sZonal Cr-spinels from Serpentinites in North Western Part of the Greater Caucasus

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Abstract. Formation homogenity and geodynamic conditions for the formation of apohyperbasites is an actual problem in geological study of the Paleozoic complexes of the Greater Caucasus. Study results of chromespinelids from serpentinite fragments of Paleozoic tectonic melange in the Western part of the Greater Caucasus (outcrops in Dakhovskiy uplift and Kisha river) tested with electron microprobe methods and processing of the results of elemental analysis using non-parametric statistics lead to the conclusion that apohyperbasites belong to ophiolites of subduction environments. Their composition is close to chromespinelids’ of ophiolite complexes of supra-subduction zones (SSZ) composition. Chromespinelides from the flank of Dakhovskoye uplift are represented by subferrochromite cores with rims of magnetite; transformation of subferrochromites during obduction process (Cr# ~0.80-0.81, Mg# ~0.35-0.40 in the least modified cores) in to chromites occurred under the conditions of the greenshist facies and was accompanied with redistribution and removal of aluminum and magnesium, and enrichment with iron and chromium. Chromespinelides from the serpentinites of contact Agarinskiy and Kizilkol’skiy thrust sheets presented with cores of aluminumchromite with relics of chrompiocotites (Cr# ~0.50-0.70, Mg# ~0.39-0.64), surrounded by rims of ferrochromite – chromomagnetite. This transformation occurred on the boundary of the greenschist and low-temperature zone of the amphibolite facies and was accompanied by the substitution with iron for both two-and trivalent cations.

1. Introduction
Serpentinites in the Greater Caucasus occur mainly in the form of small tectonic lenses and plates at the edges of the Hercynian crystalline core blocks, showing signs of repeated intense deformations, and they are poorly characterized by the results of precision analytical studies. The formation and geodynamic affiliation, age, and conditions of metamorphic transformations of hyperbasites are the subject of long-term discussions [1].

2. Relevance
Chromespinelides are the most important source of such data in serpentinized hyperbasites that have lost their primary composition. However, the interpretation of mineralogical and geochemical data is complicated due to allochemical transformations, which are a function of the level of metamorphism and the fluid-rock ratio [2, 3]. This requires determining of the degree and direction of changes in the composition of chromespinelides. Their zonal grains are the most informative in this regard.
3. Object of study and problem

The subject of a study is two serpentinite outcrops located in the Western part of the Greater Caucasus in the Belaya river basin. These outcrops are fragments of tectonic melange: tectonic plates and lenses are pushed over the flanks of the Hercynian crystalline core blocks – Dakhovskiy shield and the Atsgarinskiy thrust sheet. The blocks are formed by upper Proterozoic (?) metamorphic complexes containing middle to late Paleozoic diorite and granitoid intrusions. The goal of the work is to study the nature of zoning of chromespinelids, to determine its causes, and to interpret the typomorphic features that have preserved relic features of grains or fragments of their cores.

4. Methods and approaches

The composition of chromespinelides was studied using a Tescan VEGA II LMU scanning electron microscope equipped with INCA ENERGY 450/XT energy dispersive microanalysis (EDX) and INCA Wave 700 wave dispersive analysis systems. To identify grain zoning, element mapping was performed (using SmartMap INCA software). Elemental composition was determined by quantitative electron-microprobe analysis. Fe\(^{3+}\) was calculated based on stoichiometric considerations according to [4]. Statistical processing of the results of elemental analysis was performed using nonparametric statistics. The main part of the research was performed at "Mineral and environment research center" of the Southern Federal University.

5. Results of the research

Serpentinites from the flank of Dakhovskiy shield are presented by β-lisarite-chrysotile and chrysotile-antigorite variations [5]. Accessory chromespinelides almost always contain veins and outer edges of magnetite (Cr\(_2\)O\(_3\) up to 2-4 wt.%), which are often surrounded by chlorite-serpentine aggregate [6]. The methods of element mapping (X-ray maps EDX) reveal a gradual transition from homogeneous cores (with an Al\(_2\)O\(_3\) content of 8.5-9.5 wt.%), through the formation of "cloud" zones in the inner parts of the grains (Al\(_2\)O\(_3\) ~4.5-9 wt.% ) to a contrast distribution with the formation of aluminum-saturated (Al\(_2\)O\(_3\) more than 10 wt.% ) peripheral zones adjacent to the magnetite edges and strongly depleted internal parts (Al\(_2\)O\(_3\) less than 2 wt.% ) (Fig. 1.1-1.3). Central areas of homogeneous chromespinelides correspond to subferrochromites (Fig. 2.1). Cr# value corresponds to ~0.80-0.81, Mg# ~ 0.35-0.40, MnO content up to ~0.8 wt.%, Zn up to ~0.4 wt.%, NiO up to ~0.2 wt.% for them.
On the contact of the Agarinsky and Kizildol’skiy (composed of middle-upper Devonian strata) thrust sheets, serpentinites are represented by tectonic breccia, have a chrysotile-antigorite and antigorite composition, talc-altered, and quartz-carbonate veins are developed in places between their fragments. Chromespinelides are mostly do not have magnetite rims. The grains have a pronounced zonation: the rim is formed by ferrochromium chromomagnetic, the cores are composed of alumochrome-chromepicotite (Fig. 1.4-1.5), while chromepicotites (Cr₂O₃ ~37-38%) are in the form of relict sites (size up to 10 microns). Core values of the Cr# are 0.50-0.70, Mg# ~0.39-0.64. MnO content is up to ~2 wt.%, ZnO up to ~0.9 wt.%, NiO up to ~0.4 wt.% in alumochrome-chromepicotites.

The results of statistical processing of the results of electron microprobe analysis of chromespinelid cores (without magnetite rims) indicate a different nature of isomorphic substitutions in the chromespinelids of the considered outputs. In Dakhovski chromespinelides, positive correlations were found (at the level of p <0.05) between aluminum and magnesium (Spearman's rank correlation coefficient +0.61), negative correlations were found between aluminum and chromium (-0.76), iron and magnesium (-0.52). Consequently, the formation of zoning was determined primarily by the removal of aluminum and magnesium, addition of iron, and the relative enrichment of chromium. In the Kisha river chromespinelids positive relationships were found between aluminum and magnesium (+0.48), magnesium and chromium (+0.57), aluminum and chromium (+0.77); significant negative relationships were found in iron with chromium (-0.80), aluminum (-0.83), and magnesium (-0.69). These dependences reflect the substitution of both two - (Mg) and trivalent (Al, Cr) cations by iron.

Features of the composition of Dakhovski chromespinelides indicate their transformation in to chromites under the conditions of the greenschist facies (for which Mg# is 0.4 - 0.7 [3]) with diffusion removal of Al and Mg, which was accompanied by the formation of chlorite in accordance with the reaction (Mg,Fe)(Al,Cr₃)O₄ + fluid → Mg₅Si₃O₁₀(OH)₈ + (Fe,Mg)(Cr,Al)₃O₄ [16], which under the conditions of the greenschist facies is realized during the joint serpentinization of olivine and pyroxene.
The absence of well-defined chromagnetite rims around the aluminum-rich outer zones indicates the absence of long-term heating of rocks [8], and the presence of magnetite rims is associated with the final stage of transformation under oxidative conditions with intensive filtration in serpentinites of hydrothermal fluids (with temperatures above 300°C) [9]. Serpentinites of Kisha river are signs of transformation into a more high-temperature conditions of metamorphism (at the border of greenschist - low-temperature zone of the amphibolite facies), which was accompanied by the replacement of aluomochrome - chromepicotites forming external zone ferrochromite - chromomagnesite. The formation of secondary chromite or chrommagnetite shells is associated with the degree of fluid reduction and the fluid/rock ratio [10]: chromites are formed at a high fluid/rock ratio, when fluids are strongly reduced and Fe$^{2+}$ prevails.

![Figure 2](image)

**Figure 2.** The position of the compositions of chromespinelids (internal parts) on the diagrams: 1.1 – fields of compositions in the classification diagram (in accordance with the nomenclature developed by N. In. Pavlov [11]: 1 – chromites, 2 – subferrichromites, 3 – aluomochromites, 4 – subferrialumochromites, 5 – ferrialumochromites, 6 – subaluoferrichromites, 7 – ferrichromites, 8 – chromepicotites, 11 - chromomagnesites, 12 - picotites, 13 - magnetites); 1.2 – metamorphic grade: GS – green, LA – low-temperature amphibolite, UA – high temperature amphibolite, GR – granulite ([12]); 2 – the compositions of chromespinelids from rocks of different geodynamic settings (after ([13, 14, 15, 16, 17])); 2.1 – ultramafites of MORB, 2.2 – ultramafites deepwater trenches, 2.3 – xenoliths of ultramafites from basalts, 3.1 – oceanic islands, 3.2 – island arcs; 3.3 - ultramafic massifs of the median ridges of the Atlantic and Indian oceans, 3.4 - conical seamounts (serpentinite diapirs) of frontal parts of the Mariana and Izu-Buninskoj island arcs, 3.5 - Nidar peridotites; MORB - basalts of middle-ocean ridges; SSZP - oceanic suprasubduction peridotites. Compositions of the internal parts of chromespinelids: a, d - initial subferrichromites; b - modified parts of the grains (Dakhovskiy shield), c, e - initial subferrichromites (Kisha river).

The composition of the least affected by allochemical transformations of chromespinelid cores corresponds to the chromespinelids of ophiolite complexes of supra-subduction zones (SSZ) (fig. 2.2) and is most similar to the compositions typical of pre-arc ophiolites (forearc peridotite), including serpentinite diapirs of the frontal parts of the Mariana and Izu-Bunin island arcs and the ophiolite associations of folded belts identified with them, for example, the Nidar Neotetis complex (fig. 2.3).

6. **Conclusions**

Thus, the serpentinites of the tectonic melange of the Western part of the Greater Caucasus belong to the ophiolite complex, whose fragments, judging by the composition of chromespinelids, correspond to ophiolites of supra-subduction zones (SSZ). During the formation of the cover-thrust structure of the Greater Caucasus at the stage of the Hercynian collision, ophiolite fragments underwent
transformations under different conditions: serpentinites exposed on the Kisha river, lying between tectonic plates, were transformed under higher temperature conditions with a relatively reduced fluid/rock ratio.

7. References

[1] Snezhko V A and Snezhko V V 2019 On the age of apoharzburgite Bedenskiy complex Modern problems of Geology, Geophysics and Geocology of the North Caucasus. Collective monograph based on the materials of the IX all-Russian scientific and technical conference (Moscow: Vavilov Institute of history of natural science and technology Russian Academy of Sciences) pp 60-65

[2] Barnes S J and Roeder P L 2001 The range of spinel compositions in terrestrial mafic and ultramafic rocks J. Petrol vol 42 pp 2279-2302

[3] Farahat Eman S A 2008 Chrome-spinels in serpentinites and talc carbonates of the El Ideid-El Sodmein District, central Eastern Desert, Egypt: their metamorphism and petrogenetic implications Geochemistry vol 68 pp 193-205

[4] Droop G T R 1987 A general equation for estimating Fe3+ concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria Mineralogical Magazine vol 51 (3) pp 431-435

[5] Popov Yu V, Zhabin F V and Pustovit O E 2019 Mineral composition of serpentinites of the tectonic melange of the Dakhovsky crystalline protrusion (Greater Caucasus) Geology and Geophysics of Russian South 4 pp 38-48

[6] Popov Yu V, Pustovit O E and Tereshchenko A V 2020 Accessory chrome spinels of serpentinites of tectonic melange of the Dakhov uplift (Greater Caucasus) Geology and Geophysics of Russian South 2 pp 38-55

[7] Bach W, Paullick H, Garrido C J, Ildefonse B, Meurer W and Humphris S E 2006 Unravelling the sequence of serpentinization reactions: petrography, mineral chemistry, and petrophysics of serpentinites from MAR 15ºN (ODP Leg 209, Site 1274) Geophysical Research Letters vol 25 pp 1467-1470

[8] Eckstrand O D 1975 The Dumont serpentinite: a model for control of nickeliferous opaque mineral assemblages by alteration reactions in ultramafic rocks Economic Geology vol 70 pp 183-201

[9] Ahmed A H and Surour A A 2016 Fluid-related modifications of Cr-spinel and olivine from ophiolitic peridotites by contact metamorphism of granitic intrusions in the Ablah area, Saudi Arabia Journal of Asian Earth Sciences vol 122 pp 58–79

[10] Barnes S J and Roeder P L 2001 The range of spinel compositions in terrestrial mafic and ultramafic rocks J. Petrol vol 42 pp 2279-2302

[11] Pavlov N V 1949 Chemical composition of chrome spinelides in connection with the petrographic composition of rocks of ultrabasic intrusions Works of the Geological Institute of the Russian Academy of Sciences Issue 103 p 91

[12] Saumur B M and Hattori K 2012 Zoned Cr-spinel and ferritchromite alteration in forearc mantle serpentinites of the Rio San Juan Complex, Dominican Republic Mineralogical Magazine vol 77 (1) pp 117-136

[13] Jan M Q and Windley B F 1990 Chromium-spinel silicate chemistry in ultramafic rocks of the Jijal complex. Northwestern Pakistan Journal of Petrology vol 31 pp 667–715

[14] Zaemnia F, Kananian A, Arai S, Mirmohammadi M, Imamali pour A, Khedr M Z, Miura M, Abbou-Kebir K 2017 Mineral chemistry and petrogenesis of chromitites from the Khoi ophiolite complex, Northwestern Iran: Implications for aggregation of two ophiolites Island Arc 26 (6) e12211

[15] Ghazi J M, Mouzzen M, Rahghoshay M and Moghadam H S 2011 The geodynamic setting of the Nain ophiolites, Central Iran: evidence from chromian spinels in the chromitites and associated rocks Ofioliti vol 36 (1) pp 59–76
[16] Kamenetsky V S, Crawford A J and Meffre S 2001 Factors controlling chemistry of magmatic spinel: An empirical study of associated olivine, Cr-spinel and melt inclusions from primitive rocks *Journal of Petrology* **42** pp 655-671

[17] Rollinson H and Adetunji J 2015 The geochemistry and oxidation state of podiform chromitites from the mantle section of the Oman ophiolite: A review *Gondwana Research* **27** (2) pp 543-554