

Platinum-Group Element Mineralogy and Geochemistry in Chromitites of the Nurali Mafic-Ultramafic Complex (Southern Urals, Russia)

Federica Zaccarini¹, V. Evgeny Pushkarev², B. German Fershtater²,
Roberto Cabella³ and Giorgio Garuti¹

¹Department of Earth Sciences, University of Modena, (Italy)

²Institute of Geology and Geochemistry, Ekaterinburg (Russia)

³Department for the study of the Territory and its Resources, University of Genoa, (Italy)

e-mail: fedezac@tsc4.com

Introduction

The Nurali lherzolite-gabbro complex (Fig. 1) is located in the Southern Urals (Russia), approximately 45 km South-West of the city of Miass. The complex has been initially considered as an ophiolite sequence characterized by weakly-depleted oceanic mantle (Savelieva 1987, Savelieva and Saveliev 1992), although, it distinguishes from the other ophiolites of the Urals because of i) the lack of a sheeted dyke complex and pillow lava, and ii) the calc-alkaline affinity of gabbros and diorites, displaying remarkable enrichment in K and LILE compared with oceanic tholeiites (Fershtater and Bea, 1996). Basing on the geochemistry of trace elements, including Platinum-group elements (PGE), it has been proposed that the lherzolites of Nurali may represent lithospheric mantle exhumed from the continent-ocean transition zone (Garuti et al. 1997a, Fershtater et al. 2000).

Several sub-economic chromitite bodies occur in the Nurali Complex. Two distinct chromitite-rich zones (Fig. 1), which proved to be the largest in the complex, were discovered by Smirnov S.V. in 1990, and previously described by Smirnov and Volchenko (1992) and Moloshag and Smirnov (1996). One (CHR-I) consists of a concordant lens of massive chromite (10m x 3m)

located within interlayered dunite-websterite, 150m above the contact with the dunite. The other (CHR-II) covers an area of about 3 x 30 m, and consists of the rhythmic repetition of massive chromite seams interbedded with clinopyroxenite, inside a large ultramafic block isolated within the “melange” formation bordering the East side of the Nurali complex. In this paper we report the results of the mineralogical and geochemical study of chromitite samples from the two main localities, with special regard to the composition of chromite, distribution of the PGE, and the composition and mineral assemblage of the Platinum-group minerals (PGM).

Chromite composition

At both localities, the chromitites display the effects of hydrothermal metamorphism by which chromite grains are rimmed by abundant ferrian-chromite, and the interstitial primary silicates have been replaced by secondary phases, consisting of chlorite, serpentine, talc, and Cr-rich garnets. Relics of primary orthopyroxene and clinopyroxene have been preserved in CHR-I and CHR-II, respectively. The primary composition of chromite was investigated by analyzing the unaltered cores of chromite grains with the electron microprobe.

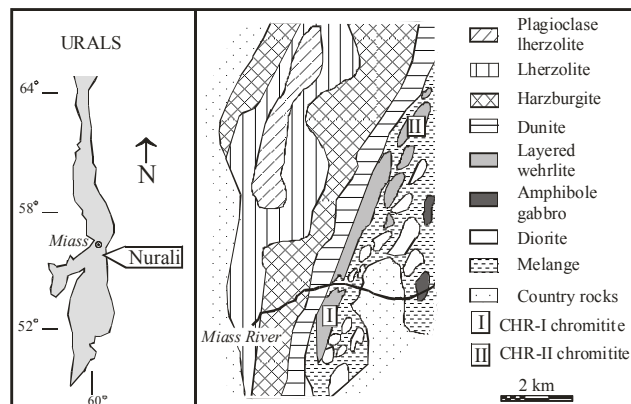


Figure 1. Geological sketch map of the Nurali complex (from Garuti et al. 1997a).

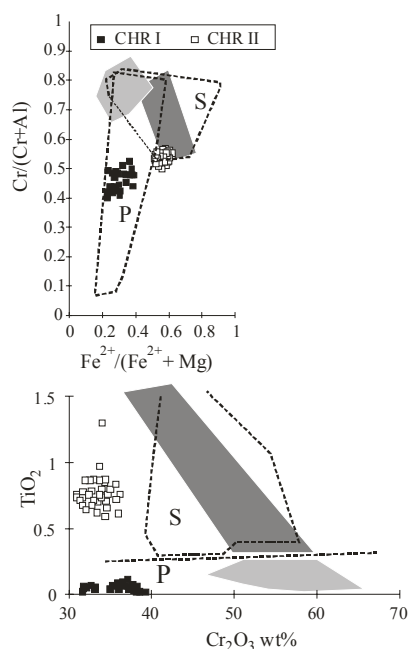


Figure 2. Chemical composition of chromite from chromitites of the Nurali complex. Light grey field: compositions of chromite from the ore deposits of Kempirsai, Kluchevskoy, Ray-Iz, and Kraka ophiolites; dark grey field: chromitites from alaskan-type dunites of Kytlym, Kachkanar, Nizni Tagil, Uktus (unpublished data from the authors). P = podiform chromitite, S = stratiform chromitite.

The results confirm the previous observation by Moloshag and Smirnov (1996) that the Nurali chromitites are characterized by different chromite compositions, showing remarkable increases in Cr/Al, Fe/Mg, and TiO₂ from CHR-I to CHR-II. Figure 2 shows that compositions from CHR-I plot in the field of Al-rich, Ti-poor podiform chromitites, whereas those from CHR-II display affinity with the Fe-rich, Ti-rich chromitites from layered intrusions or alaskan-type complexes of the Urals. Both types are definitely different from the Cr-rich chromitites hosted in the mantle tectonite or in the transition zone of other ophiolite complexes of the Urals (Kempirsai, Ray-Iz, Kluchevskoy, Kraka).

The Platinum Group Element and Au distribution

Overall PGE contents of the order of 3.8 ppm and 7.75 ppm, and Au concentrations up to 232 ppb and 436 ppb were obtained for two chromitite samples from the CHR-I and CHR-II, respectively. The (Pt+Pd)/(Os+Ir+Ru) ratios varies from 0.62 in CHR-I to 33.2 in CHR-II, giving rise to rather different PGE distribution patterns (Fig. 3).

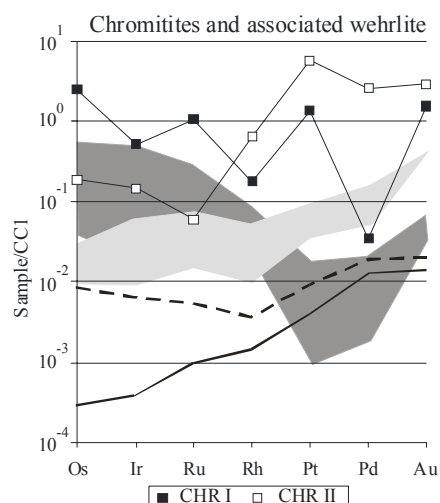


Figure 3. Chondrite-normalized PGE patterns for chromitites and wehrlite host from Nurali. Dashed line = wehrlite below CHR I, continued line = wehrlite above CHR I. Chondrite values from Naldrett and Duke (1980). Dark grey field = IPGE rich chromitites from Kempirsai; light grey field: PPGE rich chromitites from Kempirsai (unpublished data from the authors and from Melker et al. 1999).

The contrast between PGE-Au distribution in chromitites of the Nurali and Kempirsai ophiolite complex is apparent. The positive slope of the CHR-II sample rather recalls the PGE patterns of the MG and UG chromitites of the Bushveld complex, and may have derived from the original presence of a sulfide melt in the chromite forming system (Naldrett and Von Gruenewaldt 1989). The profile of CHR-I is definitely unusual compared with the profiles of both stratiform and podiform chromitites, and its origin is unclear. However, relationships with the PGE distribution in two samples of wehrlite from 10 meters below and above the chromitite lens would indicate that the (Pt+Pd)/(Os+Ir+Ru) ratio changes from 1.7 to 10.6, after precipitation of abundant IPGE (Os, Ir, Ru) in the chromitite layer. The low (Pt+Pd)/(Os+Ir+Ru) ratio of the CHR-I chromitite suggests that sulfur saturation was not achieved in the system, and PGM predominantly composed of the refractory IPGE precipitated early from the magma and were subsequently included in the chromite.

The Platinum Group Minerals

The investigation of 30 polished sections by reflected-light microscopy at 250-800X magnification, allowed the identification of more than 400 PGM up to 80 μ m in size. The mineralogical study of PGM grains by electron

microscope and microprobe confirmed that the CHR-I and CHR-II chromitites contain two distinct populations of PGM (Moloshag and Smirnov 1996), the first one consisting of Ru-Os-Ir minerals, the second one dominated by Pt- and Pd-phases. Basing on textural and paragenetical evidence, the PGM can be divided into two groups:

1) The primary PGM occur as euhedral crystals locked in fresh chromite grains, and therefore are believed to have formed in the high-temperature magmatic stage. They consist of laurite, erlichmanite, Os-Ir-Ru and Pt-Fe alloys, along with rare cooperite and unidentified Ir-Ru-Rh sulfide, possibly kashinite. Minerals of the laurite-erlichmanite serie are the most abundant in both chromitites CHR-1 and CHR-2. Both laurite and erlichmanite display enrichment in Ir, and in some cases in Pd (up to 1.1 wt. %). Compositional zoning has been checked for the largest grains, and it frequently shows slight enrichment in Os at the rims, although the opposite zoning also exists and, in some cases, erlichmanite and laurite coexist in the same crystal. The Pt-Fe alloys have been found exclusively in the CHR-2 chromitites. They generally are less than 10 μ m and constantly occur associated with pyrrhotite (Fig. 4A). The compositions suggest an isoferroplatinum-type stoichiometry (Pt_3Fe), although precise

classification of these alloys is hampered by the lack of structural data.

2) The secondary PGM occur closely associated with serpentine, chlorite, Cr-rich garnets, ferrian-chromite and magnetite, and therefore are believed to have formed at relatively low temperature, possibly during the hydrothermal event that affected the Nurali chromitites. They consist of Ru-Os-Ir-Fe oxides, Pt-Pd-Fe-Cu-Ni alloys, potarite and PGE-bearing awaruite. Preliminary results of the chemical composition and physical properties of the Ru-Os-Ir-Fe oxides have been reported by Garuti et al. (1997b) and these minerals are presently considered as new species (Jambor and Roberts 1999). Their composition suggest an origin by desulfurization and further oxidation of pre-existing laurite or erlichmanite crystals. The secondary Pt-Pd-Fe-Cu-Ni alloys occur as irregular composite grains, frequently associated with potarite, awaruite, wairuite and relics of magmatic sulfides (Fig. 4 B,C,D). They may have derived from either in-situ alteration of primary PGM, or deposition of PGE mobilized at relatively low temperature. The former hypothesis is preferred as it better explains textural relations and paragenesis of these PGM.

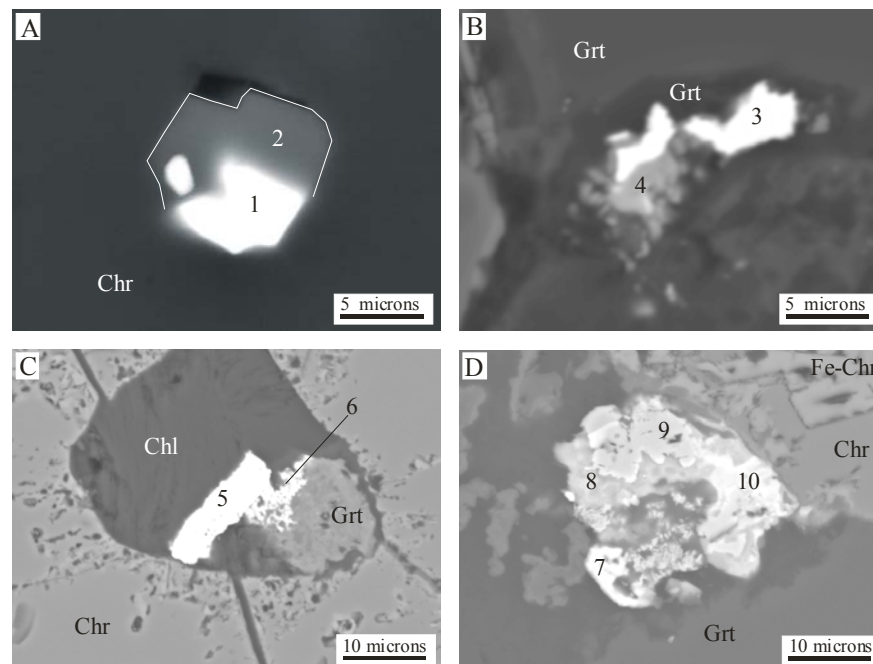


Figure 4. BSE images of PGM from the Nurali chromitites. A) Magmatic grain composed of Pt-Fe alloy (1) and pyrrhotite (2) included in fresh chromite (Chr). B) Secondary PGM composed of potarite (3) and Cu-Pd-Fe-Pt alloy (4) in contact with garnet (Grt). C) Secondary Pt-Fe-Pd-Ni-Cu alloy (5) and porous Pd-Pt-Fe-Cu-Ni alloy (6) in contact with garnet (Grt), engulfed in chlorite (chl), Chr = chromite. D) = Secondary PGM composed of: Cu-Pt-Pd-Rh alloy (7), Cu-Pt-Pd sulfide (8), awaruite (9) and Cu-Pt-Pd alloy (10) in contact with garnet (Grt), chromite (Chr) and ferrian-chromite (Fe-Chr).

Concluding remarks

1. The relative stratigraphic position of the investigated chromitites within the layered sequence of the Nurali complex is difficult to be established, since the CHR-II layer occurs in a dislocated block, within the “melange” formation. However, the trend of increasing Fe/Mg, and TiO₂ from CHR-I to CHR-II may possibly reflect a higher differentiation of the magma parent to the CHR-II chromitite.

2. Both the PGE distribution and the assemblage of primary PGM indicate that the two chromitites formed under increasing sulfur fugacity, and possibly that sulfur saturation was achieved only during formation of the CHR-II chromitite, as accounted for by the high values of (Pt+Pd)/(Os+Ir+Ru), and the abundance of Pd+Pt PGM.

3. The study of PGM indicates that hydrothermal metamorphism caused substantial modifications of the primary PGM assemblage in the Nurali chromitites. However, the most relevant effect would appear to have been the alteration in-situ of primary phases, by which the PGE were not mobilized over long distances, that did not change the original PGE distribution at the scale of the hand sample.

4. The chromite composition as well as the PGE-Au abundance and distribution patterns of the Nurali chromitites do not fit the fields of the ophiolitic chromitites of the Urals. This may possibly reflect the peculiarity of conditions of magma genesis and fractionation in the continental margin with respect to the supra-subduction zone, as it has already been proposed on the basis of bulk rock chemistry (Garuti et al. 1997a, Fershtater et al. 2000).

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