Zonality of ore-forming chrome spinels of medium-chrome and aluminous chromitites of the Voikaro-Syninsky massif

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Abstract

Relevance of the work. The conditions for the formation of chromium ores in alpine-type ultramafites remain a topical subject of research. In recent years, scientific papers have focused on the issue of changing the chemical composition of ore-forming minerals and chromium ores under the influence of deformation and dynamic recrystallization processes accompanying metamorphism. The results of such studies make it possible to formulate a new model of the formation of chromium mineralization taking into account a significant amount of geological data indicating that alpine-type ultramafic rocks are “mantle tectonites”. In our work, we have studied zonal ore-forming spinels from chrome ores of the Polar Urals. The results of the study make it possible to associate the formation of chemical zoning in minerals and ore bodies with recrystallization under the influence of stress tension.

Purpose of the work – study of the conditions for the formation of chemical zoning of chromium spinels from alumina and medium chromium ores of the Voikaro-Syninsky massif.

Results. Zonal ore-forming spinels from medium-chromium and aluminous chromitites of the Voikaro-Syninsky massif (Polar Urals) have been studied. It was found that replacement rims are developed along the grains of ore-forming spinels with an increased content of Cr_2O_3 and an oxidation state of iron in relation to the core, as well as a reduced content of Al_2O_3 . The oxidation state of iron in the rims of most grains does not exceed the values typical for unaltered ore-forming spinels. $T\text{-fO}_2$ parameters of zoning formation in spinels were determined by oxythermobarometry. Comparison with zoned chrome spinels of the Golyamo Kamenyane massif (Bulgaria).

Conclusion. Metamorphic transformations of alumina and medium-chromium chromitites of the Voikaro-Syninsky massif, occurring under subcrustal conditions under the action of directional stress at relatively constant $T\text{-fO}_2$ parameters, lead to an increase in the chromium content of the ore mineral.

Keywords: Polar Urals, chromium ores, chemical zoning, dynamic recrystallization, stress, strain.

Introduction

The zoning of ore-forming and accessory chrome spinels from alpine-type ultramafic rocks is the subject of numerous studies. It is formed because of metamorphic transformations of rocks and chromium ores [1–5]; under the influence of directed stress [6, 7]; because of the redistribution of iron and magnesium between spinel and olivine when the temperature changes [8, 9].

Previously, we studied the chemical zoning of chromium spinels and olivines from high-chromium chromitites and ore-bearing rocks of the Tsentralnoye deposit and medium-chromium chromitites of the Yengayskoe-1 ore occurrence in the Rai-Iz massif [10, 11]. It was found that the chemical zoning of spinels is formed under conditions of a decrease in temperature and an increase in oxygen fugacity. The amount of aluminum oxide decreases to the edges of the grains of the mineral; the iron content and the degree of oxidation of iron increase. The Cr_2O_3 content in spinels from the ores of the Tsentralnoye deposit and the Yengayskoe-1 ore occurrence varies from the centre to the edge of the grain in different ways: in the first case, it increases, in the second – decreases. This may

be due to the different pressures at which the zoning of the mineral was formed. The ore-hosting meta-ultramafic rocks, amphibole-enstatite-olivine rocks, contain elongated spinel grains with asymmetric zoning in Al, Cr, Mg content, the formation of which occurs under conditions of one-sided compression [10, 11].

The topic of this study is the chemical zoning of spinels from ores of the aluminous and medium chromium types of the Voikaro-Syninsky massif. The compositions of the ore-forming spinels of the Voikaro-Syninsky massif were studied by A.B. Makeev and co-authors [12, 13]; they are covered in the geological reports of I. S. Chashchukhin, V. Yu. Alimov, N. V. Vakhrusheva; A. B. Makeev; B. V. Pechenkin, and V. G. Kotelnikov.

In his monographs A.B. Makeev presents the results of a study of the mineralogy of ultramafic rocks of the Polar Urals. The chemical compositions of ore-forming chrome spinels of the Syum-Keu, Rai-Iz and Voikaro-Syninsky massifs have been characterized. It is noted that spinels have either a homogeneous internal structure, or zonal, with a later rim of ferrichromite and magnetite [12, 13].

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In their report I. S. Chashchukhin, V. Yu. Alimov, N. V. Vakhrusheva [14] discuss the chemical composition of ore-forming spinels of most of the main ore occurrences in the northern part of the Voikaro-Syninsky massif. The zoning of ore bodies by the chemical composition of ore-forming chromium spinel, in particular, body 3415 of the Arkashorskoe ore occurrence, has been studied. A microprobe study of the distribution of chemical components inside grains of accessory chromium spinels during metamorphism has been carried out. It was found that metamorphism leads to the formation of magnetite and chromomagnetite rims in the studied spinels. Rims are formed both by the overgrowth of spinel grains with magnetite and as a result of changes in the chemical composition of its marginal part during retrograde metamorphism.

Features of the geological structure of the studied ore occurrences

In this paper, alumina chromitites of ore body no. 118 of the Yambotyviskaya area and medium-chromium chromitites of ore body no. 3415 of the Arkashorskoe ore occurrence have been studied.

Ore body no. 118 is located at the watershed of the Levaya Payera River and the Yambotyvis stream. It lies in the rocks of the dunite-harzburgite complex with a dunite content of 10–30%. Harzburgites underwent non-equilibrium metamorphism, as a result of which an aggregate of talc and amphibole developed along enstatite. Chromitites are surrounded by a dunite rim, the thickness of which varies from 0.1 m to a few meters. The ore body is column-shaped. Its apparent thickness is 8–9 m, its length is 12–13 m. The central part of the ore body is solid, with areas of densely disseminated, medium-grained chromitites.

Ore body no. 3415 exposed in the wall of the left side of the valley Arkashore stream. Ores occur in meta-ultramafic amphibole-olivine-antigorite rocks. Chromitites are surrounded by a dunite rim, the thickness of which ranges from 0.5 to 1.5 m. The length of the ore body is 40 m, with a maximum outlet width of 12 m; the shape is lenticular with complexly oriented contacts. The ore body plunges westward at an angle of 50–80°. The ores are mainly represented by moderately disseminated varieties with separate lenticular and spotty areas, composed of coarse-grained densely disseminated chromitite with serpentine-olivine cement. At the endocontacts, the density of dissemination of ore-forming spinel decreases.

According to the chemical composition of the ore-forming spinel, two blocks are distinguished within the ore body – western and eastern, which have similar thicknesses. Ore-forming chrome spinels of the western block contain on average Cr_2O_3 – 46–49 wt.%; Al_2O_3 – 14–18 wt.%; MgO – 13–14 wt.%. The chemical composition of the spinels of the eastern block of the ore body is characterized by a higher content of Cr_2O_3 – 54–58 wt.% and lower Al_2O_3 – 6–13 wt.% and MgO – 8–12 wt.%. It should be noted that the composition of the ore-forming spinels of the ore body was determined by the method of wet chemical analysis and reflects the composition of the grains of the mineral as a whole.

Research results

The study of the chemical composition and zoning of mineral grains in this work was carried out using microprobe analysis (Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences, Cameca SX-100, the analysts are I. A. Danilenko,

Figure 1. Distribution of chemical elements in grains of ore-forming chrome spinels from ore body no. 118 of the Yambotyviskaya area. The image was obtained using a scanning electron microscope

Рисунок 1. Распределение химических элементов в зернах рудообразующих хромовых шпинелей из рудного тела № 118 Ямботывисской площади. Изображение получено при помощи сканирующего электронного микроскопа

Figure 2. Compositional variations in grains of ore-forming spinel and contacting olivine from sample no. X-1507/8 (ore body no. 118, Yambotyvissskaya area)

Рисунок 2. Вариации содержаний химических элементов в зернах рудообразующей шпинели и контактирующего с ней оливина из обр. X-1507/8 (рудное тело № 118, Ямботывисская площадь)

D. A. Zamyatin) and using a scanning electron microscope (Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences, Jeol JSM-6390LV with an energy dispersive prefix INCA Energy 450 X-Max 80, the analyst is L. V. Leonova).

Spinel grains of ore body no. 118 are surrounded by a border having an average thickness of 1–10 microns, which in some cases reaches 100–150 microns. The boundary between the rim and the core of the grain is sharp; directly at the contact, silicate microinclusions

Figure 3. Ratio of trivalent cations in the centers and edges of grains of ore-forming chromium spinels of the Voikaro-Syninsky massif. Yambotyviskaya area: 1 – core, 2 – rim; Arkashorskoye ore occurrence: 3 – core, 4 – rim

Fields of compositions according to the classification by N. V. Pavlov: 1 – chromite; 2 – subferrichromite; 3 – aluminochromite; 4 – subferrialuminochromite; 5 – ferrialuminochromite; 6 – subalumoferrichromite; 7 – ferrichromite; 8 – chrompicotite; 9 – subferrichrompicotite

Рисунок 3. Соотношение трехвалентных катионов в центрах и краях зерен рудообразующих хромовых шпинелей Войкаро-Сыньинского массива. Ямботывисская площадь: 1 – центр, 2 – кайма; Аркашорское рудопроявление: 3 – центр, 4 – кайма

Поля составов по классификации Н. В. Павлова: 1 – хромит; 2 – субферрихромит; 3 – алюмохромит; 4 – субферриалюмохромит; 5 – ферриалюмохромит; 6 – субалюмоферрихромит; 7 – феррихромит; 8 – хромпикотит; 9 – субферрихромпикотит

are concentrated. Rim spinel is lighter in color both in reflected light and in backscattered electrons. It can be seen that the border consists of individual grains ranging in size from 5–10 microns to 50 microns, associated with chlorite flakes, the size of which is 5–10 microns. Chrome spinel, similar in chemical composition and reflectivity to the spinel, is developed along grain boundaries and around cracks and inside deformation zones (fig. 1). This indicates that the rims develop by replacing grains of chromium spinel, and not growing on them.

In the cores of spinel grains of ore body no. 118 of the Yambotyviskaya area from the center towards the rim, a slight (from 41 to 40 wt.% on average) decrease in the content of Cr_2O_3 , as well as MgO from 17–17.5 wt.% is observed up to 16–16.5 wt.% (points X-2–X-4 and X-6–X-9 in fig. 2). At the same time, towards the border, the iron content of the mineral increases from 23–24% to 26%, i. e. by 2–3% (in ore-forming spinels of the Rai-Iz massif, the iron content increases towards the edge of the grain by 5–10% [11]). The content of Al_2O_3 in the grain cores varies between 26–27 wt.%, FeO – 13–14 wt.%.

Spinel, forming replacement rims, is characterized by an increased content of Cr_2O_3 – 51–52 wt.% and FeO – 20–21 wt.% and additionally reduced Al_2O_3 – 9–12 wt.% and MgO – 12–14 wt.%. The oxidation state of

iron varies widely from 13 to 70%, on average taking values in the range from 35–40%. Spinels with the highest $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ ratio are found in the edge part of the rim, at the contact with silicates, and with the lowest one, in the inner parts of grains, in recrystallization zones. In the oxidized spinels of the rim, an increase in the $\text{FeO}_{\text{total}}$ content occurs due to the enrichment of the mineral with trivalent iron (fig. 2, point X-1). As can be seen on the maps of the distribution of chemical elements in spinel grains, the border between the rim and the core of the grain is sharp (fig. 1). The rim is well enriched in Cr and Fe and depleted in Mg and Al. That is, the composition of the mineral corresponds to the ore-forming spinels of medium-chromium chromitites of the Voikaro-Syninsky massif, although in most analyses it has an increased degree of iron oxidation by 10–15% (fig. 3). Thus, in the ores of ore occurrence 118, the development of medium-chromium, ferruginous chromium spinels over alumina ones is observed.

The iron content of olivine ($\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$) decreases from the centre of the grain to the edge by 0.5–1%, while the content of Cr_2O_3 in the mineral is less than 0.02 wt.%, that is, below the detection limit in the study by microprobe analysis.

Around the spinel grains composing ore body 3415, a rim is also developed, the thickness of which is up to 100–300 μm on average. The border is composed of lighter spinel in reflected light, as well as chlorite, which forms regularly oriented inclusions, due to which the border acquires a structure similar to a graphic one. The chlorite content in the border is 7–10%, the grain size of the mineral is on average 10–30 microns. The smallest thickness of the rim is characteristic for the chrome spinels of the western block of the ore body, the highest – for the spinels of the eastern block, where there are mineral grains completely replaced by a chlorite-spinel aggregate.

The content of Cr_2O_3 in spinel cores varies between 47–48 wt.%; Al_2O_3 = 18–19 wt.%; FeO = 18–20 wt.%; MgO = 13–15 wt.%; $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ = 28–30 %. In a rim composed of a spinel-chlorite aggregate, the content of Cr_2O_3 increases to 51–55 wt.%, and FeO = up to 21–25 wt.%. This reduces the of Al_2O_3 content to 7–14 wt.% and MgO up to 9–11 wt.%. The oxidation state of iron in the spinel of the rim is lower than in the core and averages 22–24% (fig. 3, 4). In some cases, at the contact with the silicate part of chromitite in spinel, increased (up to 30–35%) values of $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ are observed.

The maps of the element distribution (fig. 5) show that the decrease in the Al content towards the grain edge is well expressed, compared with the change in the Cr, Fe, and Mg contents. In the rim, angular blocks with different amounts of Al are distinguished. The rim is unevenly developed along the periphery of the grains.

In olivine grains from the silicate part of chromitites of ore body no. 3415, the iron content gradually decreases towards the contact with the ore-forming chromium spinel from 5.5–5.7% in the core of the grain to 5–5.2% in the rim. The content of Cr_2O_3 in the rims of the mineral grains reaches 0.2 wt.% (the detection limit of the element is lower – 0.02 wt.%).

Figure 4. Compositional variation in the grain of ore-forming spinel and olivine from sample no. 3701 (ore body no. 3415, Arkashorskoye ore occurrence)

Рисунок 4. Вариации содержаний химических элементов в зерне рудообразующей шпинели и контактирующего с ней оливина из обр. 3701 (рудное тело № 3415, Аркашорское рудопоявление)

Using an Ballhaus-Berry-Green olivine-spinel geothermometer and a oxybarometer [15], the temperature of olivine-spinel equilibrium and oxygen fugacity were estimated at which the zoning of ore-forming spinels of the studied ore bodies was formed. The temperatures values calculated on the basis of the compositions of the spinel cores from the chromium ore of the Yambotyvissskaya ore occurrence are 760 ± 20 °C, the oxygen fugacity values are 1.9–2.1 units above the FMQ buffer. The temperature of the olivine-spinel equilibrium in the rim also corresponds to the indicated range but the oxygen fugacity is higher: +3...+3.2 log units relative to the FMQ buffer. In areas of the border with a low oxidation state of iron ($\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}) = 13\%$) the value of $f\text{O}_2 = 0.7$ log units

above the FMQ buffer. The scatter in the values of oxygen fugacity and the degree of iron oxidation in the grain rims of ore-forming spinels in the Yambotyvissskaya area indicates that the conditions for the formation of these rims were nonequilibrium.

In the studied chromitite of the Arkashorskoye ore occurrence, the temperature of the olivine-spinel equilibrium is 650 ± 20 °C, the oxygen fugacity varies within +2...+2.3 log units relative to the FMQ buffer. From the grain core to its rim, the oxygen fugacity increases by 0.1–0.2 log units, and the temperature of the olivine-spinel equilibrium decreases by 40 °C, which is lower than the error of the oxybarometer and geothermometer. It follows from this that the formation of the zoning of

Figure 5. Distribution of chemical elements in grains of ore-forming chromium spinels of ore body no. 3415 of the Arkashorskoye ore occurrence. The image was obtained using a scanning electron microscope

Рисунок 5. Распределение химических элементов в зернах рудообразующих хромовых шпинелей рудного тела № 3415 Аркашорского рудопроявления. Изображение получено при помощи сканирующего электронного микроскопа

the ore-forming spinels of the Arkashorskoye ore occurrence took place at relatively constant T - fO_2 parameters.

Discussion of the results

The ratios of the compositions of the cores and rims of grains of ore-forming spinels of the considered objects are close to the compositions of zonal spinels of the Golyamo Kamenyane massif studied in [4]. Researchers have found that the formation of a replacement rim for high-chromium, and relatively ferrous spinels for medium-chromium, is associated with regressive water metamorphism that took place under reducing conditions [4]. Later, the zoned spinels of the Golyamo Kamenyane massif were studied by the EBSD method. It was found that the rim is composed of an aggregate of chrome spinel grains [7]. The analysis of their orientation made it possible to determine that the formation of a rim occurs as a result of dynamic recrystallization of spinel. The authors conclude that spinels have undergone metamorphism in the shear deformation zone under mid-crustal conditions [7].

Ore body 3415 of the Arkashorskoye ore occurrence consists of two blocks, the spinels of which differ in composition. The ore-forming mineral has zoning manifested in the development of a rim of recrystallization of more chromium spinel around less chromium. The chemical zoning of the ore body is due to the fact that the degree of recrystallization of the mineral increases from west to east, up to the complete replacement of grains with a chromite-chlorite aggregate. In the ores of the eastern part of the ore body, the development of such rims is significant, up to the complete replacement of the mineral. Due to the fact that the compositions of the chromium

spinel of the ore body were determined by the method of wet chemistry in monomineral fractions, the effect of changing the chemical composition with an increase in the degree of recrystallization of the mineral is clearly expressed. At the same time, ore body 3415 lies in a petrographically homogeneous section, composed of amphibole-olivine-antigorite rocks. In the case of ore metamorphism together with the host rocks, the ores should have been completely recrystallized, or symmetrical zoning would have formed. It follows that the zoning of ore body 3415 and an increase in the chromium content of newly formed spinels occurred under the action of a directed (one-sided) stress effect on the ore body. The results of oxythermobarometry of chromium ores allow us to conclude that the transformations of chromitites took place in subcrustal conditions at constant T - fO_2 parameters. The grain rims consist of blocks with different compositions, primarily aluminum content. This may be a consequence of the dynamic recrystallization of spinel.

In the chromitites of the Yambotyviskaya area, the increase in the chromium content of the ore-forming spinel from the core to the rim of the grain occurs under nonequilibrium conditions. As a result, spinel microblocks are present in the rim, both with an increased content of ferric iron and with a normal one, typical of ore-forming spinels of the Yambotyviskaya area. The composition of the grain rim of the ore-forming spinel of the Yambotyviskaya area in some areas becomes close to that of the central parts of spinel grains of medium-chromium ores of the Arkashorskoye ore occurrence.

The study of the zoning of ore-forming chromium spinels allows us to conclude that metamorphic transformations of alumina and medium-chromium chromitites occurring in crustal conditions under the action of directional stress at relatively constant T - fO_2 parameters lead to an increase in the chromium content of the ore mineral.

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Зональность рудообразующих хромовых шпинелей среднехромистых и глиноземистых хромовых руд Войкаро-Сыньинского массива

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Аннотация

Актуальность работы. Условия образования хромовых руд в альпинотипных гипербазитах остаются актуальным предметом исследований. В научных работах последних лет стало уделяться внимание вопросу изменения химического состава рудообразующих минералов и хромовых руд под действием процессов деформации и динамической рекристаллизации, сопровождающих метаморфизм. Результаты таких исследований позволяют сформулировать новую модель образования хромового оруденения, учитывающую значительный объем геологических данных, указывающих на то, что альпинотипные ультрамафиты являются «мантийными тектонитами». В нашей работе изучены зональные рудообразующие шпинели из хромовых руд Полярного Урала. Результаты исследования позволяют связать образование химической зональности в минералах и рудных телах с рекристаллизацией под действием стрессовых напряжений.

Цель работы – исследование условий образования химической зональности хромовых шпинелей из глиноземистых и среднехромистых хромовых руд Войкаро-Сыньинского массива.

Результаты. Изучены зональные рудообразующие шпинели из среднехромистых и глиноземистых хромовых руд Войкаро-Сыньинского массива (Полярный Урал). Установлено, что по зернам рудообразующих шпинелей развиты каймы замещения с повышенным по отношению к ядру содержанием Cr_2O_3 и степенью окисления железа, а также пониженным содержанием Al_2O_3 . Степень окисления железа в каймах большинства зерен не превышает значений, типичных для неизмененных рудообразующих шпинелидов. Методами окситермобарометрии определены T-fO_2 -параметры образования зональности в шпинелидах. Произведено сравнение с зональными хромовыми шпинелями массива Голямо-Каменяне (Болгария).

Вывод. Метаморфические преобразования глиноземистых и среднехромистых хромитов Войкаро-Сыньинского массива, происходящие в субкоровых условиях под действием направленного стресса при относительно постоянных T-fO_2 -параметрах, приводят к увеличению хромистости рудного минерала.

Ключевые слова: Полярный Урал, хромовые руды, химическая зональность, динамическая кристаллизация, стрессовые напряжения.

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