineral grains are filled with drops, which leads to the formation of a nodule.

According to the second concept [6], nodular chromitites are formed under the influence of the fluid phase. Fluid bubbles in the basaltic melt collect chromite microcrystals and lift them to the upper part of the magmatic column. Here, the crystals accumulate in segregation, the density of which is higher than the density of the basalt melt; then they descend to the bottom of the magma chamber forming an ellipsoidal shape in the melt.

The latest study [7] is based on the results of X-ray tomography of the nodular chromitites of the Oman massif and the determination of the orientation of the chrome-spinel grains using the EBSD attachment. The authors found that the nodules studied by them are formed by solid chromitite rims growing on skeletal spinel crystals or segregation of mineral grains. The rounded shape of the nodule is a consequence of their partial dissolution. Formation of chromite rims occurs in a Cr-saturated melt.

The members of the Institute of Geology of Ufa Scientific Center of the Russian Academy of Sciences (Ufa) are engaged in the study of nodular chromitites. So, D. E. Saveliev studied one of the deposits of the Kraka massif, within which both nodular and solid chromitites are found [3]. The author concluded that nodular chromitites have a tectonic origin and are formed during a shear flow due to massive ones. Inside the body of massive chromitites, nodular ores trace weakened zones and are associated with the most rheologically weak dunites. The rounded shape of the nodule is formed due to the high total pressure and temperature at which breccia would form under surface conditions.

The nodular chromitites of the Engayskoe-3 occurrence, which are the subject of discussion of this work, were previously studied using electron microscopy by V. Yu. Alimov and L. A. Sherstobitova [9]. According to the results of the study, it was
The purpose of this work is to study the chemical zoning of the chrome-spinel nodule from chromitites of the ore body no. 11 of the Engayskoe-3 occurrence.

Chemical compositions of ore-forming chrome-spinels and olivines were determined using electron probe microanalysis (microanalyzer CAMECA SX 100, Ural Branch of the Russian Academy of Sciences, analyst is A. V. Mikheeva).

The mineral composition of chromitites

Within the ore body No 11 represented by chromitites of a disseminated-banded texture, podiform separation of nodular chromitites with a visible thickness of 55 cm is exposed (Fig. 1). The lens is oriented submeridionally, in accordance with the banding of slightly disseminated chromitites, and has a subvertical dip.

The body of nodular chromitites lies in the dunite body, in which jets, packs, disseminated-banded, slightly impregnated ores occur fixing fracture zones.

In the cross-section, the nodules have an oval shape with a length to width ratio 3:2, at least 2:1. Nodule sizes range from 6 to 20 mm along the long axis averaging 14–16 mm. Most large nodules have a zonal structure and consist of two zones. The inner zone (core) is represented by a medium or rare impregnation of chrome-spinel crystals, whose dimensions are 0.3–1.0 mm, located among the grains of olivine and chlorite. In the general case, the core configuration corresponds to the nodule form [10].

Figure 1. Exposure of nodular chromitites. Ore body no. 11, Engayskoe-3 occurrence, left bank of the Enga-Yu river.
Рисунок 1. Коренной выход нодулярных хромититов. Рудное тело № 11, рудопроявление Енгайское-3, левый берег р. Енга-Ю.

Figure 2. The development of talc Tlc, chromic clinohlore Chl, serpentine Srp and tremolite Amf in pressure shadows at the nodule border of chrome-spinel Spl with serpentinized olivine Ol. Thin section photo in cross-polarized light.
Рисунок 2. Развитие талька Tlc, хромового клинохлора Chl, серпентина Srp и тромолита Amf в тенях давления на границе нодуля хромовой шпинели Spl с серпентинизированным оливином Ol. Фото шлифа с анализатором.
The outer zone is represented by a single crystal rim of a 3–4 mm chrome-spinel. As you can see in the photograph of the thin section, the rim is not developed along the entire periphery of the studied nodule – it is absent in its upper part (Fig. 3, profile b–b’). The single-crystal structure of the outer zone is traced due to the identical orientation of the individual cracks. Cracks in the rims of the nodule are often filled with serpentinized olivine. In addition to them, there are stepped cracks, which cut the entire nodule (not going beyond its limits) and are made by a parallel-columnar chlorite aggregate.

The nodules are immersed in a silicate matrix, which is represented by serpentinized olivine with separate long-prismatic amphibole grains. At the outer boundary of the nodule, in the pressure shadows, a parallel-columnar aggregate of chrome clinohlore, tremolite and talc is developed (Fig. 2). In the space between the nodules, lenses, and chains of chromium, spinel crystals of 0.1–1.0 mm in size are distinguished.

**Chemical zoning of nodules. Oxythermobarometry of nodular chromitites**

Variation in the composition of chrome-spinel within a nodule were studied in two mutually perpendicular directions – along the long and short axes (Fig. 3). The compositions of chrome-spinel in the core and rim of the nodule are different. The content of Cr₂O₃ in the rim gradually decreases to the edge of the nodule and to the contact of the rim with the core; it varies within 61–62 wt. %. The contents of MgO and Al₂O₃ change in a similar way. Along the short axis of the nodule (Fig. 3, profile a–a’), Cr₂O₃ content and Fe⁺⁺⁺⁺(Fe⁺⁺⁺⁺⁺Fe⁺⁺⁺⁺⁺) (herein after, Fe#) in the spinel edge is higher than along the long axis (Fig. 3, b–b’ profile). Such zoning cannot be explained by the kinetic redistribution of components inside the spinel grains under the action of stress similar to [11, 12] since chromium enrichment would occur in a different way than in the studied nodule: Cr – along the compression axis (short), and Al – along the axis of stretching (long). It is possible that chromium enrichment along the long axis occurs due to the removal of aluminum from the mineral, which was redistributed to chlorite forming a parallel-columnar aggregate (together with talc and tremolite) in pressure shadows along the axis of stretching of the nodule (Fig. 2).

The composition of spinel in the nodule core is noticeably variable. From the center to the edge of the grains of the mineral the content of Cr₂O₃ increases from 61–62 wt. % to 62–66 wt. % (it averages about 64 wt. %), at the same time, the content of Al₂O₃ decreases from 6–8 wt. % to 2–5 wt. %. Fe# in the edges of the spinel grains is 3–5% lower than in the central parts.

The chrome-spinels that compose the core of the investigated nodule have a higher Cr-content compared to the ore spinels of the Tsentralnoye deposit (Fig. 4). The spinels that make up the nodule rim, on the contrary, have a similar compositions. The spinel grains forming an impregnation in the space between the nodules are close in composition to the marginal parts of their rim.

The change in the ratio of trivalent cations in the spinels of the nodule rim (from its inner part towards the edge and core) occurs mainly by replacing Al³⁺ ↔ Fe⁺⁺⁺, as indicated by the inverse proportionality of the amounts of these cations in the unit cell of the mineral (Fig. 5, a). Grains of spinel forming an impregnation in the space between nodules (one of the studied grains is in direct contact with tremolite grain) have a similarly chemical zoning (one of the studied grains is in direct contact with the tremolite grain). This type of isomorphism may be due to late processes, which spinel has undergone during serpentinization [13].

For chrome-spinels from the nodule core, the change in the composition of the mineral grain from the center to the edge is due to the isomorphic replacement of Al³⁺ ↔ Cr⁴⁺ (Fig. 5, b). This type of isomorphism in ore-forming spinels is associated with the development of chlorite during the secondary transformation of mineral [14].

Olivines from the inner part of the nodule have the lowest Fa-content within the studied sample of chromitite (Fa = 2...3%). Fa outside the nodule increases slightly with distance from it, reaching values of up to 3.5%.

Using the geothermometer and oxybarometer [15], the temperature of the olivine-spinel equilibrium and oxygen fugacity were calculated. The central parts of the spinel and olivine grains from the nodule core fix the lowest oxygen fugacity values to...
The ratio of trivalent cations in octahedra of chrome-spinel, which composes the nodule from chromitites of the Engayskoe-3 occurrence. Legend keys – see figure 4.

As described above, chrome-spinels from the core and rims of the chromitites nodule of the ore body 11 of the Engayskoe-3 occurrence have different compositional trends, as well as different microstructure. This indicates the different conditions of their formation. The parameters determined in our work correspond to the stage of the crustal (metamorphic) transformations of ultramafites. The core of nodules often have an angular shape; then the rim will have the same shape. The boundary of the core and rim is sharp, without a gradual change in the density of the chrome-spinel impregnation. The thickness of the rim is stable and does not depend on the size of the core. These observations together with the obtained data suggest that the core of the studied nodules (like the nodules from the chromitites of the Oman massif studied in [7]) are fragments (chips) of earlier embedded chromitites. The symmetric zoning of the rim indicates that its composition has not undergone changes due to the superimposed processes, but it is basic one. Its variation from internal parts to external occurred against the backdrop of changes in the fugacity of oxygen and chemical properties of the ore-forming system. The formation of nodules rims is associated with a stage of metamorphism, in which the paragenesis of chlorite, tremolite, and talc was formed in the silicate part of chromitites; and olivine re-

0.7 logarithmic units above the FMQ buffer, on average, about FMQ + 2 logarithmic units. The edge parts of the grains are much more oxidized: oxygen fugacity, defined for them, is 3.1–3.3 logarithmic units above FMQ buffer. The central parts of the nodule rim and olivine grains in contact with the nodule are also more reduced (FO2 = FMQ + 1.2...+ 1.7 logarithmic units) as compared to the marginal (FO2 3.3–3.6 logarithmic units above FMQ buffer). The temperature of olivine-spinel equilibrium is at the level of 550–600 °C.

Conclusion
As described above, chrome-spinels from the core and rims of the chromitites nodule of the ore body 11 of the Engayskoe-3 occurrence have different compositional trends, as well as different microstructure. This indicates the different conditions of their formation. The parameters determined in our work correspond to the stage of the crustal (metamorphic) transformations of ultramafites. The core of nodules often have an angular shape; then the rim will have the same shape. The boundary of the core and rim is sharp, without a gradual change in the density of the chrome-spinel impregnation. The thickness of the rim is stable and does not depend on the size of the core. These observations together with the obtained data suggest that the core of the studied nodules (like the nodules from the chromitites of the Oman massif studied in [7]) are fragments (chips) of earlier embedded chromitites. The symmetric zoning of the rim indicates that its composition has not undergone changes due to the superimposed processes, but it is basic one. Its variation from internal parts to external occurred against the backdrop of changes in the fugacity of oxygen and chemical properties of the ore-forming system. The formation of nodules rims is associated with a stage of metamorphism, in which the paragenesis of chlorite, tremolite, and talc was formed in the silicate part of chromitites; and olivine retained its plasticity. In addition, the results obtained in this work show that large-scale redeposition of the ore substance is possible (when the metamorphism of ultramafites) without a significant change in the chemical composition of the ore-forming spinel.

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Химическая зональность нодулей хромовой шпинели и оксинтермобарометрия нодулярных хромитов рудопроявления Енгайское-3 массива Рай-Из (Полярный Урал)

Павел Борисович ШИРЯЕВ1, 2,*
Надежда Владимировна ВАХРУШЕВА1, 2**

1 Институт геологии и геохимии им. акад. А. Н. Заварницкого УрО РАН, Россия, Екатеринбург
2 Уральский государственный горный университет, Россия, Екатеринбург

Актуальность работы. Хромиты нодулярной текстуры встречаются на всех хромитоносных аллувиальных ультрафилитовых массивах мира. Вопросы геохимических и термодинамических условий их образования на протяжении столетий занимает исследователей и по-прежнему остается открытым. Геология, минералогия и петрогенез хромитов эталонных оффиолитовых массивов Полярного Урала, результаты исследований которых представлены в настоящей работе, слабо освещены в отечественной и зарубежной литературе. 

Цель работы. Изучить химическую зональность нодулей хромовой шпинели из хромитовых рудопроявления Енгайское-3 массива Рай-Из (Полярный Урал), установить закономерности изменения содержания химических элементов в ядрах и каемах нодулей, определить T–FO2 параметры образования исследованных хромитов.

Результаты. Нодули хромитов рудопроявления Енгайское-3 состоят из ядра, сложенного вкрапленным хромитом, которое окружено каймой сплошного. Изменение соотношения трехвалентных катионов в шпинелях каймы нодуля (от ее внутренней части до ее края) происходит главным образом путем замещения Al3+ ↔ Fe3+, на что указывает обратная пропорциональность количества этих катионов в элементной ячейке шпинели. Аналогично изменяются составы зерен шпинели, образующие вкрапленность в пространстве между нодулями. Для хромовых шпинелей из ядра нодуля изменение состава зерна минерала от центра к краю обусловлено изоморфным замещением Al3+ ↔ Cr3+. Центральные части зерен шпинели из ядра нодуля фиксируют значения фугитивности кислорода до 0,7 л. ед. выше буфера FMQ, в среднем около FMQ + 2 л. ед. Краевые части зерен значительно более окислены: фугитивность кислорода, определенная для них, составляет FMQ + 3,1…+3,3 л. ед. Внутренняя часть ядра нодуля является более восстановленной (IO2 (FMQ) = +1,2…+1,7 л. ед.) по сравнению с краевой (IO2 (FMQ) = +3,3…+3,6 л. ед. выше буфера FMQ). Температура охлаждения шпинеля равновесия находится на уровне 550–600 °С.

Вывод. Следует предположить, что ядра исследованных нодулей являются фрагментами более ранних вкрапленных хромитов. Образование каймы нодулей сопряжено с этапом метаморфизма, на котором в силликатной части хромитов формировался парагенезис хлорита, амфибола и талька, а оливин сохранил пластичность.

Ключевые слова: нодулярные хромиты, химическая зональность, Полярный Урал, оффиолиты, оксинтермобарометрия.

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* shiryayev@igg.uran.ru
** vakhruscheva@igg.uran.ru

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