Primary Magmatic and Secondary Postmagmatic Compositional Trends of Chromian Spinel From Dunite of the Uralian-Alaskan Type Complexes

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Accessory and ore-forming chromian spinels are important petrogenetic indicators reflecting geotectonic environments, compositions, and crystallization conditions of mafic-ultramafic rocks. However, the latest global database (Barnes and Roeder 2001), which includes over 26 000 spinel analyses, contains only about 400 from Uralian-Alaskan type mafic-ultramafic intrusions. Several recent publications (Garuti et al. 2003; Krause et al. 2007; Scheel et al. 2009) add important information to this topic, but many aspects of the evolution of chromian spinels associated with dunites in Uralian-Alaskan type complexes are still not solved. This is due to the fact that large amounts of data on the chemistry of chromian spinels are published in the Russian literature, and are generally inaccessible to the international geological community. Most of these spinel analyses were obtained from dunite and chromium-platinum ores of the Ural Platinum Belt where 14 huge duniteclinopyroxenite-gabbro massifs crop out over a distance of 900 km along the 60th meridian. In this contribution, three main questions relating to variations of chromian spinel compositions in dunites in Uralian-Alaskan type ultramafic complexes, are discussed: 1) What is the primary magmatic trend of spinel evolution in dunite and what controls the trend? 2) What happens with the composition of chromian spinel during high temperature subsolidus deformation of dunite involving tectonic emplacement, re-crystallization, and re-equilibration processes? 3) When do ore-forming systems begin to separate from the host dunite, in what direction does the ore chromite composition develop, and under what conditions does this occur?

On the basis of studying several dunite-clinopyroxenite massifs in the Ural Platinum Belt (Russia), I support the opinion by Alex Efimov (Efimov et al. 1993) that most are strongly recrystallized and suffered high temperature plastic deformation under subsolidus conditions. These observations are supported by the wide development of equigranular textures and also by the formation of coarse-grained and pegmatitic dunite with mineralized miarolitic cavities. These types of ultramafites occur mainly in the central parts of the dunite bodies where Pt-rich chromite lenses, schlieren, and veinlets are widespread. Deformation and re-crystallization are the main reasons why a primary magmatic chromian spinel trend is normally not preserved. Such a trend was observed only in the Uktus dunite-clinopyroxenite-gabbro massif, Central Urals, and for large dunite layers in dunite-clinopyroxenite-tilasite bedding sequence in the Kytlym massif, Northern Urals (Pushkarev 2000).

1) The magmatic trend of chromian spinel evolution includes variations resulting from direct crystallization from primary melts and also re-equilibration of chromian spinel with evolved intragranular melt. On a ternary Al-Cr- Fe^{3+} diagram, this trend appears as a linear field extending from the Cr apex, where the Cr/(Cr+Al) ratio is about 0.8, to the Al-Fe³⁺ side, where the Al/ Fe³⁺ ratio varies from 1:1 to 2:3, up to the point where it goes through the chromian spinel solvus (Figure 1). Along this trend the Cr/(Cr+Al) ratio decreases from 0.8 to 0.5 and Mg/(Mg+Fe²⁺) decreases from 0.6 to 0.3. Below the solvus, chromian spinel exsolves and forms two phases: Al-rich chromian picotite and Fe-rich chromian titanomagnetite, which define the miscibility gap. The direction of magmatic evolution with increasing of Al, Fe²⁺, Fe³⁺, and Ti, and decreasing Cr in chromian spinel is controlled by Ol-Cpx±Cr-spinel fractionation from the primary ankaramite-like

melts with high CaO/Al₂O₃ ratios. Estimated temperatures of Ol-CrSp equilibrium reflect subsolidus conditions and correspond to 1100-950°C. The redox state for this mineral assemblage is generally +2 to +3 log fO_2 units above FMQ. Synmagmatic concentrations of chromian spinel in dunites are generally very small in size and do not contain economic concentrations of PGE.



Figure 1. A) Cr-Al-Fe³⁺ diagram for chromian spinel compositions from dunite in the Ural Platinum Belt (Russia). 1-4 – Uktus dunite-clinopyroxenite-gabbro massif (Central Urals): 1 – accessory and ore chromite, 2 – hypersolvus chromite, 3 – Al-rich exsolved spinel (picotite), 4 – Fe-rich exsolved spinel (Cr-titanomagnetite); 5 – accessory chromian spinel from different types of recrystallized dunite in the Ural Platinum Belt (Ivanov 1997); 6 – accessory chromian spinel and exsolved phases from dunite layers in the Kytlym massif, Northern Urals; 7 – Pt enriched ore chromitites. **B)** Schematic view of chromian spinel development: 1 – magmatic trend; 2 – dunite recrystallization trend; 3 – Pt-enriched ore chromitite trend.

2) Post-magmatic re-crystallization of chromian spinel occurred during subsolidus cooling, probably with intensive interaction between oxides and porous fluids, as typical of large dunite bodies in the Ural Platinum Belt. During this stage, the rocks in the central parts of the dunite bodies strongly recrystallize and the textures are transformed into equigranular, coarse-grained and pegmatitic (Ivanov 1997). Some coarse-grained and pegmatitic dunite contains large crystals of Crrich spinel (up to 5-10 mm) and miarolitic cavities, often filled by intermediate and lower temperature minerals, such as Cr-diopside, forsterite, Cr-pargasite, Cr-Na-phlogopite, Na-chlorite (glagolevite), serpentine, Cr-Ti-Ca-rich garnet, high Cr-spinel, native Cu, etc. Estimated temperatures of Ol-CrSp equilibrium for recrystallized coarse-grained dunite of the central parts of the bodies are 900-700°C. The redox state is similar to the magmatic trend and is +2 to $+3 \log fO_2$ units above FMQ. During the recrystallization process, chromian spinel compositions move in the opposite direction of the magmatic trend. From fine-grained to coarse-grained dunite, Cr and Mg increases and Fe_{tot} decreases in chromian spinel. $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ and Cr/(Cr+Al) slightly increases. On a ternary Al-Cr-Fe³⁺ diagram, the field of chromite from recrystallized dunite has a similar orientation as the magmatic trend, but is slightly shifted to the Cr- Fe³⁺ side of the diagram (Figure 1). Olivine also becomes more Mg-rich. This type of dunite is accompanied by chromitites, usually with high concentrations of PGE and PGM (e.g., the famous Uralian lode platinum deposits). We don't consider here the effect of lower temperature oxidizing and formation of Cr-magnetite rims around chromite grains.



Figure 2. Typical compositional variations of the chromian spinel through a Pt-rich chromitite vein within dunite.

3) The Pt ore-forming chromian spinel trend is reflected in the zoning of ore chromitites (Figure 2). In general, it follows the same direction on the Al-Cr-Fe³⁺ diagram as the trend of recrystallization, only shifted to Cr- Fe³⁺ side (Figure 1). During chromitite formation from the marginal to the central parts of schlieren and veins, the composition of chromian spinel becomes more Cr-, Mg-, and slightly Al-rich, with an almost constant Cr/(Cr+Al) ratio. Fe content in chromite decreases, but Fe³⁺/(Fe³⁺+Fe²⁺) increases. There is no pronounced gap between the post-magmatic re-crystallization and ore-forming trends, but the difference is statistically important in terms of chromite chemistry, because most ore-related Cr-spinels have higher chromium contents and few of the chromites in the marginal parts of veins are close to the accessory minerals in composition. It appears that the ore-forming system separates from the dunite host close to the end of high-temperature plastic deformation. Estimated temperatures for PGM-rich chromitites are close to those for re-crystallized dunite (900-700°C), but the redox state is clearly high and is +4 log/O₂ units above FMQ, reflecting more oxidized conditions during ore formation.

On the basis of all available data, including that from the Russian literature, I suggest that the most magnesian and Cr-rich ore chromitites enriched in PGM formed during the latest stage of dunite development close to the end of subsolidus deformation and recrystallization. This is in contrast with general opinion that high chromian and magnesian chromites formed in the earlier stages of magmatic crystallization. Usually, in each dunite body only one or maximum two above-

described trends are visible. One known exception is the Turnagain Alaskan-type ultramafic intrusion in Northern British Columbia (Scheel et al. 2009), where it appears that all trends or parts of them are represented. However, some trends, especially trend 4 (see Scheel et al. 2009), is oriented in the opposite direction to those observed in the Uralian complexes. The reason for this difference is not yet understood.

These data allow me to conclude that the composition of chromian spinels from dunite of the Uralian-Alaskan type complexes can be easily transformed, reflecting changes in the composition of the melt, the chemistry of the host rock, fluid, deformation, and redox state. Therefore, it is a highly sensitive indicator of geological processes. In many cases it is difficult to distinguish the influence of different geological events on the chromian spinel composition. Therefore, I believe that this is one of the reasons why primary magmatic chromite compositions are rarely preserved in the Ural-Alaskan-type complexes that have undergone high-temperature plastic deformation. However, the presence of the re-crystallization type of chromian spinel is a positive signal for chromite-PGM ore and platinum placer deposit exploration.

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