

## Accessory mineralisations in lherzolites of Northern Kraka massif (South Urals)

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**Abstract.** The findings of platinum group metal mineralization (PGM) and the distribution of platinum group elements (PGE) in lherzolites of the Northern Kraka massif are described. The total contents of PGE are approximately two orders of magnitude lower than those in chondrite and are close to pyrolite, relative to which the studied lherzolites are enriched in Pd and depleted in Ru. In segregations of PGMs, the presence of all PGEs (except rhodium) in various proportions was established. All found grains are divided into three contrasting types: the refractory triad Os–Ir–Ru, essentially platinum with the participation of Pd, and Cu–Pd. Almost all found PGM grains are localized either in the peripheral parts of grains of altered sulfides (heazlewoodite, pentlandite) or in the silicate matrix in the immediate vicinity of sulfide segregations. Based on the mineral associations and PGE distribution, a probable genesis of segregations has been suggested. Associations of Cu–Pd and Pd–Pt(+Cu) composition most likely formed during the crystallization of sulfides from the extracted partial melts. This is indicated by their close association with clinopyroxenes and the presence of relatively fusible platinoids and copper. The associations of Pt–Ir and Os–Ir–Ru(+Pt) composition are most likely restitic, formed in place of primary mantle sulfides as a result of extraction of more fusible elements and further desulphurization. The isolation of platinoids as their own mineral phases is associated with the influence of superimposed low-temperature processes – subsolidus redistribution during cooling and subsequent serpentinization.

**Keywords:** ultramafic rocks, ophiolite, lherzolite, platinum group metal mineralization, platinum group elements

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### Introduction

The Kraka ultramafic massifs are located in the northern closure of the Zilair megasynclorium (Fig. 1). These are four bodies with a total area of about 900 km<sup>2</sup>, separated by fields of Paleozoic volcanic-sedimentary strata. From north to south there are Northern, Middle, Uzyansky and Southern Kraka. The Northern Kraka massif is characterized by an isometric shape in plan and large dimensions (20 × 15 km), slightly inferior in area only to the southern massif of the group. At the same time, the ultramafic rocks of the Northern Kraka massif are characterized by the best preservation of primary upper mantle parageneses and a fairly homogeneous composition. Approximately 90% of the massif area is occupied by spinel lherzolites with a small proportion

of spinel-plagioclase varieties, the remaining 10% are dunites, marginal serpentinites and mafic dykes (diabases, gabbros and products of their metamorphism). In most of the territory occupied by lherzolites, the rocks contain no more than 40% mesh serpentine.

Interest in the massif as a promising source of platinum group metals arose at the turn of the 1990s–2000s, when thematic programs for the search for chromitites and noble metals mineralization began to be actively implemented in the region (Snachev et al., 2001; Snachev et al., 2000; Kovalev et al., 1997). The main objects of the search were chromitites, several occurrences of which have been known in the massif since the end of the 19th century (Kvyatkovsky, 1931; Farfontiev, 1937). The second most important object was plagioclase lherzolites, in which, according to the report of V.P. Loginov (1933), signs of platinum content were discovered in the form of “small grains of platinum group metals among rare and uniform dissemination of nickel sulfides”. As a result of the analyses, it was

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found that the concentration of platinum in these rocks was 300–800 mg/t.

Unfortunately, during the period of thematic work on chromitites, new deposits with promising reserves were not identified; the significance of small ore occurrences, even with fairly high concentrations of platinum group elements (PGE) in them, is small. The search for platinum-bearing plagioclase lherzolites also did not give a positive result; the total contents of platinum group metals in the studied samples ranged from 10 to 50 mg/t (Snachev et al., 2001).

In the meantime, the significant size of the massif and the wide distribution of fresh ultramafic rocks make the search for mineralized zones a very promising task, since when areas with elevated PGE concentrations and native platinum group metals are discovered, there is a possibility of identifying large-volume deposits. In this regard, the main goal of our research was to explore the mineral forms of platinum group metals in lherzolites.

### Materials and methods

The object of the study was lherzolite samples collected during field trips in 2018–2022. The main office methods of study were standard petrographic and mineralographic methods (polarizing microscope POLAM R-311); to determine the bulk composition of the rocks, chemical analysis was carried out for petrogenic oxides (“wet chemistry”, X-ray fluorescence analysis). Electron microscopic studies and the study of the composition of minerals were carried out in polished sections and blocks on a Tescan VEGA 4 Compact scanning electron microscope (Tescan, Czech Republic) with an Xplorer 15 energy-dispersive analyzer (Oxford Instruments, UK) (IG UFRC RAS, Ufa). The spectra were processed automatically using the AzTec One software package using the TrueQ technique. When shooting, the following settings were used: accelerating voltage 20 kV, probe current in the range of 3–4 nA, spectrum accumulation time at a point of 60 s in the Point&ID mode. Determinations of Pt, Pd, Rh, Ru, Ir in lherzolites of the Northern Kraka were carried out in VSEGEI (St. Petersburg) using the method of mass spectrometry with inductively coupled plasma (ICP MS) in a colloidal salt solution of deionized water containing particles of the fraction of the test sample with sizes of 1–1000 nm.

### Geological setting

As noted in the introduction, the Northern Kraka massif is a large geological body composed of fresh ultramafic rocks (Fig. 1). The massif is characterized by highly dissected relief and relatively good exposure. Route studies covered most of the massif, characterized the petrographic, petrochemical and mineral composition

of the rocks (Savelyev et al., 2008; Savelyev, 2022), structural studies were carried out, as a result of which it was possible to identify patterns of internal structure, reflected in the corresponding geological schematic map and diagrams (Fig. 1, b–d). As follows from these constructions, lherzolites are most characterized by the orientation of banding and mineral schistosity in a sublatitudinal direction with a predominant strike to the southeast (100–150°) and a relatively gentle dip to the southwestern point at an angle of 30–45°.

In outcrops, lherzolites look quite homogeneous (Fig. 2); on the surface, against the background of light brown olivine, tabular crystals of enstatite of a light greenish-yellow color (2–5 mm), smaller bright green grains of diopside (0.5–1 mm) and small black grains of accessory Cr-spinel (0.1–1 mm). Most of the studied lherzolites are represented by the spinel facies, where the only accessory mineral is Cr-spinel of variable composition. Among them there are areas composed of spinel-plagioclase varieties of lherzolites, in which plagioclase or products of its replacement occur along with Cr-spinel and in close association with it.

The rock-forming minerals of spinel lherzolites are olivine, orthorhombic and monoclinic pyroxenes (Fig. 2,c). Previously carried out petrographic and mineralogical-geochemical studies (Savelyev, 2022) made it possible to identify in the ultramafic rocks of the massif various types of combinations of microstructures and mineral composition, the formation of which is interpreted as the result of several mantle processes - partial melting, percolation of melts through restite, plastic flow and deformation-induced decomposition of pyroxenes. Accessory minerals in ultramafic rocks are represented by Cr-spinel, iron sulfides, copper-nickel and iron-nickel alloys, and platinum group minerals.

In the inner part of the massif, among the peridotites, there are rare thin dykes of mafic rocks, which composition usually corresponds to gabbro. In addition, we have identified zones of mylonitization, within which lherzolites are subject to intense plastic deformation with the formation of ultrabasic mylonites – rocks consisting of lenticular grains of ortho- and clinopyroxene, surrounded by a fine-grained mass of the same minerals, as well as Cr-spinel and predominant olivine.

### Results

Route studies on a scale of 1:50,000 cover most of the central and northern parts of the massif, where significant areas are composed of weakly serpentinized massive rocks. Spinel lherzolites predominate to a large extent; spinel-plagioclase varieties and dunites are of subordinate importance.

Accessory Cr-spinels of ultramafic rocks are characterized by significant variations in aluminum

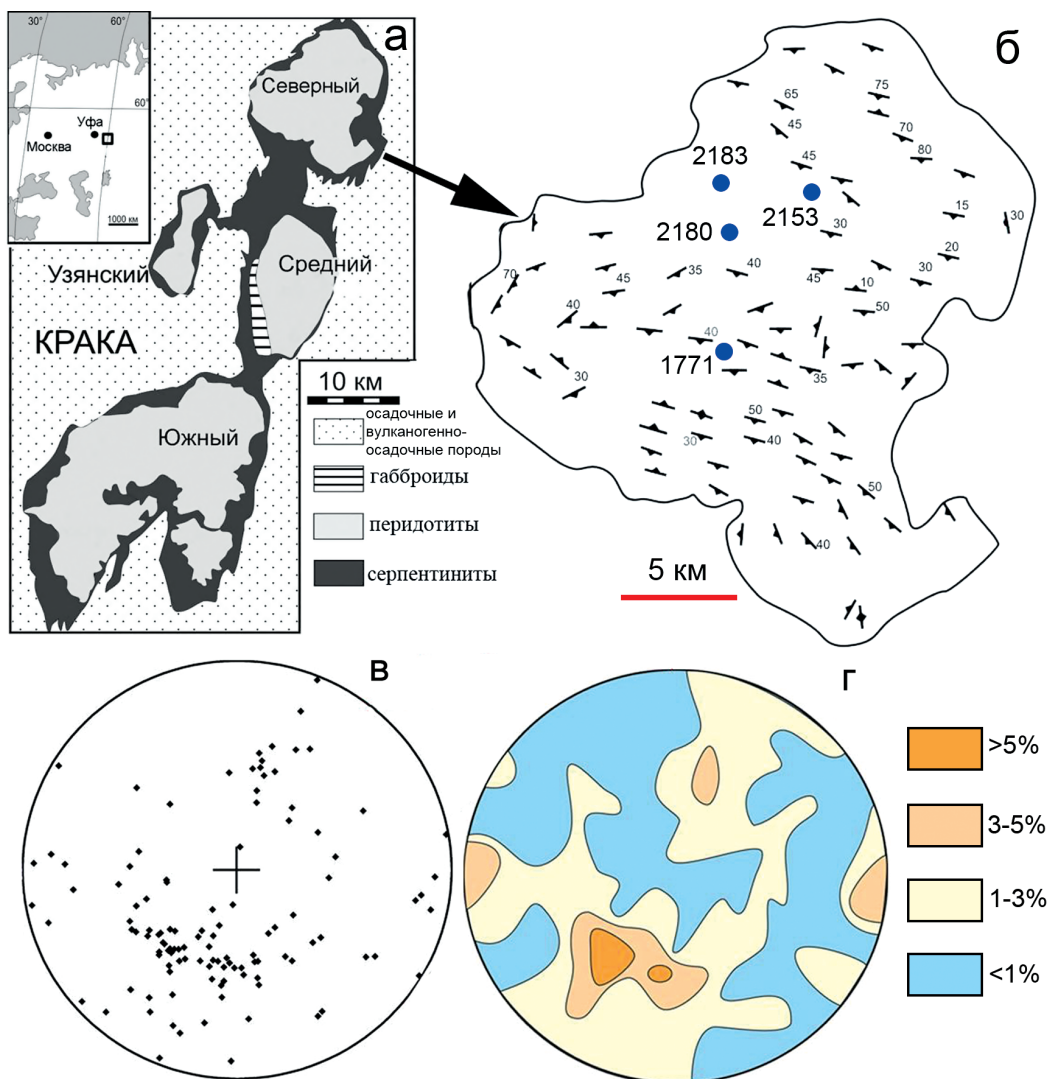


Fig. 1. Internal structure of the Northern Kraka massif: a – overview geological scheme of the Kraka massif region, b – elements of occurrence of mineral schistosity and banding in peridotites (according to (Moskaleva, 1974; Savelyev, 2012)) and the position of the studied samples with platinum-metal mineralization; c – distribution of normals to the plane of mineral foliation on the upper hemisphere of an equal-area projection; d – diagram constructed based on the results of statistical processing (c) (color scale indicates the frequency of occurrence of values)

and chromium contents and contain little ferric iron. Lherzolites are dominated by high-alumina Cr-spinels (picotite, chrompicotite with Cr# = 0.2–0.4), higher-chromium varieties are found in harzburgites (chrompicotite, aluminochromite with Cr# = 0.4–0.7), and in dunites and chromitites they predominate high-chromium aluminum-chromite and chromite (Cr# = 0.7–0.85). The composition of rock-forming minerals from the rocks of the massif is described in detail in (Savelyev, Gataullin, 2021).

The study of polished sections of lherzolites showed a wide distribution of rare dissemination of base metal sulfides (BMS), among which the most widespread are heazlewoodite Ni<sub>3</sub>S<sub>2</sub>, pyrrhotite Fe<sub>1-x</sub>S, pentlandite (Fe,Ni)<sub>9</sub>S<sub>8</sub> and its cobalt-containing variety (Fe,Ni,Co)<sub>9</sub>S<sub>8</sub>, less common are chalcopyrite (CuFeS<sub>2</sub>), millerite (NiS). In addition to sulfides, minerals of native elements were also discovered – awaruite Ni<sub>3</sub>Fe, wairauite CoFe, native

copper Cu and arsenides (nickeline NiAs). Typically, the BMS content in peridotites is hundredths to tenths of a percent, reaching 0.5–1 vol. in some cases. %.

The bulk PGE contents were determined in several lherzolites samples (Table 1). In all studied samples, the concentrations of platinum group elements are lower than in chondrite by one or two orders of magnitude, but are comparable to the expected concentrations of PGE in pyrolite.

The studied lherzolites are characterized by depletion in ruthenium compared to the original pyrolite material and enrichment in palladium. The concentrations of rhodium, iridium, and platinum differ little from those for pyrolite (Fig. 3). The average content of platinum group metals is 0.028 g/t, which differs significantly from the content of the found own platinum group minerals in lherzolites.

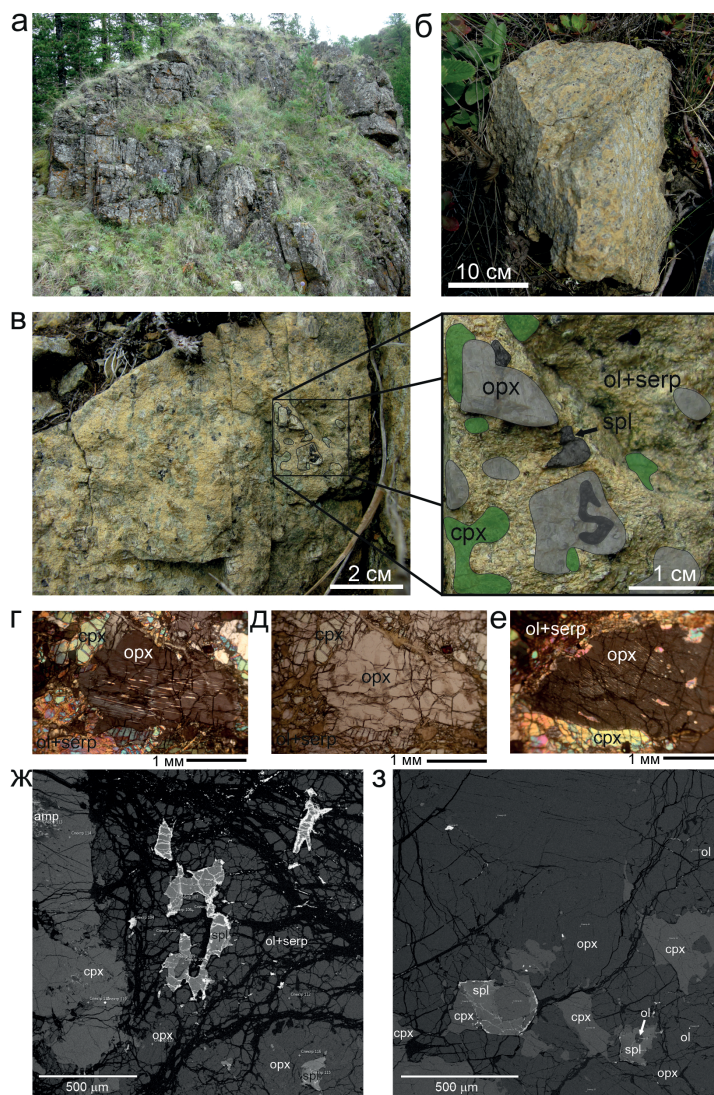


Fig. 2. General view of outcrops, samples and preparations of lherzolites in reflected light and back-scattered electrons: a – general view of the outcrop; b, c – samples of lherzolite with a naturally prepared surface, Cr-spinels and pyroxenes protrude above the main mass of olivine; c, right – enlarged fragment highlighting minerals; d – image of a thin section in crossed nicols, an orthopyroxene grain contains lamellae of minerals with high interference colors, surrounded by small grains of olivine and clinopyroxene; d – the same image in parallel nicols; e – lamellas and rounded inclusions of monoclinic pyroxene in orthorhombic pyroxene; g – SEM image of one of the characteristic xenomorphic forms of Cr-spinel segregations in lherzolites; h – clinopyroxene segregations on the periphery of large orthopyroxene grains. Designations: amp – amphibole, ol – olivine, opx – orthopyroxene, cpx – clinopyroxene, spl – Cr-spinel, serp – serpentine

No.	Sample	Ru	Rh	Pd	Ir	Pt	$\Sigma$ PGE (without Os)
1	Sek - 1771	2.3	< 2	20	2.1	12.0	36.4
2	Sek - 2153	3.5	< 2	13	4.0	5.8	26.3
3	Sek - 2180	3.2	< 2	7.3	2.8	3.0	16.3
4	Sek - 2183	2.8	3.5	18	3.3	6.3	33.9

Table 1. Gross contents of platinum group elements in lherzolites of Northern Kraka (mg/t)

Among the 20 polished sections we studied, isolations of platinum group minerals were found in four samples: Sek-1771, Sek-2153, Sek-2180, Sek-2183, which are represented by fairly fresh lherzolites with good preservation of primary mantle minerals – olivine, orthorhombic and monoclinic pyroxenes, Cr-spinel (Fig. 4, 5). Isolations of platinum group minerals

(PGMs) are always spatially associated with BMS – pyrrhotite (Fig. 4, a, b), pentlandite (Fig. 4, c, e, f) and heazlewoodite (Fig. 5). Due to the very small sizes of PGMs (a few micrometers), it is rarely possible to obtain quantitative data on their composition, but mineral phases can be identified quite reliably from qualitative spectra (Fig. 4, d, g).

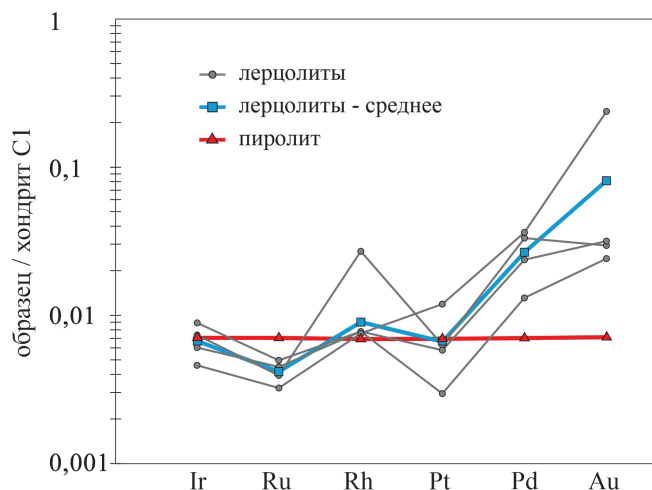


Fig. 3. Chondrite-normalized contents of platinum group elements in lherzolites of the Northern Kraka massif in comparison with their concentrations in pyroclite. Data on the composition of chondrite and pyroclite according to (McDonough, Sun, 1995)

Calculation of the composition of PGM mineral phases for constructing triangular diagrams was carried out using normalization to 100% after excluding the matrix material. As a result, three contrasting types of platinum-metal mineralization were established: 1) high-melting alloys (Os–Ir–Ru), 2) with a predominance of platinum and 3) palladium type (Fig. 6). It should be noted that the identified types are often combined in the same samples. Minerals are represented by alloys of Os–Ir–Ru composition with a predominance of ruthenium,

less commonly laurite, and alloys of Pt–Ir, Cu–Pt–Ni–Pd and Cu–Pd composition.

**Discussion**

Elevated average PGE contents in ultramafic rocks is a well-known fact, but most of the research on platinum content and mineralogy of platinum group metals is associated with the study of chromitites, where PGMs occur as rare accessory minerals, while the ultramafic host rocks themselves rarely become the object of research.

Nevertheless, in the last 20 years, many works have appeared on the mineralogy of PGE in peridotites from xenoliths and massifs of the so-called “subcontinental mantle”, for example (Ferraris, Lorand, 2015; Lorand et al., 2010; Luguet et al., 2007). One of the latest major reviews on this issue indicates that studying the features of PGE mineralogy in peridotites is of great importance for understanding the geochemical behavior of highly siderophile elements in the upper mantle (González-Jiménez et al., 2020).

Previous studies of PGMs in peridotites derived from the upper mantle showed that most of the PGEs are mainly concentrated in accessory polymetallic sulfides of the Ni–Fe–Cu system (BMS), rather than in alloys (Luguet and Reisberg, 2016), as was suggested by based on experimental data showing very high PGE distribution coefficients (105–108) in the metal – silicate melt system (Brenan et al., 2016; Mann et al., 2012). In addition, in the Earth’s upper mantle, PGE can also

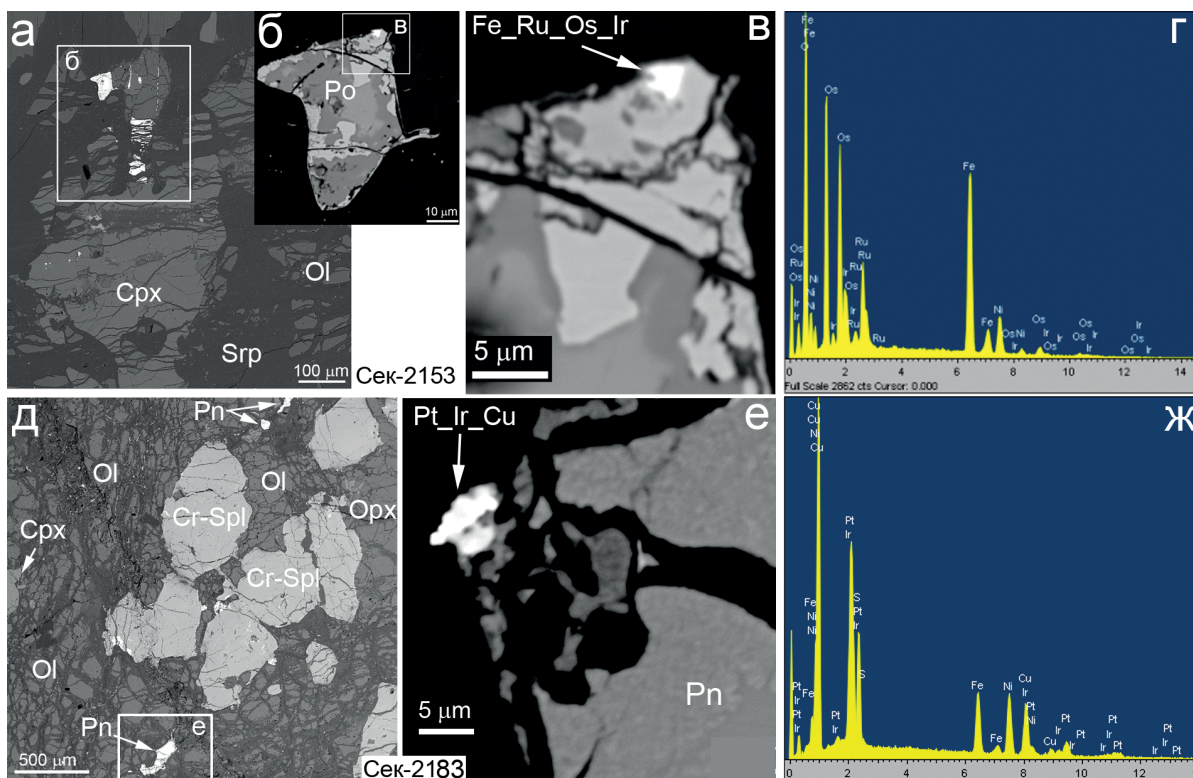


Fig. 4. Submicron segregations of platinum group minerals in lherzolites of Northern Kraka and EDS spectra of their compositions. Designations: Cpx – clinopyroxene, Ol – olivine, Opx – orthopyroxene, Pn – pentlandite, Po – pyrrhotite, Srp – serpentine

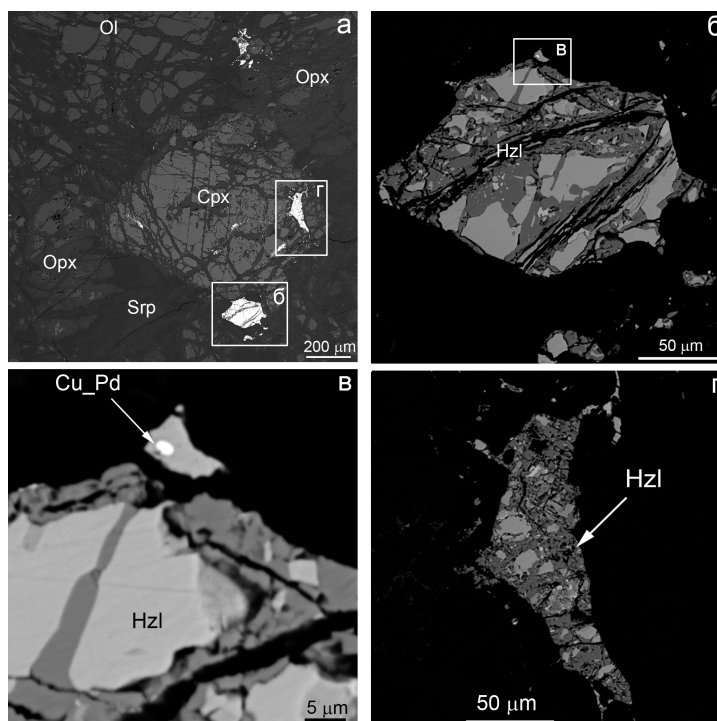


Fig. 5. Heazlewoodite in association with clinopyroxene and submicron formation of palladium copper at its periphery (sample Sec-2180). Designations: Cpx – clinopyroxene, Hzl – heazlewoodite, Ol – olivine, Opx – orthopyroxene, Srp – serpentine

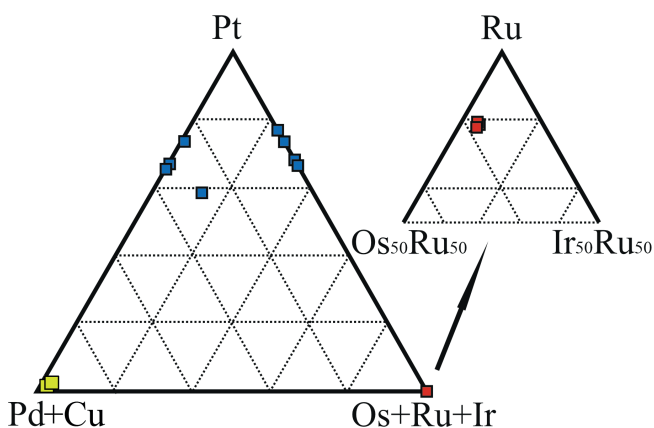


Fig. 6. Diagrams of platinumid compositions from the studied lherzolites of the Northern Kraka massif

form their own minerals, including alloys, sulfides, arsenides, sulfarsenides, tellurides, bismuthides or stannides (O'Driscoll, González-Jiménez, 2016).

Our studies indicate that almost all PGM finds were made in the marginal parts of BMS grains or in the serpentine shell near the boundary of these grains. In this case, the BMS grains were in spatial association with either olivine (Fig. 4) or clinopyroxene (Fig. 5), and these differences were reflected in the composition of the PGM: 1) in the case when the sulfide grain was located on the periphery of the diopside, a mineral of Cu–Pd composition was precipitated in it, 2) in a grain located inside the olivine, an alloy of Pt–Ir composition with a small proportion of copper was formed, 3) in the grain at the contact of olivine and orthorhombic pyroxene, the

release of high-melting Os–Ir–Ru association occurred.

Most likely, PGE were originally part of iron and nickel sulfides, which, in turn, were formed from a monosulfide solid solution. However, the processes that led to the formation of the discharges in question could be different. The observed mineral associations and PGM composition indicate the following probable mechanisms for the formation of PGE-enriched sulfides. Associations of Cu–Pd and Pd–Pt(+Cu) composition most likely formed during the crystallization of sulfides from extracted partial melts, as evidenced by their close association with clinopyroxenes and the presence of relatively low-T PGE (Pd, Pt) and copper. Associations of Pt–Ir- and Os–Ir–Ru(+Pt) composition are probably restite, formed in place of primary mantle sulfides as a result of extraction of more fusible elements and further desulfurization. This is confirmed by the data that refractory PGE (Os, Ir, Ru) can easily enter the crystal structure of pentlandite (Godel et al., 2007; Luguet et al., 2001, 2004), in association with which their precipitations were observed.

Regardless of how sulfides with increased concentrations of platinum group metals were formed, the release of the latter in the form of their own mineral phases was apparently influenced by superimposed low-temperature processes - subsolidus redistribution during cooling and subsequent serpentinization. A number of studies have established that during serpentinization, PGE are redistributed into discrete ultrafine phases (from micro- to nanoscale) at the boundaries of partially destabilized associations of sulfide minerals in the

mantle (Abrajano et al., 1988; Edwards, 1990; Lorand, 1987; Lorand, Luguët, 2016; Luguët et al., 2004, 2001; Ohnenstetter, 1992; Peregoedova et al., 2004; Prichard et al., 1994, etc.). This conclusion is fully confirmed by our research. The close association in peridotites between Ni–Fe sulfides and PGMs suggests that PGE remobilization is largely limited to the microscale (Lorand et al., 2010; O’Driscoll and González-Jiménez, 2016; Prichard et al., 1994; Lawley et al., 2020).

Nevertheless, the experience of studying peridotites of the Kraka massifs indicates that the number of PGM finds shows a clear negative dependence on the degree of manifestation of serpentinization processes. Fully serpentinized ultramafic rocks usually contain only heazlewoodite and awaruite without inclusions of platinum group minerals. Thus, we can conclude that the mobility of PGE increases simultaneously with an increase in the degree of serpentinization of rocks.

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IN RUSSIAN

## Акцессорная платиноидная минерализация в лерцолитах массива Северный Крака (Южный Урал)

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Описаны находки платинометальной минерализации и распределение элементов платиновой группы в лерцолитах массива Северный Крака. Валовые содержания элементов платиновой группы (ЭПГ) приблизительно на два порядка ниже таковых в хондрите и близки к пиролитовым, относительно которого исследованные лерцолиты обогащены Pd и обеднены Ru. В выделениях минералов платиновой группы (МПГ) установлено присутствие всех ЭПГ (кроме родия) в различных соотношениях. Все выделения подразделяются на три контрастных типа: тугоплавкая триада Os–Ir–Ru, существенно платиновый с участием палладия и палладиево-медный. Практически все найденные зерна МПГ локализованы либо в периферических частях зерен измененных сульфидов (хизлевудит, пентландит), либо в силикатном матриксе в непосредственной близости от сульфидных выделений. На основе установленных минеральных ассоциаций и распределения в них ЭПГ предположен вероятный генезис выделений. Ассоциации Cu–Pd- и Pd–Pt(+Cu)-состава, скорее всего, образовались при кристаллизации сульфидов из экстрагировавшихся

частичных расплавов, на что указывают их тесная ассоциация с клинопироксенами и присутствие относительно легкоплавких платиноидов и меди. Ассоциации Pt–Ir- и Os–Ir–Ru(+Pt)-состава, вероятнее всего, являются реститовыми, образованными на месте первичных мантийных сульфидов в результате экстракции более легкоплавких элементов и дальнейшей десульфуризации. Выделение платиноидов в виде собственных минеральных фаз связано с влиянием наложенных низкотемпературных процессов – субсолидусного перераспределения при остывании и последующей серпентинизации.

**Ключевые слова:** ультрамафиты, офиолиты, лерцолиты, минералы платиновой группы, элементы платиновой группы

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