

CHEMICAL ZONING OF SPINELS AND OLIVINES FROM CHROMITITES AND THE ENCLOSING ULTRAMAFITES OF THE RAI-IZ MASSIF TSENTRALNOYE DEPOSIT (THE POLAR URALS)

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Химическая зональность шпинелей и оливинов из хромититов и вмещающих ультрамафитов месторождения Центральное массива Рай-Из (Полярный Урал)

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Изучена химическая зональность сосуществующих оливинов и хромовых шпинелей из хромититов и вмещающих пород месторождения Центральное массива Рай-Из. Установлено два типа зональности. Первый тип проявлен как в аксессуарных, так и в рудообразующих шпинелях и оливинах и возникает на контакте минералов, вследствие перераспределения между ними катионов Fe и Mg. К контакту зерен железистость оливина убывает, а шпинели – возрастает. В обоих минералах к краю увеличивается количество Cr_2O_3 . Такая зональность формируется в условиях понижения температуры и повышения фугитивности кислорода. Второй тип зональности наблюдается в пластически деформированных энстатит-оливиновых породах, продуктах метаморфизма гарибургитов. Он характеризуется понижением железистости и повышением количества Cr_2O_3 от внутренних частей зерен оливина и шпинели к их контактам. Образование такой зональности происходило при постоянной температуре и фугитивности кислорода. Если первый тип зональности хорошо изучен и широко обсуждается в литературе, то зональность второго типа является сравнительно редкой. Аналогичное распределение элементов наблюдается в зернах аксессуарных шпинелей массивов Миямори и Хироман (Япония), где оно интерпретируется как результат кинетического перераспределения химических компонентов в структуре минерала, которое происходит под действием диффузионной ползучести Набарро-Херрника в условиях направленного стресса. Присутствие в энстатит-оливиновой породе признаков пластических деформаций – зон динамической рекристаллизации, – полисинтетическое двойникование в зернах оливина также позволяют интерпретировать зональность аксессуарных шпинелей как результат кинетического диффузионного перераспределения компонентов в зерне минерала под действием стресса.

Ключевые слова: оливин; хромовая шпинель; химическая зональность; хромититы; гипербазиты; массив Рай-Из; Полярный Урал.

The authors studied the chemical zoning of coexisting olivines and chromium spinels from chromitites and near-ore rocks of the of the Rai-Iz massif Tsentralnoye deposit. There are two types of zoning. The first type appears both in accessory and in ore-forming spinels and olivines and occurs at the contact of minerals due to the redistribution of Fe and Mg cations between them. On approaching the grain contact the Fe/(Fe + Mg) in olivine decreases while in spinel it increases. In both minerals the Cr_2O_3 content increases to the grain rims. This zoning has been formed under the conditions of temperature decreasing and oxygen fugacity rising. The second type of spinel zoning can be observed in plastically deformed enstatite-olivine rocks, the products of harzburgite metamorphism. It is characterized by the Fe content decrease and the Cr_2O_3 increase from the inner parts of spinel and olivine grains to their contact. The formation of this zoning occurred at a constant temperature and oxygen fugacity. The first type of zoning is well studied and widely discussed in literature, but zoning of the second type is relatively rare. The similar distribution of elements is observed in the grains of accessory spinels of the Miyamori and Hiroman massifs (Japan), where it is considered as the result of kinetic redistribution of chemical components in the mineral structure that occurs under the influence of Nabarro-Herring diffusion creep in conditions of directed stress. The presence of plastic deformation signs (dynamic recrystallization zones and polysynthetic twinning in olivine grains) in the studied enstatite-olivine rock sample also permits the authors to interpret the zoning of accessory spinels as the result of kinetic diffusion redistribution of components in the mineral grain under stress conditions.

Keywords: olivine; chrome-spinel; chemical zoning; chromitites; ultramafic rocks; Rai-Iz massif; Polar Urals.

In the grains of ore-forming and accessory chrome-spinels, as well as in olivines of the Rai-Iz massif one can observe a chemical zoning – heterogeneous distribution of chemical components. A variety of publications discusses the zoning in chromium spinels from various associations, but practically no publications touch upon a topic of the olivine chemical zoning, both in meta-ultramafites and chromitites. Most authors associate zoning formation in spinels with metamorphism [1, 2–4 and many others]. For zonal accessory spinels of the Rai-Iz massif I. S. Chashchukhin shows [1] that the type of zoning depends mainly on the type of metamorphic associations in which the mineral is located. In spinels from the olivine-enstatite rocks (the highest-temperature metamorphites of the

Rai-Iz massif) from the center to the edge of the grain FeO total increases, the Al_2O_3 and MgO contents decrease, distribution of the remaining elements chromium, manganese, titanium, etc. stay relatively uniform. In olivine-talc amphibole rocks towards the spinel grain edge the content of iron, titanium, and manganese rises, while the the content of magnesium, chromium and aluminum oxides falls. At the edge part of the spinel grains from olivine-antigorite rocks relatively the central one, the FeO and TiO_2 content increases and MgO and Al_2O_3 decreases, the content of Cr_2O_3 within the grain varies insignificantly [1].

An alternative model of zoning formation in spinels is suggested in works [5–7]. According to this model redistribution of chemical components in the initially homogeneous spinel occurs under the action of Nabarro-Herring diffusion creep. Stress chemical zoning (kinetic demixing) appears when the diffusivities of two final components are unequal. Lighter ions are concentrated at the crystal faces in tensions and the heavier ones – on the compression faces, so the spinel grains acquire a “multipolar” zoning. A number of natural objects demonstrate reliability of the model – plastically deformed harzburgites of the Miyamori and Horoman (Japan) complexes, peridotites of the Golyamo-Kamenyane (Bulgaria), the chromitites of Oman (Turkey). An increase in the Cr content to the grain edge along the short axis (compression) for this mechanism of zoning formation in spinel is accompanied by an increase in the Mg cation number. On the long (stretching) axis to the grain rim Al content increases together with Fe^{2+} [5].

Generally, the works devoted to the spinel zoning do not consider or do not discuss the composition of coexisting olivine. However, heterogeneity of the chemical composition of this mineral can allow to interpret the zonal distribution of Fe and Mg in spinel grains and estimate the conditions for the formation of its zones.

In this paper the authors present the results of studying of the zoning of the coexisting spinels and olivines from chromitite and ore-hosting ultramafites of the Tsentralnoye deposit southern block

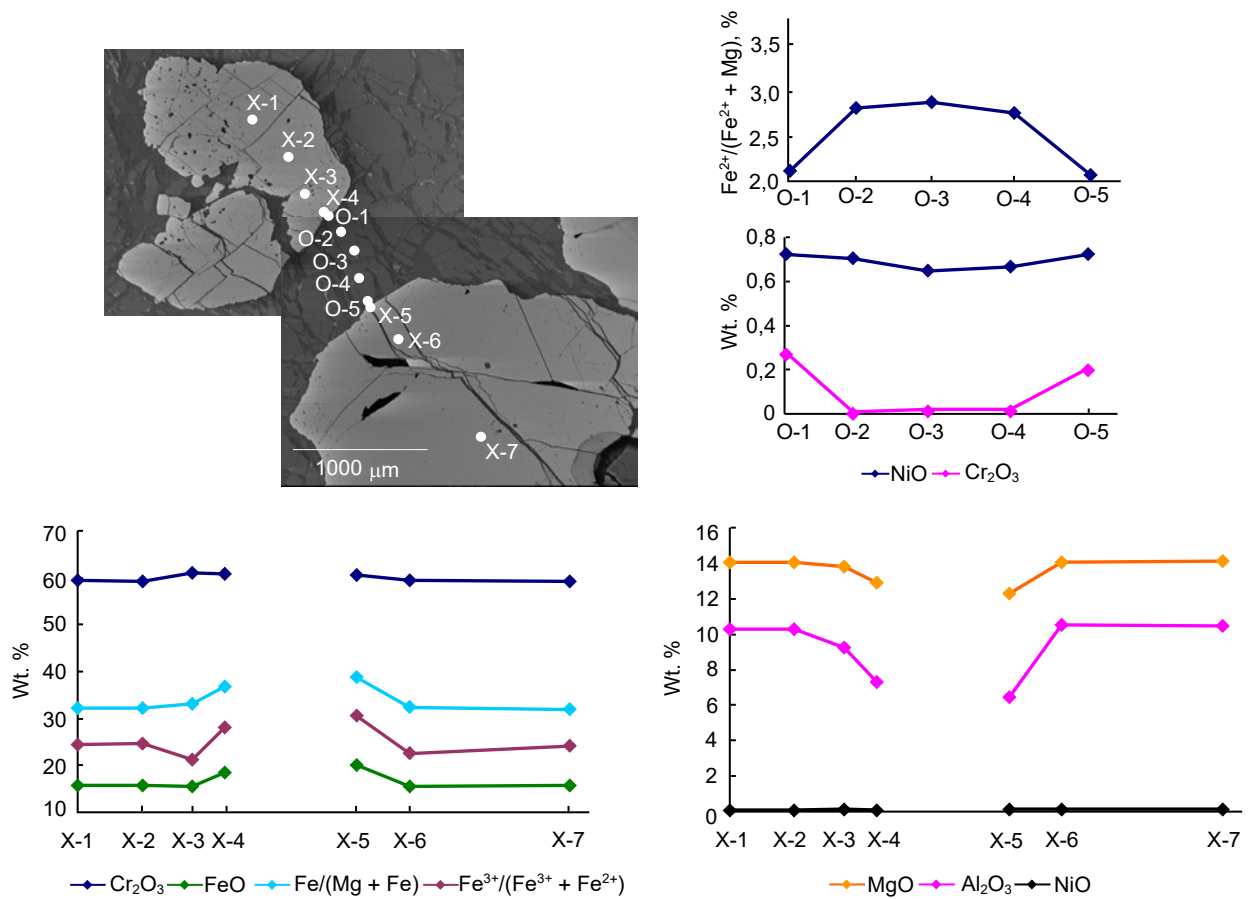


Figure 1. Ore-forming chrome spinel (light-gray, the analysis points X-1...X-4 and X-5...X-7) and olivine (gray, the analysis points O-1...O-5) grains contact from the sample P-3. BSE image, CAMECA SX 100. The diagrams show variations in composition within the grains of minerals.

Table 1. Chrome-spinel chemical composition.

Oxide	Sample number							
	P-1		P-1		P-1		P-2	
	Point number							
	X-1	X-2	X-3	X-4	X-5	X-1	X-2	
TiO ₂	0,07	0,07	0,07	0,07	0,03	0,09	0,14	
Cr ₂ O ₃	34,30	31,48	33,14	33,42	40,89	48,21	34,72	
Al ₂ O ₃	1,11	0,96	0,96	1,01	1,16	1,48	1,15	
FeO	54,61	57,88	57,49	56,29	49,11	43,17	55,69	
MgO	4,10	3,79	3,84	3,83	4,16	3,91	3,30	
MnO	0,29	0,27	0,24	0,37	0,52	0,52	0,37	
NiO	0,64	0,77	0,65	0,78	0,42	0,34	0,67	
V ₂ O ₃	0,14	0,14	0,17	0,14	0,12	0,22	0,25	
ZnO	0,13	0,10	0,14	0,09	0,22	0,11	0,25	
CoO	0,02	0,00	0,00	0,00	0,04	0,00	0,00	
Total	95,41	95,46	96,70	96,00	96,67	98,05	96,56	
<i>Formula units normalized to 3 cations</i>								
Cr	1,00	0,92	0,96	0,97	1,18	1,38	1,01	
Al	0,05	0,04	0,04	0,04	0,05	0,06	0,05	
V	0,00	0,00	0,00	0,00	0,00	0,01	0,01	
Fe	1,69	1,79	1,76	1,73	1,50	1,31	1,71	
Mg	0,23	0,21	0,21	0,21	0,23	0,21	0,18	
Ni	0,02	0,02	0,02	0,02	0,01	0,01	0,02	
Mn	0,01	0,01	0,01	0,01	0,02	0,02	0,01	
Zn	0,00	0,00	0,00	0,00	0,01	0,00	0,01	
Fe ³⁺	0,94	1,03	0,99	0,98	0,76	0,55	0,93	
Fe ²⁺	0,74	0,76	0,76	0,75	0,74	0,76	0,78	
xFe _{sp} ²⁺	76,7	78,4	78,4	78,2	76,5	78,3	81,2	
XCr _{sp}	95,4	95,7	95,9	95,7	95,9	95,6	95,3	
#Fe	56,0	57,7	56,7	56,5	50,9	41,9	54,4	

Oxide	Sample number						
	P-3	P-3	P-3	P-3	P-3	P-3	P-3
	Point number						
	X-1	X-2	X-3	X-4	X-5	X-6	X-7
TiO ₂	0,12	0,13	0,10	0,14	0,15	0,10	0,12
Cr ₂ O ₃	59,49	59,10	61,25	60,76	60,13	59,43	58,99
Al ₂ O ₃	10,29	10,22	9,30	7,28	6,38	10,54	10,43
FeO	15,86	15,68	15,56	18,58	19,98	15,52	15,63
MgO	14,10	14,02	13,86	12,88	12,24	14,06	14,07
MnO	0,14	0,19	0,16	0,18	0,21	0,16	0,15
NiO	0,08	0,09	0,11	0,08	0,11	0,12	0,11
V ₂ O ₃	0,09	0,11	0,10	0,10	0,10	0,08	0,08
ZnO	0,03	0,06	0,01	0,02	0,04	0,00	0,04
CoO	0,03	0,04	0,01	0,00	0,03	0,01	0,02
Total	100,23	99,64	100,46	100,02	99,37	100,02	99,64
<i>Formula units normalized to 3 cations</i>							
Cr	1,50	1,50	1,55	1,57	1,58	1,50	1,50
Al	0,39	0,39	0,35	0,28	0,25	0,40	0,39
Fe	0,42	0,42	0,42	0,51	0,55	0,42	0,42
Mg	0,67	0,67	0,66	0,63	0,60	0,67	0,67
Mn	0,00	0,01	0,00	0,00	0,01	0,00	0,00
Fe ³⁺	0,10	0,10	0,09	0,14	0,17	0,09	0,10
Fe ²⁺	0,32	0,32	0,33	0,36	0,38	0,32	0,32
XFe _{Sp} ²⁺	32,3	32,1	33,2	36,8	38,9	32,4	32,1
XCr _{Sp}	79,5	79,5	81,5	84,8	86,3	79,1	79,1
#Fe	24,4	24,6	21,2	28,2	30,5	22,6	24,3

Note: $XFe_{Sp}^{2+} = Fe^{2+} \times 100 / (Fe^{2+} + Mg)$; $XCr_{Sp} = Cr \times 100 / (Cr + Al)$; $\#Fe = Fe^{3+} \times 100 / (Fe^{3+} + Fe^{2+})$.

(ore pool 9). In this part of the deposit chromitites occur among the rocks of the dunite-harzburgite complex, in which the dunite component gradually decreases in the southwestern direction. Ultramafic rock samples were collected from the deposit tunnel at a distance from the ore body (sample P-1) and from the ore body contact 9 (sample P-2), while the chromitites (sample P-3) – from its inner part. The sample P-1 presents itself an enstatite-olivine rock of poikiloblastic structure, directive texture, with the content of olivine – 80–85 %, enstatite – 12–15 %, chrome-spinel – 1–2 % as well of some flakes of clinocllore and antigorite. The rock contains two generations of olivine grains, differing in size and internal structure features. The cross sections of the grains of the first generation usually are slightly elongated according to directivity and vary in size from 2 to 7 mm. Such grains have cleavage cracks, kink bands and (or) undulose extinction. Orthopyroxene (enstatite) also occurs as single large (2–3 mm) porphyroblasts, saturated with poikilitic inclusions of olivine and chrome spinel.

The cross sections of the olivine grains of the second generation are isometric or slightly elongated; their average size is 0.3–0.5 mm, rarely more. Grains were not affected by internal stress and often form aggregates with a mosaic texture. Olivine grains of the second generation together with the enstatite neoblasts form 3–5 mm wide linear zones oriented subparallel to general mineral lineation in the rock. Chrome-spinel grains, localized within recrystallization zones, have irregular, elongated/flattened shape, 0.7–1.5 mm in length and 0.3–1 mm in width. Spinel inclusions in olivine grains of the first generation, on the contrary, have octahedral shape, and their size does not exceed 0.5 mm.

The presence of linear zones composed of olivine and enstatite of the second generation in the rock and the kink bands in olivine grains of the first generation indicate that the rock undergone plastic deformations with recrystallization.

The amphibole-enstatite-olivine rock of poikiloblastic texture with foliated structure (sample P-2) consists in olivine (75–80 %) and enstatite (12–15 %), which, as in the sample P-1, are presented by two generations with identical average grain sizes. Apart from these min-

erals the rock contains prismatic grains of amphibole (tremolite) of 5–7 % with length up to 3–5 mm, sometimes more. Amphibole is often found within the bands formed by recrystallized olivine and enstatite. Spinel is present as an elongated/flattened grains of irregular shape localized within the zones of recrystallization and as octahedral crystals with the same dimensions as that of spinel grains from enstatite-olivine rock of sample P-1.

Chromitite (sample P-3) is densely disseminated and has a medium-grained texture and massive structure. The chromitite is composed of chrome spinel (70–75 %), olivine (17–20 %), chlorite (3–5 %), serpentine (2–3 %). Chrome spinel grains are usually isometric or slightly elongated in shape with smoothed edges up to 5 mm in size. Olivine grains are xenomorphic and elongated and also occur in two size fractions/generations – the first one is 3–5 mm and the second one is 1–1.5 mm long. Kink bands and undulose extinction appear in the grains of both generations, but they are much less common than in olivines from the near-ore rocks. Both of olivine generations are serpentinized, in a number of cases clinocllore flakes are developed at olivine and spinel boundaries.

Compositions of olivines and spinels studied in this work were obtained from mineral grains that are in direct contact with each other. The analyses have been carried out on the CAMECA SX 100 electron probe microanalyzer by D. A. Zamyatin (IGG UB RAS, Yekaterinburg). The change in the composition of the ore-forming spinel and the contacting olivine grain from chromite (sample P-3) is shown in Fig. 1 and in Table 1 and 2. Fayalite content (Fa, $f = Fe \times 100 / (Fe + Mg)$) in olivine grains varies from 2.9 % at the core to 2.1 % at the rim. Spinel grains have another component distribution: the iron content of the mineral increases towards the grain rim reaching 36–39 %, whereas at the center of grains its value is close to 32 %. Similar zoning of minerals occurs during the ion exchange of Mg and Fe between olivine and spinel as the temperature is decreasing [8, 9]. Cr₂O₃ content at the grain rims increases, in olivine at the olivine-spinel contact its value varies from 0.2 to 0.3 %. Cr₂O₃ content at the cores of spinel

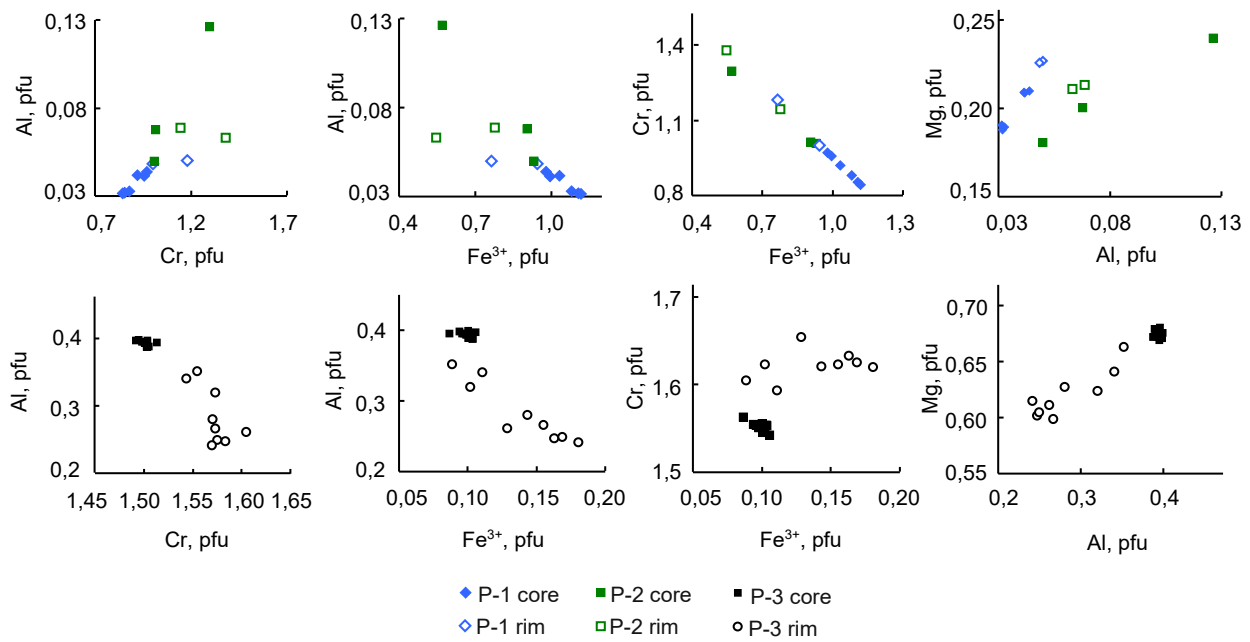


Figure 2. The main correlation dependences of the component contents in the studied chrome spinels.

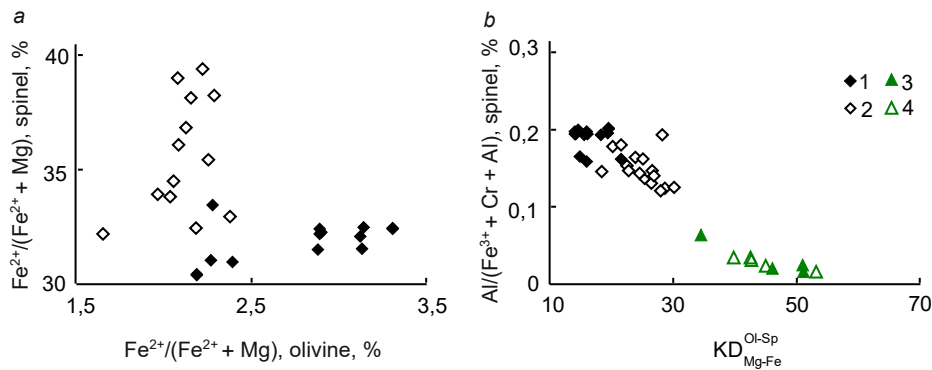


Figure 3. Compositional variation of coexisting olivines and spinels from the studied samples. 1 – olivine and spinel grain cores from chromite; 2 – olivine and spinel grain rims from chromite; 3 – olivine and spinel grain cores from meta-ultramafites; 4 – olivine and spinel grain rims from meta-ultramafites.

grains is around 59 %, at the rims – 61 %. The component content in spinel increases quite sharply and is accompanied by an increase in #Fe ($Fe^{3+}/(Fe^{3+} + Fe^{2+})$, pfu).

For all these #Fe decreases at 200 μm from the grain rim which is accompanied by a sharp Cr₂O₃ content increase. At the spinel rim (analysis point is located at 5 μm from the grain boundary) Cr₂O₃ content slightly decreases, and #Fe in spinel, on the contrary, sharply increases. Al₂O₃ content gradually decreases to the rims of the spinel grains, along with MgO lowering. NiO content in chromium spinel smoothly increases from grain cores to rims from 0.08 to 0.11–0.12 % and sharply decreases to 0.02 % at the contact with olivine grain. Olivine grains demonstrate the increase in NiO from the center to the rim (from 0.65 % to 0.72 %). We also have studied several more grains of spinel and olivine from this sample. All of them have similar zoning. For more reliable reconstruction of chemical transformations occurring in spinel, a number of scatter charts has been done. They characterize the behavior of bivalent and trivalent cations at the cores and rims of spinel grains (Fig. 2). At the grain rims the proportionality of amount of Fe³⁺ and Fe²⁺ cations with Al is inverse, while the amount of Al and Mg is directly proportional. Cr and Fe³⁺ proportionality in the grain cores is inverse. It is noticeable that the internal parts of the grains are uniform in composition, and the obtained dependences characterize its change from one grain to another. In the rims the content of chromium and ferric iron increases and the alumina content decreases.

There are two different groups with a different inclination of the trend line on the diagram Fa – XFe_{sp}²⁺ (Fig. 3, a) for the analysis of cores and rims of the grains. As the reason for this can serve the fact that the rims of the spinel grains are depleted with Al and enriched with chromium and trivalent iron which increase KD_{Mg-Fe}^{Ol-Sp} at a constant temperature. Consequently a more intensive redistribution of magnesium into olivine and of iron – into spinel takes place in the olivine-spinel pair. Fig. 3, b shows the proportionality of KD_{Mg-Fe}^{Ol-Sp} and the fraction of Al ($Al/(Fe^{3+} + Al + Cr)$) at the rims and cores of spinel grains, which confirms this assumption. The addition of ferric iron ensures the stability of the spinel lattice during its depletion with aluminum cations (Fig. 2). The grains of rock-forming olivine from the enstatite-olivine rock (sample P-1, Fig. 4) are also zonal: grain cores contain 7.3 % Fa, and to the rim its content decreases to 6.2%. Iron distribution in an accessory spinel is similar – $XFe_{sp}^{2+} = 78.4$ % at the core, and 76.5 % at the grain rim. The content of chromium and aluminum oxides increases to the grain rims in both minerals. The content of NiO in the grains of accessory spinel (0.43–0.81 %) is higher than in the grains of rock-forming olivine (0.31–0.5 %). XFe³⁺ in spinel decreases to the rim from 59 % to 58.4 % in the first and from 58 % to 51 % in the second grain. The content of Al cations in spinel is extremely low (Fig. 2), but despite this there is clear direct Al proportionality to Mg and Cr. The content of Cr cations is inversely proportional to the content of Fe³⁺.

The fayalite molecule content in olivines from amphibole-enstatite-olivine rock (sample P-2, fig. 5) also decreases to the grain rims.

Table 2. Olivine chemical composition.

Oxide	Sample number							
	P-1		P-1		P-1		P-2	
	Point number							
	O-1	O-2	O-3	O-4	O-5	O-1	O-2	
SiO ₂	41,03	41,60	40,86	40,55	40,89	40,63	40,53	
MgO	50,91	50,74	50,96	50,78	52,58	50,26	50,79	
CaO	0,02	0,01	0,00	0,00	0,00	0,00	0,01	
Cr ₂ O ₃	0,02	0,00	0,08	0,24	0,57	0,00	0,04	
FeO	7,05	7,15	6,86	6,61	6,18	7,60	7,63	
MnO	0,04	0,11	0,15	0,06	0,07	0,08	0,11	
NiO	0,43	0,50	0,28	0,31	0,31	0,41	0,44	
Al ₂ O ₃	0,00	0,00	0,00	0,01	0,01	0,00	0,01	
TiO ₂	0,00	0,01	0,00	0,00	0,01	0,00	0,00	
CoO	0,08	0,07	0,10	0,00	0,07	0,04	0,00	
Total	99,58	100,19	99,29	98,56	100,69	99,02	99,56	
<i>Formula units normalized to 3 cations</i>								
Si	1,00	1,01	1,00	1,00	0,98	1,00	0,99	
Mg	1,85	1,83	1,85	1,86	1,88	1,84	1,85	
Cr	0,00	0,00	0,00	0,00	0,01	0,00	0,00	
Fe	0,14	0,14	0,14	0,14	0,12	0,16	0,16	
Ni	0,01	0,01	0,01	0,01	0,01	0,01	0,01	
Fa, %	7,21	7,33	7,02	6,81	6,19	7,82	7,77	

Oxide	Sample number							
	P-2		P-3		P-3		P-3	
	Point number							
	O-3	O-1	O-2	O-3	O-4	O-5		
SiO ₂	40,43	43,22	43,05	43,19	43,00	43,47		
MgO	50,87	54,53	53,86	53,60	53,79	54,43		
CaO	0,01	0,00	0,00	0,00	0,00	0,00		
Cr ₂ O ₃	0,16	0,27	0,00	0,01	0,01	0,20		
FeO	7,65	2,11	2,79	2,84	2,73	2,06		
MnO	0,15	0,03	0,05	0,04	0,03	0,03		
NiO	0,44	0,73	0,71	0,65	0,67	0,73		
Al ₂ O ₃	0,00	0,00	0,01	0,01	0,01	0,00		
TiO ₂	0,00	0,00	0,00	0,02	0,00	0,01		
Total	99,71	100,89	100,47	100,36	100,24	100,93		
<i>Formula units normalized to 3 cations</i>								
Si	0,99	1,01	1,02	1,02	1,02	1,02		
Mg	1,85	1,91	1,90	1,89	1,90	1,90		
Cr	0,00	0,01	0,00	0,00	0,00	0,00		
Fe	0,16	0,04	0,06	0,06	0,05	0,04		
Ni	0,01	0,01	0,01	0,01	0,01	0,01		
Fa, %	7,78	2,12	2,82	2,89	2,77	2,08		

Note: Fa = Fe × 100/(Fe + Mg).

The iron content decreases to the rims of accessory spinel grains from 79–81 % to 75–78 %. This process is accompanied by the Cr₂O₃ content growth of both minerals. At the contact of olivine grains with spinel Cr₂O₃ reaches 0.16 %. Cr₂O₃ content increases from 36–41 % at the center of chromium spinel grain to 47–49 % at the rim. Al₂O₃ in spinel also increases towards the rim. In both minerals NiO content changes upon nearing their contact. In olivine the component content of increases from 0.41 to 0.44%, while in spinel it decreases from 0.5–0.6 % to 0.24–0.35 % from the core to the rim's grain. #Fe³⁺ decreases in spinel grains from core to rim varying from 50–54 % to 40–41 %. It is observed Fe³⁺ and Cr inverse proportionality and Mg and Al direct proportionality (Fig. 2).

A thermometer and an oxybarometer [10] were used to evaluate the parameters under which the mineral composition was changed and their chemical zoning has been formed. In chromitite (sample P-1), the temperature of the olivine-spinel equilibrium estimated using an ion-exchange geothermometer for the pressure of 1 GPa comprised 673 °C at the grain core and 579 °C at the rim. With the growth

of the assumed pressure to 3 GPa, the estimated temperature increases for 22 °C, while the difference in its value between grain rims and cores remains close to 100 °C. Oxygen fugacity for the grain cores is 2.5 log. units above the FMQ buffer and for the rims FMQ + 4.2 log units.

The temperature and oxygen fugacity within the studied grains in olivine-enstatite rock remain practically unchanged. The temperature for the grain cores of olivine and spinel is 665–662 °C, for the rims – 662–651 °C. Oxygen fugacity for the rims and cores of grains is within the range of dlog fO₂(FMQ) + 5,0...+5,2 log units. Variations of the studied parameters from the core to the rim of the grain are within the error of the method that indicates to their constancy in the process of grain formation.

The central parts of olivine and spinel grains from the amphibole-enstatite-olivine rock show the temperatures of 636–648 °C and oxygen fugacity 3.7–4.7 units above the FMQ buffer. The grain rims have been formed at the temperature of 618–659 °C and the oxygen fugacity of FMQ + 3.8 ... + 4.3 log units. Variations in temperature of

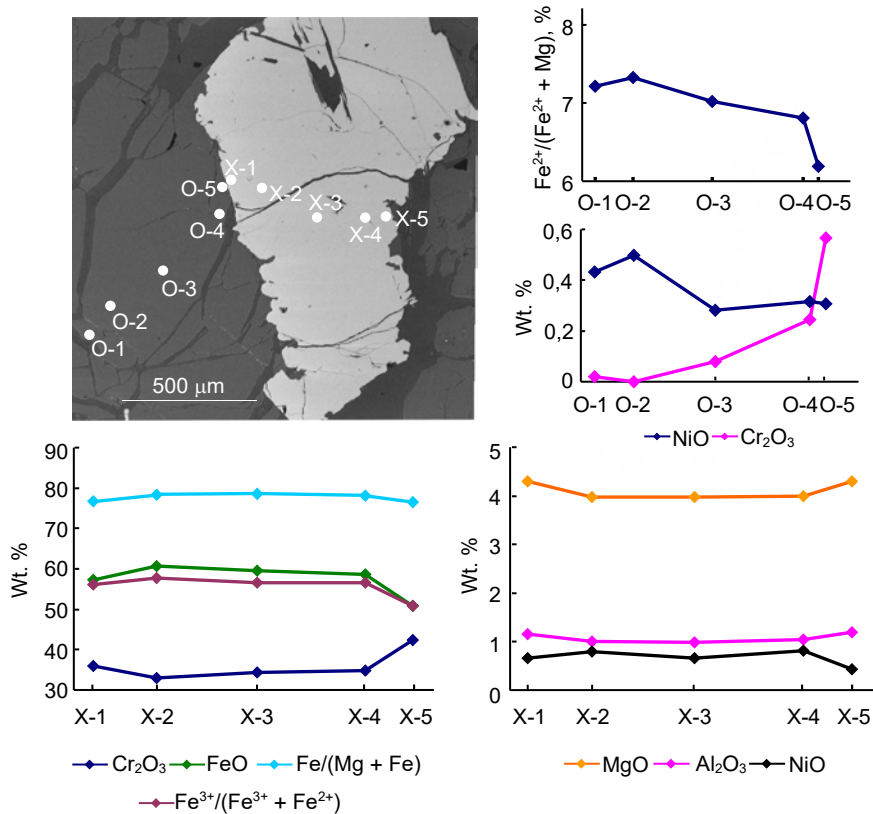


Figure 4. Accessory spinel (light gray, analysis points X-1...X-5) in contact with olivine (gray, analysis points O-1...O-5) from sample P-1. BSE image, CAMECA SX 100. The diagrams show variations in composition within the grains of minerals.

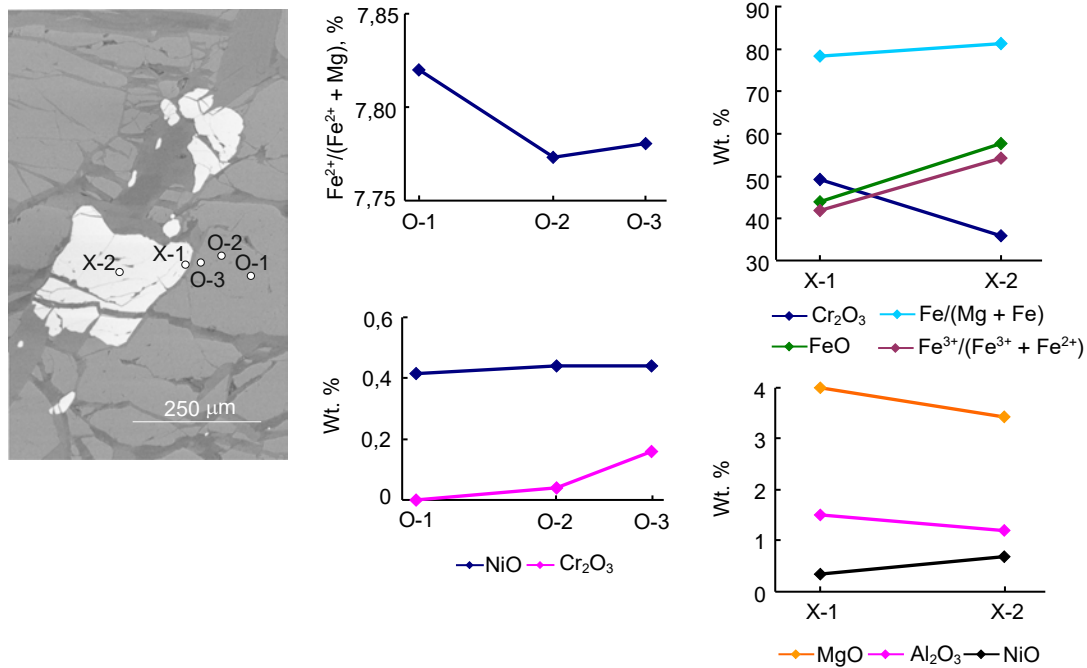


Figure 5. Accessory spinel (light gray, X-1, X-2 analysis points) in contact with olivine (gray, analysis points O-1...O-3) from P-2 sample. BSE image, CAMECA SX 100. The diagrams show variations in composition within the grains of minerals.

the olivine-spinel equilibrium are also insignificant. In the elongated grain of the accessory spinel, located inside the recrystallization zone along with amphibole and enstatite $\log f_{O_2}$ (FMQ) decreases from the core (+4.7 log units) to the rim (+3.8 log units), accompanied by a decrease in temperature from 636°C up to 618 °C. In the spinel grain, which shape is close to the isometric, the oxygen fugacity rises to the grain edge (from 3.7 to 4.4 log units above the

FMQ buffer) together with the decrease in temperature (from 658 °C to 649 °C).

The temperature interval within which the evolution of the olivine and spinel compositions occurred and their chemical zoning were formed according to the olivine-spinel thermometry data is about 100 °C. Temperature interval for chromitite is the highest among the studied samples. In the ore-forming spinels under the conditions of

the oxygen fugacity increasing for 2 log units it occurs the depletion of the grain rims with aluminum, that is compensated by an increase in Fe^{3+} content. Olivine grain rim composition is in equilibrium with the spinel one. Previously established direct proportionality of the olivine and spinel iron content which monotonically increases from chromites to ultramafites testifies to the existence of equilibrium in the ore-rock system [11].

The formation of spinel zoning in enstatite-olivine rock takes place under constant T-fO₂ conditions, thus, the change in these parameters cannot be the factor leading to its formation. The enrichment of the spinel grain rims with trivalent cations Al and Cr occurs simultaneously and along with that the magnesiality of the mineral grain rim increases. The direct proportionality of Cr and Mg in the profile oriented perpendicular to the grain elongation may testify to the observed zoning formed by deformation events [5]. The traces of plastic deformation established in the rock can also serve as the basis for this.

In the spinel from amphibole-enstatite-olivine rock one can observe two types of zoning: the first one (in an elongated grain) is close to that of the enstatite-olivine rock. The difference is that during the growth in the Cr and Al content from the core to the grain rim the content of Fe^{3+} reduces, that affects the decrease in the calculated value of oxygen fugacity for 1 log unit. In an isometric grain (the second one), the content of Cr and Al decreases to the grain rim, that is accompanied by the increase of the content of trivalent iron. At the same time, the growth in the Fe^{3+} content compensates the decrease in the component content. Oxygen fugacity at which the grain rim has been formed is 0.5–0.7 units higher than the one determined in the core. Formation of zoning in both cases occurs under the conditions of the temperature falling. The different ways of zoning formation can also be explained by different behavior of the components in the grains.

During studying of meta-ultramafites and chromitite from the southern block of the Rai-Iz massif Tsentralnoye deposit the authors determined two main types of chemical zoning of chromium spinel and the coexisting olivine. The first one, manifested both in chromites and rocks, appears as a result of growth in the oxygen fugacity against the background of the temperature decrease in accompanied by Mg–

Fe diffusion exchange between olivine and spinel is well-known for many objects and is repeatedly discussed in literature. The second one fixes the deformation stage of meta-ultramafites development and is accompanied by the redistribution of components, both in chromic spinel and in olivine in the stress field without noticeable effect of temperature and oxygen fugacity.

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