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ORIGINAL ARTICLE

Geochemistry and mineralogy of platinum-group elements (PGE) in chromites from Centralnoye I, Polar Urals, Russia

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Abstract The Polar Urals region of northern Russia is well known for large chromium (Cr)-bearing massifs with major chromite orebodies, including the Centralnoye I deposit in the Ray-Iz ultramafic massif of the Ural ophiolite belt. New data on platinum (Pt)-group elements (PGE), geochemistry and mineralogy of the host dunite shows that the deposit has anomalous iridium (Ir) values. These values indicate the predominance of ruthenium–osmium–iridium (Ru–Os–Ir)-bearing phases among the platinum-group mineral (PGM) assemblage that is typical of mantle-hosted chromite ores. Low Pt values in chromites and increased Pt values in host dunites might reflect the presence of cumulus PGM grains. The most abundant PGM found in the chromite is erlichmanite (up to 15 μm). Less common are cuproiridsite (up to 5 μm), irarsite (up to 4–5 μm), and laurite (up to 4 μm). The predominant sulfide is heazlewoodite, in intergrowth with Ni–Fe alloys, sporadically with pentlandite, and rarely with pure nickel. Based on the average PGE values and estimated Cr-ore resources, the Centralnoye I deposit can be considered as an important resource of PGE.

1. Introduction

The Urals ophiolitic complexes of central Russia host both large chromite deposits, as for example Kempirsai in Kazakhstan (Distler et al., 2008), Centralnoye I, Centralnoye II, Zapadnoye, Yugo-Zapadnoye, Engai, Sklonovoye, Rybiy Khvost and other deposits in the Ray-Iz massif located in the Polar Urals (e.g. Gurskaya et al., 2004; Kenig et al., 2004), and smaller occurrences (e.g. Kraka, Kluchevskoy and others). Geochemistry and mineralogy of platinum-group elements (PGE) in the chromite ores of the Ray-Iz massif have been studied by Volchenko (1990), Gurskaya (1995), Gurskaya et al. (2004) and others.

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The study of chromite samples from the south-eastern part of the Centralnoye II deposit (orebody No. 31) confirmed significant concentrations of IPGE and also occurrence of platinum-group minerals (PGM) (Garuti et al., 1999) as well as gold (Au) (Kojonen et al., 2003).

Here, we report new mineralogical and geochemical data for chromite orebodies from the Centralnoye I deposit and compare them with previous results from the Centralnoye II deposit. This contribution follows the study by Pašava et al. (2009).

2. Geology

The Centralnoye I deposit (N 66°50′04.46″, E 65°25′01.12″) is located in the SW part of the Ray-Iz ultramafic massif, which is composed mainly of dunite and harzburgite, and which together with other chromite deposits (Centralnoye II, Zapadnoye, Yugo-Zapadnoye and others), is hosted by a Polar Urals ophiolitic complex (Fig. 1). This complex covers an area of about 400 km^2 and is one of several thought to represent fragments of the upper mantle–crust transition, that were exhumed from the Ordovician–Silurian lower oceanic lithosphere during closure of an oceanic basin (Gurskaya, 1995).

With an annual exploitation of about 600,000 t of ore, the deposit has a recovery expectation of about 7–8 years (ore reserves of about 4.5 mil. t of ore averaging 35%–38% Cr_2O_3 calculated in July 2007). The Centralnoye I deposit is represented by a complex ore-bearing zone, which is about 1700 m long, up to 450 m wide, the host to 79 orebodies, and is tectonically divided into northern and southern blocks (Fig. 1). The size of individual orebodies varies from 30 to 35 m in length with variable thickness from 0.2 to 11.5 m (avg. 1.9 m). Three types of Cr-mineralization can be distinguished: (1) low-grade segregations in dunite; (2) high-grade remobilized ore in tectonicized zones within dunite and harzburgite; and (3) a mixed type of (1) and (2) according to Kenig et al. (2004).

Table 1 Ranges and average values of PGE, Au (in ppb) and Cr_2O_3 (wt.%) in studied chromite and dunite from the Centralnoye I compared to the PGE values from the Centralnoye II deposit (data from Gurskaya et al., 2004) and Au from the Centralnoye II deposit (data from Kojonen et al., 2003).

		Centralnoye I		Centralnoye II
		Cr-ore	Dunite	Cr-ore
Ir	Min–max	6.8–116.7	1.9–4.6	32–110
	Avg.	47.5	3.3	63
Ru	Min–max	18.1–169.7	0.3–1.9	13–260
	Avg.	69.9	1.3	113
Rh	Min–max	1.9–14.5	0.7–2.3	5–14
	Avg.	6.4	1.4	9
Pt	Min–max	0.3–3.8	6.9–28.3	<5–20
	Avg.	1.6	15.0	6
Pd	Min–max	0.2–1.2	9.0–46.3	<10–90
	Avg.	0.4	22.4	27
Au	Min–max	0.5–4.0	0.5–5.0	
	Avg.	1.3	2.6	<0.78
Cr_2O_3	Min–max	27.4–51.2	0.012–0.027	33–44
	Avg.	42.7	0.018	

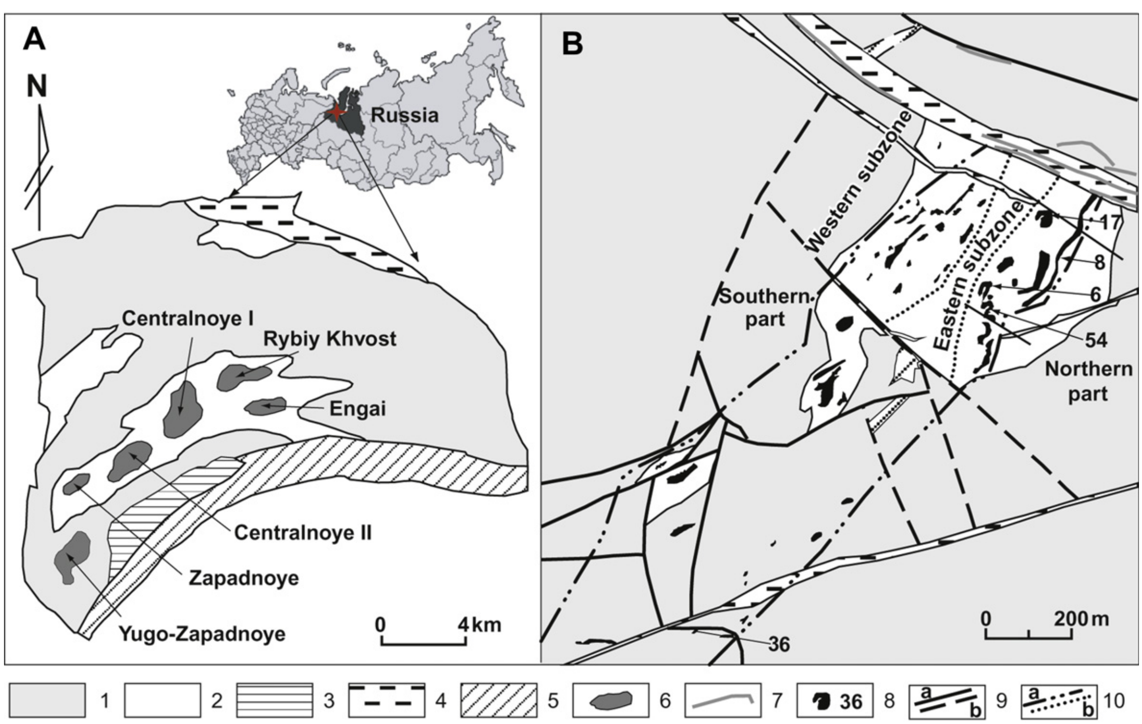

Figure 1 Simplified geological map showing A. Ray-Iz ophiolite with location of major chromite orebodies (after Kojonen et al., 2003). B. Centralnoye I deposit (N 66°50′04.46″, E 65°25′01.12″) with localization of studied orebodies (adapted from Kenig et al., 2004). 1–harzburgite; 2–dunite; 3–pyroxenite-wehrlite; 4–serpentinite; 5–gabbro; 6–dunite with Cr-deposits; 7–diabase dyke; 8– chromite orebody; numbers of orebodies; 9–faults: a) observed; b) inferred; 10–borders: a) orebodies blocks; b) orebodies subzones.

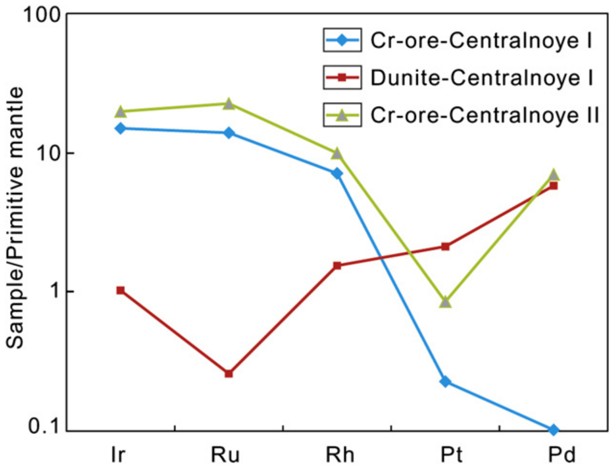

Figure 2 PGE mantle normalized patterns for average chromite and dunite from the Centralnoye I deposit (mantle data from McDonough and Sun, 1995) and chromite from the Centralnoye II deposit (data from Gurskaya et al., 2004).

3. Sampling and methods

Eight representative samples of massive chromite ore (about 2 kg) and four samples of barren host dunite (about 1 kg) from different blocks and orebodies were collected from the open pit of the Centralnoye I deposit. In the Centralnoye I deposit itself, massive ore and host dunite from northern block orebodies Nos. 6 (level 635), 8 (level 610), 17 (level 610) and 54 (level 635), and southern block orebody No. 36, were sampled (see Fig. 1).

Preconcentration of PGE (ruthenium-Ru, rhodium-Rh, palladium-Pd, iridium-Ir, platinum-Pt) into nickel (Ni)-buttons were carried out in the labs of the Czech Geological Survey in Prague. The PGE were determined using inductively coupled plasma mass spectrometry (ICP-MS) at the Faculty of Science, Charles University, Prague (Dr. V. Strnad, analyst). Gold and other elements were determined using ICP-MS in the ACME Analytical Laboratories Ltd (Vancouver, Canada). Preliminary mineralogical observations were carried out with a reflected light microscope. Chemical analyses of sulfides were performed in the labs of the Czech Geological Survey on a Microspec WDX-3PC wavelength-dispersion electron microprobe, using a focused beam. Accelerating voltage was set to 20 kV, and the beam current was 20 nA; spectrum acquisition time was 50 s.

The PGM grains were analyzed in the lab of the Geological Institute (Academy of Sciences, Prague) using the Cameca SX-100 electron microprobe with the wave-length-dispersion mode. Accelerating voltage was set to 15 keV, and the beam current was 10 nA. Pure metals were used as primary standards for PGE. The samples were analyzed using: $L\alpha$ for Ru, Rh, Pd, Ir, Pt, $M\alpha$ for Os, and $L\alpha$ for S, Fe, Cu and Ni. A scanning electron microscope CamScan 4 with an energy-dispersive analyzer Oxford Link ISIS 300 was used for a preliminary examination of samples and for taking backscattered electron images (BEI). Totals of the electron microprobe analyses reflect the small size of the PGM grains; grains smaller than 5 μm were calculated based on atomic proportion to attribute the mineral species.

4. Results and discussion

PGE, Au and Cr data are given in Table 1. The PGE and Au can be classified into two sub-groups on the basis of their geochemical behavior: the Ir group (I-PGE; Os, Ir, and Ru) and the Pd group (P-PGE; Rh, Pt, Pd, and Au). Generally, chromites related to ophiolites are known for their low P-PGE content (Economu-Eliopoulos, 1996). In contrast, chromium ores from the Centralnoye I deposit are characterized by high I-PGE. Slightly higher average Ir, Ru, Rh, Pt and significantly higher average Pd values in chromites from the Centralnoye II deposit were reported by Gurskaya et al. (2004) (see Table 1, Fig. 2). The average Au concentration in chromites (1.3 ppb) at the Centralnoye I deposit is higher than that reported from the Centralnoye II deposit (<0.78 ppb) by Kojonen et al. (2003) who, despite finding such a low concentration, described the presence of native gold.

Significant positive correlations were calculated between Cr and IPGE in our ore samples (correlation coefficients: $Cr/Ir_{cc} = 0.79$, $Cr/Ru_{cc} = 0.80$), indicating the presence of Os-, Ir-, and Ru-, bearing phases within the PGM assemblage at the Centralnoye I deposit. This was confirmed by our preliminary mineralogical study (see Table 2). PGM occur as inclusions (Fig. 3A–C), usually less than 10 μm across, in chromite. Erlichmanite is the most abundant PGM, forming small inclusions (up to 15 μm) in chromite, and also was observed in intergrowth with laurite. Less common are cuproiridsite (up to 5 μm), irarsite (up to 4–5 μm) and laurite (up to 4 μm). Heazlewoodite (about 20 μm in across; Fig. 3D–E), was observed in intergrowth with Ni–Fe alloys (with about 20 wt.% of Fe), sporadically with pentlandite (of a variable admixture of Co 1.5 wt.%–2.2 wt.%),

Table 2 Representative compositions of PGE minerals from the Centralnoye I deposit.

	Weight%						Atomic%				
	Os	Ir	Ru	Cu	S	Total	Os	Ir	Ru	Cu	S
Erlichmanite											
RC3_2/34	66.62	7.49	0.00	0.12	25.45	99.68	29.56	3.29	0.00	0.16	66.99
RC3_2/35	59.53	9.94	1.34	0.00	26.22	97.04	26.00	4.34	1.09	0.00	68.58
RC3_2/36	60.45	8.65	3.71	0.00	26.39	99.19	26.13	3.67	3.00	0.00	67.20
RC3_2/37	62.78	8.65	0.00	0.00	25.65	97.08	28.11	3.83	0.00	0.00	68.14
RC3_2/38	62.37	8.59	0.42	0.00	25.12	96.50	28.26	3.85	0.36	0.00	67.52
RC3_2/39	60.62	10.41	2.26	0.26	25.55	99.09	26.64	4.52	1.86	0.34	66.63
Cuproiridsite											
RC3_1/40	0.12	65.46	0.00	9.54	23.10	98.23	0.05	28.10	0.00	12.39	59.45
RC3_1/41	0.01	64.05	0.00	9.60	23.09	96.74	0.00	27.67	0.00	12.54	59.80

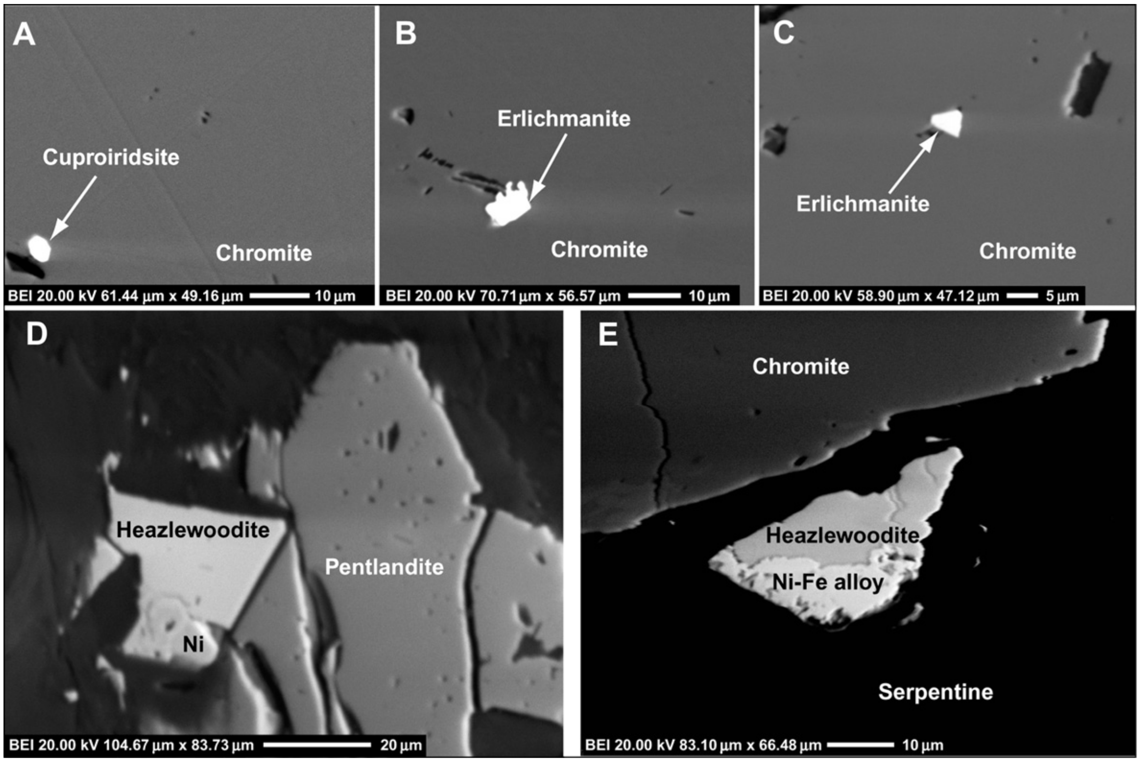

Figure 3 Back-scattered electron images of typical mineral assemblages in Cr-bearing samples.

and rarely with native nickel. Millerite was not observed in the studied samples.

Our preliminary mineralogical observations are in agreement with the results reported by Garuti et al. (1999), and Gurskaya et al. (2004) from the Centralnoye II deposit. However, these authors identified a greater complexity of the PGM assemblage (laurite, erlichmanite, Os–Ir–(Ru) alloys, cuproiridsite, kashinite, rhodian pentlandite, irarsite, cherepanovite, hollingworthite, tolovkite, unknown Ir–Rh–Ni sulfides and an unknown Rh–Ni arsenide). Garuti et al. (1999) suggested that such PGM paragenesis indicates deposition through an unusually wide range of $f(S_2)$ and T compared with mantle-hosted chromitites from other ophiolite complexes. This wide range is ascribed to the crystallization of PGM and chromite down to a relatively low temperature, enabling the relative increase of $f(S_2)$ (Garuti et al., 1999). As an example, the presence of a heazlewoodite-pentlandite-native nickel assemblage associated with chromite alteration was also described by Ahmed and Hall (1982) from the Sakhakot-Qila ultramafic complex in Pakistan as indicating highly reducing conditions with $f(O_2)$ and $f(S_2)$ much below those yielding nickel sulfide ores.

The studied high-grade chromite ores in dunite (Cr_2O_3 = 27.4 wt.%–51.2 wt.%, avg. 42.67 wt.%, and the average Cr/(Cr + Al) ~ 1) are close to data (Cr_2O_3 = 33 wt.%–44 wt.%) from the Centralnoye II deposit (Gurskaya et al., 2004). At the Centralnoye I deposit, the barren host dunites (Cr_2O_3 = 0.01 wt.%–0.02 wt.%) reveal higher Pt, Pd and Au values than those associated with chromites. As Pt is incompatible with olivine (in contrast to Ir and Ru: see discussion in Borisov and Palme (2000)), the expected Pt content in a dunite derived from a basaltic melt with about 10 ppb Pt should be around 2–3 ppb in the trapped melt proportion (Barnes and Maier, 2002). Increased Pt values in the studied dunite samples could reflect the cumulation of PGM grains. Compared to dunites from Greek ophiolites (Economu-Eliopoulos, 1996), those from the Centralnoye I deposit show similar average concentrations of Ir, Rh and lower Ru.

The average sum of PGE (without Os) is 126 ppb in the chromite ore at the Centralnoye I deposit and 218 ppb in the Centralnoye II deposit, based on data from Gurskaya et al. (2004). Assuming the homogeneous distribution of PGE within this deposit, we can estimate the total amount of PGE in the calculated ore reserves to be about 0.567 metric ton at Centralnoye I.

5. Conclusions

Our study of massive chromite ores and host dunites of the Centralnoye I deposit leads to the following results:

1. Chromite ores are enriched in I-PGE but on average they contain lower Ir, Pt, Pd, Ru, Rh, and Au concentrations than those reported from Centralnoye II.
2. The predominance of Ru–Os–Ir-bearing mineral phases (erlichmanite, laurite, cuproiridsite, irarsite) that were identified in the PGM assemblage is typical of ophiolitic chromites.
3. The higher average Au value in Cr-ore at Centralnoye I, as compared with that of Centralnoye II indicates the possible presence of native gold.
4. Very low Pt values in chromite ore, but relatively high Pt concentrations in host dunites might reflect the cumulation of Pt-bearing PGM phases.

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