Origin of Ru-Os Sulfides from the Verkh-Neivinsk Ophiolite Massif (Middle Urals, Russia): Compositional and S-Os Isotope Evidence

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Abstract: This study presents new compositional and S-Os isotope data for primary Ru-Os sulfides within a platinum-group mineral (PGM) assemblage from placer deposits associated with the Verkh-Neivinsk massif, which is part of the mantle ophiolite association of Middle Urals (Russia). The primary nature of Ru-Os sulfides represented by laurite (RuS₂)–erlichmanite (OsS₂) series is supported by occurrence of euhedral inclusions of high-Mg olivine (Fo₉₂–₉₄) that fall within the compositional range of mantle (primitive) olivine (Fo₈₈–₉₃). The sulfur isotope signatures of Ru-Os sulfides reveal a range of δ³⁴S values from 0.3 to 3.3‰, with a mean of 2.05‰ and a standard deviation of 0.86‰ (n = 18), implying that the sulfur derived from a subchondritic source. A range of sub-chondritic initial ¹⁸⁷Os/¹⁸⁸Os values defined for Ru-Os sulfides (0.1173–0.1278) are clearly indicative of derivation from a sub-chondritic source. Re-depletion (T_{RD}) ages of the Verkh-Neivinsk Ru-Os sulfides are consistent with prolonged melt-extraction processes and likely multi-stage evolution of highly siderophile elements (HSE) within the upper mantle. A single radiogenic ¹⁸⁷Os/¹⁸⁸Os value of 0.13459 ± 0.00002 determined in the erlichmanite is indicative of a supra-chondritic source of HSE. This feature can be interpreted as evidence of a radiogenic crustal component associated with a subduction event or as an indication of an enriched mantle source. The mineralogical and Os-isotope data point to a high-temperature origin of the studied PGM and two contrasting sources for HSE in Ru-Os sulfides of the Verkh-Neivinsk massif.

Keywords: Ru-Os sulfides; laurite; erlichmanite; sulfur isotopes; osmium isotopes; ophilitic mantle; Verkh-Neivinsk massif; Urals; Russia

1. Introduction

Dominance of Ru-Os-Ir minerals over other platinum-group minerals (PGM) is considered a typical feature of podiform chromitites within the residual mantle in ophiolite-type dunite-harzburgite massifs worldwide [1–15], among others. According to equilibrium phase diagrams, experimental results, and empirical data, Ru-Os-Ir alloys and Ru-Os sulfides are considered to be formed during the very early stages of magmatic differentiation, under low fugacity of sulfur, and high-temperature conditions [11,16–23]. Ru–Os sulfides from podiform chromitites within the oceanic mantle are particularly important because they are believed to preserve the isotopic values of the sources of highly siderophile elements (HSE) and sulfur from which these Ru-Os sulfides were formed/crystallized. Usefulness of S-isotopic information collected on Ru-Os sulfides derived from the oceanic mantle has been outlined by Hattori et al. [24], whereas Os isotope data gained for Ru-Os-Ir...
alloys and sulfides from the dunite-harzburgite massifs worldwide [12,25–36], among others, and Ru-Os-Ir alloys from placer deposits [37–43] shed new insights on the multi-stage evolution history of PGM in mantle-derived ultramafic complexes. Among different points of view on the formation of chromitites and PGM, a significant place is given to the osmium isotope data of PGM, which are discussed in the framework of (i) the long-term evolution of the upper mantle, (ii) the heterogeneity of mantle derivatives, and (iii) the interaction of various sources of PGE/HSE [12,44].

The Urals is a unique structure of the Earth, where the main types of ultramafic massifs formed in various geodynamic settings (continental, oceanic, and island-arc) are found. More than a century of studies of the oceanic dunite-harzburgite massifs of the Urals have shown that both the rocks and the associated types of chromite and PGM were formed in a wide time interval, experienced complex processes of high-temperature plastic deformations, along with dynamic recrystallization; at the same time, they also experienced destruction and amalgamation of individual blocks into larger massifs (complexes).

The Verkh-Nevinsk massif, a typical representative of the mantle ophiolitic association at the Middle Urals (Figure 1a), is characterized by primary and secondary PGM assemblages [45]. The primary PGM assemblage, which is dominated by Ru-Os-Ir alloys over Ru-Os sulfides, Pt-Fe alloys, and other PGM, are typical for chromitites, whereas both the primary and secondary PGM assemblages are found in placer deposits of the Vostochny Shishim River draining different lithological units of the Verkh-Neivinsk massif (Figure 2). Secondary PGM assemblages usually form the outer part of polyphase aggregates, which contain a core composed of a Ru-Os-Ir alloy, rimmed by secondary As-bearing laurite, irarsite (IrAsS), and tolovkite (IrSbS).

Particularities of their chemistry and the physicochemical conditions of formation of Ru-Os-Ir alloys are given elsewhere [22,46–48]. The previously collected Os-isotope data for primary Ru-Os-Ir alloys and Ru-Os sulfides from the Verkh-Nevinsk massif revealed a wide range of sub-chondritic $^{187}\text{Os}/^{188}\text{Os}$ values (from 0.1162 to 0.1346 [49,50]), whereas first S-isotope data for Ru-Os sulfides showed a restricted range of $\delta^{34}\text{S}$ values (from 0.2 to 2.3‰ [51]). Both datasets were interpreted as being consistent with a deep-seated source of highly siderophile elements (HSE) and sulfur.

To gain further insight into the origin of Ru-Os sulfides, we have carried out a combined mineralogical and isotope study of laurite (Ru$_2$S$_2$)–erlichmanite (Os$_2$S$_2$) series within a primary PGM assemblage from placer deposit linked to the Verkh-Nevinsk massif. Here, we consider new S-isotope data for 18 Ru-Os sulfide grains, for which Os-isotope data were previously collected on the same spots within PGM samples (16 samples from Reference [50], and 2 new samples). These data are compared with S-isotope data for Ru-Os sulfides [24,51] and Os-isotope data for ultramafic rocks, Ru-Os sulfides and Ru-Os-Ir alloys [49,50,52–67]. Information on genetic features of PGM formation is supplemented by compositional data of solid inclusions typical of the studied Ru-Os sulfides. We integrate an application of electron microprobe analyses of Ru-Os sulfides and solid inclusions within PGM, Re-Os LA-MC-ICP-MS analyses of Ru-Os sulfides and coexistent Os-rich alloys, and S-isotope LA-ICP-MS analyses of Ru-Os sulfides, aiming at (i) evaluating compositional signatures of different morphological types of Ru-Os sulfides, and (ii) constraining the sources of HSE and sulfur within this fragment of the Uralian mantle. This study is part of a larger attempt to elucidate the mantle versus crustal origin of HSE/S in oceanic and subcontinental mantle settings [12,22,24–26,34,35,49–67], among others.
Figure 1. (a) Scheme of location of ophiolite- and zoned-type massifs of the Urals. (1) dunite-harzburgite ophiolite-type massifs, (2) dunite-clinopyroxenite-gabbro zoned-type massifs of the Platinum belt. Box corresponds to inset in Figure 1b. (b) Tectonic scheme of the Middle Urals and position of the Verkh-Neivinsk massif. (1–6) intrusive formations: (1) granitic (granite, granodiorite, alaskite); (2) granitoid (granodiorite, tonalite, granite); (3) plagiogranitic (plagiogranite, quartz diorite); (4) gabbroic (gabbro, gabbronorite, diorite); (5) dunite-harzburgite (dunite, harzburgite, serpentinite, chromitite); (6) dunite–clinopyroxenite (dunite, chromitite, wehrlite, clinopyroxenite, hornblende); (7) rocks of the amphibolite, amphibolite–gneiss, gneiss, and migmatite associations; (8) volcanogenic sedimentary rocks of the island arc sector of the Urals; (9) flysch, flyschoid, molasse, and terrigenous–carbonate, and carbonate formations of the continental sector of the Urals; (10) boundaries of mega zones ((I) Western Urals, (II) Central Urals, (III) Tagil-Magnitogorsk, (IV) Eastern Urals, (V) Transurals); (11) sampling location.
2. Geological Characteristics of Samples

The Verkh-Neivinsk massif is situated at the junction of the Tagil Megasynclinorium and the East Ural Uplift in the zone of the Serov–Mauk deep-seated fault (Figure 1b). It is composed of two complexes: dunite-harzburgite complex that comprises the inner part of the massif and dunite-clinopyroxenite-gabbro complex developed at the periphery (Figure 2). The former complex is attributed to the Late Ordovician–Early Silurian (O₃–S₁), whereas the latter has Middle Silurian–Middle Devonian (S₂–D₂) age [45]. Sixty-eight occurrences and small deposits of chromite ores were discovered in lithological units of both complexes. The main occurrences of noble metals (native gold and PGM) are related to the placer deposits of modern and ancient river valleys. Representative collection of 685 grains of Ru-Os-Ir minerals in a size range from 0.1 to 3 mm was sampled from a gold production concentrate during prospecting of the Tertiary and Quaternary sediments of the Vostochny Shishim River that are confined to the southern part of the Verkh-Neivinsk massif (Figure 2). According to Badanina et al. [47], PGM grains are mainly represented by sub-euhedral and euhedral crystals with subordinate amount of crystal aggregates, among which Ru-Os-Ir...
alloys (83.5%) prevail over Ru-Os sulfides (15.3%) and Pt-Fe alloys (1.2%). In terms of morphology, Ru-Os-Ir alloys are characterized by well-preserved combinations of basal plane, hexagonal prism, and hexagonal dipyramid, whereas Ru-Os sulfides and Pt-Fe alloys have rough, sometimes shallow surfaces of crystal grains and crystal aggregates. Majority of primary PGM are monophase. The remaining polymineralic grains are dominated by IPGE alloys (Os, Ir, and Ru), with minor amounts of one or several other PGM inclusions, including laurite RuS₂, kashinite Ir₂S₃, cuprorhodsite CuIr₂S₄, cooperite PtS, Pt-Fe alloys, irarsite IrAsS, hollingworthite RhAsS, keithconnite Pd₂₀Te₇, and ruthenarsenite RuAs [47]. The PGM grains analyzed in this study are nuggets (crystals and aggregates) that fall within a size range between 0.5 and 1.5 mm.

3. Analytical Techniques

Microprobe analyses of Ru-Os sulfides and mineral inclusions were carried out with a Cameca SX-100 equipped with five WDS spectrometers and a Bruker energy dispersive spectrometer system at Common Use Center “Geoanalyst” of Institute of Geology and Geochemistry, Ural Branch of the Russian Academy of Sciences (Ekaterinburg, Russia). Quantitative WDS analyses were performed at 25 kV accelerating voltage and 20 nA sample current, with a beam diameter of about 1 μm. The following X-ray lines and standards have been used: RuLα, RhLα, PdLβ, OsMα, IrLα, PtLα, NiKα (all native element standards), FeKα, CuKα, SKα (all chalcopyrite), and AsLα (sperrylite). Corrections were performed for the interferences involving Ru-Rh, Ru-Pd, and Ir-Cu. All elements but Os, Ir, Ru, Rh, Fe, and S were found to be below the statistically reliable detection limits under the analytical conditions. Additional details of the analytical procedures used are described in Badanina et al. [47].

Twenty-six in-situ Os-isotope analyses of Ru-Os sulfides and coexistent Ru-Os-Ir alloys were carried out at the Geochemical Analysis Unit at the CCFS/GEMOC laboratories (Macquarie University, Sydney, Australia) using analytical methods reported in other publications [32,34,64,67]. These analyses used a Nu Plasma Multi-collector ICP-MS attached to a New Wave/Merchantek UP 213 laser microprobe. Ablation was carried out with a frequency of 4 Hz, energies of 1–2 mJ/pulse, and a spot size of 15 μm. A standard NiS bead (PGE-A) with 199 ppm Os [68] and 187Os/188Os = 0.1064 [67], along with a natural Os alloy (i.e., Os₅₋₀) from the Guli massif [69,70], were analyzed between PGM samples to monitor any drift in the Faraday cups. The overlap of 187Re on 187Os was corrected by measuring the 187Re peak and using 187Re/185Re = 1.6742. All the analyzed grains have 187Re/188Os lower than 0.005, thus ensuring that the isobaric interference of 187Re on 187Os was precisely corrected [31]. The data were collected using the Nu Plasma time-resolved software, which allows the selection of the most stable intervals of the signal for integration. For laurite with grain sizes between 50 and 1000 μm and Os average contents of ~10 at.%, a typical run duration of ~75 s was achieved with an average signal intensity of Os~7.8 V on the Faraday cups. This gives a precision for 187Os/188Os ranging from 2.1 × 10⁻⁵ to 9.2 × 10⁻⁵ (SE). The external reproducibility of 187Os/188Os for the PGE-A standard during the period of measurements was 0.00013 (2σ SD, n = 15) with a mean value of 0.10652. Repeated analyses of a natural crystal of native osmium, which has been used to check the validity of the LA MC ICP-MS measurements, yield 187Os/188Os = 0.12452 ± 0.00004 (2σ SD, n = 27). This perfectly matches two previously measured LA MC ICP-MS analyses (Neptune MC ICP-MS attached to a New Wave Complex-2 DUV 193 laser microprobe, Russian Geological Institute, St. Petersburg, Russia) for the same Os grain with 187Os/188Os ranging between 0.124546 ± 0.000007 and 0.124566 ± 0.00013. Rhenium-depletion model ages (T_RD) and Re-Os model ages (T_MA) were defined previously by other authors [71,72]. Rhenium-depletion model ages (T_RD) are calculated using the equation T_RD = (1/λ) × ln((187Os/188Os)sample−(187Os/188Os)CHUR)/(187Re/188Os)CHUR + 1), where λ represent a 187Re decay constant of 1.666 × 10⁻¹¹ a⁻¹ [73], whereas sample and CHUR parameters represent present-day values. The T_RD in this study were calculated relative to an Enstatite Chondrite Reservoir (T_ECR) with 187Re/188Os = 0.421 ± 0.013 [74] and present-day
187Os/188Os = 0.1281 ± 0.0004. Alternative 187Os/188Os values for the present-day mantle, in widespread use for calculation of model ages, are 0.12736 [75], 0.1270 [71], and 0.1296 ± 0.0008 [76], where 187Re/188Os is taken as 0.40186 [71]. Calculations using the first two 187Os/188Os estimates would result in model ages that are approximately 0.15–0.2 Ga younger. If the 187Os/188Os value of primitive upper mantle (PUM) is used, the model ages of PGM are approximately 0.2 Ga older.

Eighteen S-isotope analyses were subsequently performed at the Laboratory of Stable Isotope within Common Use Center of the Far East Geological Institute, Far Eastern Branch of the Russian Academy of Sciences (Vladivostok, Russia). In situ S-isotope data were collected on the same spots within Ru-Os sulfide grains, for which Os-isotopic composition was analyzed previously. Sample preparation for mass spectrometric isotope analysis of sulfur was carried out using a femtosecond laser ablation system, NWR Femto, in combination with a reactor for sulfide aerosol conversion into SF6 gas, a cryogenic and chromatographic purification system, and an isotope ratio mass spectrometer (FsLA-GC-IRMS) [77,78]. Isotope ratios of sulfur were measured using a MAT-253 mass spectrometer (Thermo Fisher Scientific, Germany) equipped with a Faraday cup for simultaneous measurements of the ion currents at m/z 127 (32S\(^{+}\)) and 129 (34S\(^{+}\)). The measurements were carried out relative to the laboratory working standard, calibrated to the international standards IAEA-S-1, IAEA-S-2, and IAEA-S-3. The sulfur isotope composition in the sample was calculated as \(\delta^{34}S = ((34S/32S)_{sample} - (34S/32S)_{standard}) / (34S/32S)_{standard} \times 10^3\) and expressed in ‰ with respect to reference standard VCDT (Vienna Canyon Diablo Troilite). Average accuracy of \(\delta^{34}S\) analyses was better than 0.2 ‰ (2σ). Further details of analytical methods are presented elsewhere [77,78].

4. Results
4.1. Compositional Characteristics of Ru-Os Sulfides, Os-Rich Alloys, and High-Magnesian Olivine from Primary PGM Assemblage

Typical morphological features, characteristic textures of Ru-Os sulfides, formed by single relatively large grains and small inclusions in Os-Ir alloy grains (termed as type 1 and 2, respectively), and associated minerals are illustrated in Figures 3–5. Representative results of 48 electron microprobe WDS analyses of Ru-Os sulfides and associated Os-rich alloys (out of a total of 219 analyses) and 9 electron microprobe WDS analyses of high-Mg olivine inclusions are shown in Tables 1–3 and Figure 6.

Figure 3. Back-scattered images of laurite grains of type 1 at Verkh-Neivinsk: (a)—sample 153, (b)—sample 156, (c)—sample 159, (d)—sample 162, (e)—sample 166, (f)—detail of Figure 2c. LR—laurite, ERL—erlichmanite, (Os,Ir)—iridian osmium. Numbers 1–10 denote areas of electron microprobe analyses corresponding to the same numbers in Tables 1 and 2.
Figure 4. Back-scattered electron images of forsterite inclusions in: (a) osmian iridium (Os, Ir), (b–d) laurite (LR). Numbers 1–9 denote areas of electron microprobe analyses corresponding to the same numbers in Table 3.

Figure 5. X-ray maps of high-Mg olivine inclusion in laurite (sample 164). (a)—MgKα, (b)—FeKα, (c)—SiKα, (d)—RuLα, (e)—SKα.
Table 1. Electron microprobe analyses of Ru-Os sulfides of type 1 from the Verkh-Neivinsk massif.

| Analysis | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------|---|---|---|---|---|---|---|---|---|
| Sample # | 153 | 153 | 153 | 156 | 156 | 156 | 159 | 162 | 166 |
| Mineral | LR | LR | LR | LR | LR | LR | LR | ERL | ERL |
| Figure | Figure 3a | Figure 3a | Figure 3a | Figure 3b | Figure 3b | Figure 3b | Figure 3c | Figure 3d | Figure 3e |
| wt. % | | | | | | | | | |
| Fe | b.d.l. | b.d.l. | 0.17 | 0.38 | 0.40 | 0.32 | b.d.l. | b.d.l. | b.d.l. |
| Ni | b.d.l. | b.d.l. | 0.23 | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. |
| Ru | 37.24 | 36.52 | 37.10 | 39.20 | 38.08 | 38.89 | 31.69 | 12.74 | 21.48 |
| Rh | 0.27 | 0.39 | 0.27 | 0.26 | 0.25 | 0.29 | 0.04 | 0.11 | 0.01 |
| Os | 19.16 | 19.08 | 19.58 | 20.79 | 21.34 | 21.53 | 33.04 | 51.23 | 42.41 |
| Ir | 10.38 | 10.71 | 9.48 | 5.96 | 6.10 | 5.52 | 3.32 | 7.81 | 5.88 |
| S | 33.24 | 33.08 | 33.81 | 33.87 | 33.80 | 33.42 | 33.42 | 32.13 | 28.17 |
| As | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. |
| Total | 100.29 | 99.78 | 100.41 | 100.69 | 99.97 | 99.97 | 100.22 | 100.06 | 99.40 |

LR—laurite, ERL—erlichmanite, Ru# = 100 \times Ru at.%/(Ru + Os) at.%. b.d.l.—below the detection limit; the detection limits here and in Table 2 are as follows (wt.%): Os—0.15, Ir—0.75, Ru—0.24, Rh—0.01, Pt—0.09, Pd—0.27, Fe—0.15, Ni—0.18, Cu—0.15, S—0.13, As—0.01.

Table 2. Electron microprobe analyses of Ru-Os sulfides of type 2 and coexisting Os-Ir alloys from the Verkh-Neivinsk massif.

| Analysis | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|----------|----|----|----|----|----|----|----|
| Sample # | 159 | 9 | 9 | 24 | 24 | 26 | 26 |
| Mineral | (Os,Ir) laurite | (Os,Ir) laurite | (Os,Ir) laurite | (Os,Ir) laurite | (Os,Ir) laurite | (Os,Ir) laurite | (Os,Ir) laurite |
| Figure | Figure 3e | Figure 6a | Figure 6a | Figure 6b | Figure 6b | Figure 6c | Figure 6c |
| wt. % | | | | | | | |
| Fe | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.27 | 0.22 |
| Ru | 1.26 | 26.98 | 1.34 | 49.56 | 11.44 | 22.81 | 0.95 |
| Rh | b.d.l. | b.d.l. | b.d.l. | 0.25 | 0.15 | 0.18 | 0.03 |
| Os | 89.13 | 36.92 | 83.82 | 11.44 | 77.51 | 36.99 | 57.26 |
| Ir | 9.38 | 4.54 | 14.66 | 1.94 | 2.00 | 1.82 | 3.09 |
| S | 66.35 | 66.44 | 66.77 | 66.11 | 66.54 | 66.07 | 66.49 |
| Ru # | 78 | 78 | 78 | 78 | 78 | 77 | 77 |

(Los)—iridian osmium. Ru# = 100 \times Ru at.%/(Ru + Os) at.%. b.d.l.—below the detection limit; detection limits for concentrations in iridian osmium were as follows, wt.%: Os—0.15, Ir—0.85, Ru—0.27, Rh—0.11, Pt—0.99, Pd—0.30, Fe—0.16, Ni—0.18, Cu—0.15, S—0.06, As—0.03.
Table 3. Electron microprobe analyses of high-Mg olivine inclusions in osmian iridium and Ru-Os sulfides from primary PGM assemblage of the Verkh-Neivinsk massif.

| Analysis | Sample # | Figure | Host mineral (Ir,Os) LR LR LR LR LR LR LR LR | wt.% | Cations on the basis of 4 O atoms |
|----------|----------|--------|---------------------------------------------|------|----------------------------------|
|          |          |        | wt.% |                                   |      | Si | Mg | Fe | Ni | Mn | Fo |                  |
| 1        | 8        | Figure 4a | LR   | 40.33 | 7.72 | 0.14 | 0.01 | 0.00 | 93    |                  |
| 2        | 164      | Figure 4b | LR   | 40.68 | 7.73 | 0.16 | 0.01 | 0.00 | 92    |                  |
| 3        | 164      | Figure 4b | LR   | 40.55 | 7.73 | 0.34 | 0.14 | 0.00 | 92    |                  |
| 4        | 164      | Figure 4b | LR   | 40.39 | 7.78 | 0.35 | 0.11 | 0.00 | 92    |                  |
| 5        | 154      | Figure 4c | LR   | 39.72 | 6.10 | 0.13 | 0.01 | 0.00 | 92    |                  |
| 6        | 154      | Figure 4c | LR   | 40.96 | 6.41 | 0.14 | 0.01 | 0.00 | 92    |                  |
| 7        | 154      | Figure 4c | LR   | 40.74 | 6.33 | 0.14 | 0.01 | 0.00 | 92    |                  |
| 8        | 165      | Figure 4d | LR   | 40.73 | 6.19 | 0.14 | 0.01 | 0.00 | 92    |                  |
| 9        | 165      | Figure 4d | LR   | 41.21 | 5.95 | 0.17 | 0.01 | 0.00 | 92    |                  |

Two morphological groups of Ru-Os sulfides were distinguished. The first one (type 1) includes single grains ranging in size from 1.0 to 1.5 mm (Figure 3a–e). They show a complete compositional spectrum, from laurite RuS₂ to erlichmanite OsS₂ (Figure 7a, Ru # varies from 12 to 89). In addition to Ru, Os, and S, these minerals have significant contents of Ir (3.32–10.71 wt.%) and negligible abundances of Fe, Ni, and Rh, which vary within 0.17–0.40, b.d.l.–0.23, and b.d.l.–0.39 wt.%, respectively (Table 1). Ru-Os sulfides contain inclusions of iridian osmium (Os, Ir) that can be as large as 30 µm across (Figure 3c,f and Table 2, analysis 10), and high-magnesian olivine (Fo₉₂–₉₄) with grain sizes from 5 to 40 µm (Figures 4 and 5, Table 3, analyses 2–9). Ru-Os sulfides of the second morphological group (type 2) represent mineral inclusions (with typical sizes of 30–80 microns) enclosed in Os-Ir-(Ru) alloys (Figure 6, Table 2, analyses 12, 14, 16). These inclusions have higher ruthenium content (Figure 7b, Ru # varies from 54 to 100) and correspond to laurite (Table 2, analyses 11, 13, 15). Rare inclusions of high-magnesian olivine (Fo₉₃) were also revealed in Os-Ir alloy (Figure 4a, Table 3, analysis 1).
Os-Ir-Ru alloys from the primary PGM assemblage of Verkh-Neivinsk are dominated by native osmium, ruthenium, and iridium (Figure 7c). The variation of osmium and ruthenium concentrations are due to the substitution by iridium in the solid solution of osmium (the trend of compositions along the horizontal axis Os-Ir in Figure 7c) or ruthenium (vertical trend of compositions towards Ru, Figure 7c).

4.2. Sulfur Isotope Data

The $\delta^{34}$S values in Ru-Os sulfides of both morphological types show a relatively narrow range from 0.3 to 3.3‰ (Table 4, Figures 8 and 9), with a mean of 2.05‰ and a standard deviation of 0.86‰ (n = 18). The $\delta^{34}$S values in Ru–Os sulfides of type 1 have slightly narrower range from 0.3 to 2.8‰ (Table 4, Figure 10), with a mean of 1.82 ± 0.83‰ (n = 14). We note that the mean $\delta^{34}$S value for laurite (i.e., 1.64 ± 0.91‰, n = 9) corresponds, within the analytical error, to that of erlichmanite (2.16 ± 0.55‰, n = 5; Table 4, Figure 10). Laurite inclusions of type 2 are characterized by $\delta^{34}$S composition ranging from 1.5 to 3.3‰ (Table 4, Figure 10) and a slightly higher $\delta^{34}$S mean of 2.66 ± 0.73‰ (n = 4).

Table 4. Sulfur and osmium isotope data of Ru-Os sulfides and associated Os-rich alloys at Verkh-Neivinsk.

| Sample Number, Figure | Mineral, Ru# | $^{187}$Os/$^{188}$Os * | $1\sigma$ * | $^{187}$Re/$^{188}$Os * | $R^{13}$ECR (Ga) | $1\sigma$ (Ga) | $\delta^{34}$S, ‰ |
|-----------------------|--------------|--------------------------|------------|--------------------------|-----------------|-------------|----------------|
| 153, Figure 8a        | LR, 78       | 0.12135                  | 0.00003    | 0.00002                  | 0.955           | 0.004       | 2.5            |
| 154, Figure 8b        | LR, 77       | 0.12381                  | 0.00003    | 0.00009                  | 0.609           | 0.004       | 2.0            |
| 156, Figure 3b        | LR, 77       | 0.12386                  | 0.00002    | 0.00003                  | 0.602           | 0.003       | 2.2            |
| 157, Figure 8d        | LR, 75       | 0.12201                  | 0.00002    | 0.00005                  | 0.863           | 0.002       | 2.2            |
| 159-1, Figures 5c and 8e | LR, 64   | 0.11728                  | 0.00002    | 0.00001                  | 1.523           | 0.003       | 2.6            |
| 159-2, Figures 5f and 8e | (Os,Ir) | 0.11720                  | 0.00009    | 0.00023                  | 1.535           | 0.012       | -              |
Table 4. Cont.

| Sample Number, Figure | Mineral, Ru# | $^{187}\text{Os}/^{188}\text{Os}$ | 1σ | $^{187}\text{Re}/^{188}\text{Os}$ | 1σ | $T_{\text{RD}}$ ECR* (Ga) | 1σ (Ga) | $\delta^{34}\text{S}$, ‰ |
|-----------------------|-------------|-----------------------------------|-----|-------------------------------|-----|-----------------------------|---------|-------------------|
| 163, Figure 8h        | LR, 75      | 0.12503                           | 0.00001 | 0.00003                     | 0.436 | 0.002                     | 1.9     |
| 164-1, Figure 8j      | LR, 89      | 0.11946                           | 0.00003 | 0.00004                     | 1.219 | 0.004                     | 0.5     |
| 164-2, Figure 8j      | LR, 89      | 0.11943                           | 0.00004 | 0.00002                     | 1.223 | 0.005                     | 0.6     |
| 165, Figure 8l        | LR, 64      | 0.11899                           | 0.00002 | 0.00006                     | 1.298 | 0.002                     | 0.3     |
| 155, Figure 8c        | ERL, 32     | 0.12213                           | 0.00002 | 0.00002                     | 0.845 | 0.003                     | 1.9     |
| 160, Figure 8f        | ERL, 44     | 0.12788                           | 0.00003 | 0.00006                     | 0.029 | 0.005                     | 1.7     |
| 161, Figure 8i        | ERL, 12     | 0.13459                           | 0.00002 | 0.00002                     | -     | -                         | 2.8     |
| 162, Figures 3d and 8g| ERL, 32     | 0.12261                           | 0.00002 | 0.00003                     | 0.778 | 0.002                     | 1.7     |
| 166, Figures 3e and 8k| ERL, 49     | 0.12061                           | 0.00001 | 0.00002                     | 1.059 | 0.002                     | 2.7     |

Ru-Os sulfides of type 2 and associated Os-rich alloys

| Sample Number, Figure | Mineral, Ru# | $^{187}\text{Os}/^{188}\text{Os}$ | 1σ | $^{187}\text{Re}/^{188}\text{Os}$ | 1σ | $T_{\text{RD}}$ ECR* (Ga) | 1σ (Ga) | $\delta^{34}\text{S}$, ‰ |
|-----------------------|-------------|-----------------------------------|-----|-------------------------------|-----|-----------------------------|---------|-------------------|
| 9, Figure 9a          | LR, 56      | 0.12302                           | 0.00003 | 0.00002                     | 0.720 | 0.004                     | n/d     |
| 9, Figure 9a          | (Os,Ir)     | 0.12306                           | 0.00002 | 0.00009                     | 0.714 | 0.003                     | -       |
| 24, Figure 9b         | LR, 89      | 0.11774                           | 0.00004 | 0.00001                     | 1.459 | 0.006                     | 3.1     |
| 24, Figure 9b         | (Os,Ru,Ir)  | 0.12786                           | 0.00002 | 0.00003                     | 1.443 | 0.003                     | -       |
| 26, Figure 9c         | LR, 54      | 0.12506                           | 0.00002 | 0.00002                     | 0.432 | 0.003                     | 3.3     |
| 26, Figure 9c         | (Os,Ir)     | 0.12512                           | 0.00001 | 0.00036                     | 0.423 | 0.002                     | -       |
| 71                    | LR, 89      | 0.12491                           | 0.00003 | 0.00008                     | 0.453 | 0.005                     | 2.4     |
| 71                    | (Os,Ir,Ru)  | 0.12505                           | 0.00002 | 0.00033                     | 0.434 | 0.002                     | -       |
| 126                   | LR, 100     | 0.12410                           | 0.00013 | 0.00019                     | 0.568 | 0.018                     | 1.5     |
| 194                   | LR, 100     | 0.11898                           | 0.00009 | 0.00031                     | 1.286 | 0.014                     | n/d     |
| 194                   | (Ru,Os,Ir)  | 0.11891                           | 0.00003 | 0.00140                     | 1.296 | 0.004                     | -       |

Ru# = 100 × Ru at.%/(Ru + Os) at.%  *—data after Reference [50], except sample numbers 160 and 126. T$_{RD}$ ECR values estimated by Walker et al. [74] and a decay constant of $\lambda = 1.666 \times 10^{-11}$ year$^{-1}$ [73]. Uncertainties on model ages are based on within-run errors only. LR—laurite; ERL—erlichmanite; (Os,Ir), (Os, Ru, Ir), (Os,Ir,Ru)—osmium; (Ru,Os,Ir)—ruthenium; n/d—not determined.

4.3. Osmium Isotope Data

The Os-isotope data for Ru-Os sulfides and associated Os-rich alloys are provided in Table 4 and Figures 8 and 9. Solitary grains of laurite and erlichmanite of type 1 show a very wide range of $^{187}\text{Os}/^{188}\text{Os}$ values (between 0.11728 and 0.13459, and $^{187}\text{Os}/^{188}\text{Os} < 0.00009$). $^{187}\text{Os}/^{188}\text{Os}$ values in laurite and erlichmanite vary from 0.11728 to 0.12503 and from 0.12061 to 0.13459, respectively (Table 4). Thus, in addition to sub-chondritic values ($^{187}\text{Os}/^{188}\text{Os} < 0.1281$), a supra-chondrite isotope composition of osmium was detected in erlichmanite ($^{187}\text{Os}/^{188}\text{Os} = 0.13459 \pm 0.00002$). If the outliers with the most radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values in erlichmanite grains are excluded (i.e., 0.12788 and 0.13459, respectively), the Os-isotope results identify a more restricted $^{187}\text{Os}/^{188}\text{Os}$ range for erlichmanite (0.12061–0.12261) of the first morphological type. Laurite inclusions typical of the second morphological type are characterized by a similar degree of Os-isotope variations ($^{187}\text{Os}/^{188}\text{Os}$ from 0.11774 to 0.12506, Table 4, Figure 9) with that of type 1 laurites. We also note a similarity of the Os-isotopic compositions for coexisting laurite and Os-Ir-(Ru) alloys (Table 4, Figure 9a,b).
Figure 8. Back-scattered electron images of Ru-Os sulfides type 1 at Verkh-Neivinsk: (a)—sample 153, (b)—sample 154, (c)—sample 155, (d)—sample 157, (e)—sample 159, (f)—sample 160, (g)—sample 162, (h)—sample 163, (i)—sample 161, (j)—sample 164, (k)—sample 166, (l)—sample 165. Yellow circles with a diameter of 15–40 µm denote areas of Os-isotope analyses listed in Table 4. Yellow numerals in the numerator and denominator correspond to the $\delta^{34}$S (‰) value. LR—laurite, ERL—erlichmanite, (Os, Ir)—iridian osmium, OL—high-Mg olivine.

Figure 9. Back-scattered electron images of Ru-Os sulfides type 2 and associated Os-rich alloys at Verkh-Neivinsk: (a)—sample 9, (b)—sample 24, (c)—sample 26. “Craters” with a diameter of 15–40 µm denote areas of Os-isotope analyses listed in Table 4. The numerals in the numerator and denominator correspond to the $^{187}$Os/$^{188}$Os value and the measurement error, respectively. Black circles with a diameter ca. 100 µm denote spots of S-isotope analyses listed in Table 4. LR—laurite, (Os, Ir)—iridian osmium, (Os, Ru, Ir)—osmium.
Due to very low $^{187}\text{Re}/^{188}\text{Os}$ values, the Re-Os model and Re-depletion ages (i.e., $T_{\text{MA}}$ and $T_{\text{RD}}$ [71,72]) of Ru-Os sulfides are identical. $T_{\text{RD}}$ ages for laurite of the first and second type, calculated relative to an Enstatite Chondrite Reservoir (ECR) model [74], display comparable variations (436–1523 and 432–1459 Ma respectively, Table 4), whereas erlichmanites are characterized by more moderate variations ($T_{\text{RD}}$ ages from 1059 to 778 Ma).

5. Discussion

The provenance of the investigated Ru-Os sulfide and Ru-Os-Ir alloy grains is obvious: the placer deposits display a close spatial association with the Verkh-Neivinsk dunite-harzburgite massif (Figure 2). The primary nature of Ru-Os sulfides of the first morphological type is supported by occurrence of euhedral inclusions of high-Mg olivine (Fo$_{89-94}$) that fall within the compositional range of mantle (primitive) olivine (Fo$_{88-93}$) and also perfectly match the composition of olivine (with a pronounced peak between Fo$_{93}$ and Fo$_{94}$) in peridotite xenoliths from the mantle beneath Archean cratons [80–82]. The primary PGM from chromitites that form relatively small discordant bodies in residual dunites and harzburgites at Verkh-Neivinsk (unpublished data) share mineralogical and compositional characteristics with those of the detrital PGM. These chromitites are characterized by negatively sloped, chondrite-normalized platinum-group element (PGE) patterns [83], which is consistent with the preponderance of a rather limited variety of PGM of the IPGE group (i.e., dominated by laurite and Ru-Os-Ir alloy). Based on these lines of evidence, we suggest that the studied Ru-Os sulfides were derived from mantle residual rocks of the Verkh-Neivinsk massif, although the derivation of these PGM from the Moho-transition zone dunite-clinopyroxenite complex cannot be ruled out. Both options may be verified by distinct Ni concentrations in highly-magnesian olivine inclusions within the studied PGM. High Ni contents (0.33–0.42 wt.%) in all but one forsterite inclusions are consistent with a mantle origin of olivine, whereas moderate Ni abundances (0.14–0.17 wt.%) in forsterite within Os-rich laurite may indicate its derivation from different source rocks that form dunite-clinopyroxenite complex.

The composition of the laurite-erlichmanite series, plotted on the Os-Ir-Ru diagram (Figure 7a), shows common Os substitution for Ru (Ru# between 12 and 89), typical of mantle chromitites from Kempirsai and Rai-Iz (Urals), Kraubath, Eastern Alps, and Unst, Shetland Isles [5,9,11,84]. A high-temperature origin of euhedral inclusions of laurite type 2 in Os-Ir-(Ru) alloys are supported by recent experimental data [18–21] that quantitatively
evaluated the effects of T and f(S2) for laurite + alloy mineral pairs. This is consistent with the presence of a ruthenium trend in Ru-Os-Ir alloys at Verkh-Neivinsk (Figure 7c), which is indicative of high temperature and pressure values that can only be reached under mantle conditions [85]. These integrated data present irrefutable evidence that Os-Ir-Ru alloys have formed at high T-P environments and that the observed chemical compositional variations represent primary features of the grains [26,40,42,70,85–88]. Thus, these refractory alloys are considered to be representative of depleted mantle material within the mantle sections of ophiolites.

The early formation of laurite and Os-Ir alloys at high T-P conditions implies that the original S- and Os-isotope composition of these PGM reflects the source region in the mantle at the time of their formation. The sulfur-isotope results of this study display a narrow range of δ34S values for single (individual) type 1 laurite grains ranging from 0.3 to 2.8, with a mean of 1.64‰ and a standard deviation of 0.91‰ (n = 9), which is within the analytical uncertainty with that of solitary erlichmanite grains (δ34S mean of 2.66 ± 0.73‰, n = 4, Figure 10). According to Thode et al. [89], the sulfur isotope composition of the Earth’s mantle is considered to be homogeneous with a mean δ34S of 0.0‰, a value indistinguishable from that of chondrites (δ34S = 0.04 ± 0.31‰, n = 24 [90,91]). Delta δ34S values beyond ±2‰ are considered to be a result of the mantle–crust interaction processes (denoting a contribution of crustal-derived sulfur) both at mantle conditions [92] and during formation of mantle magmas under crustal conditions [93]. The sulfur isotope composition of Ru-Os sulfides from the oceanic mantle was initially studied by Hattori et al. [24], who showed that Ru-Os sulfides from placer deposits in Borneo have a mean δ34S value of 1.16 ± 0.36‰, which is consistent with a mantle source of sulfur. In a subsequent investigation of solitary grains of Ru-Os sulfides at Verkh-Neivinsk (δ34S = 1.29 ± 0.65‰) [51], they appeared to be similar to that of Ru-Os sulfides from placers in Borneo [24]. Our S-isotope study of two morphological types (i.e., individual Ru-Os sulfide grains and laurite inclusions in Os-Ir-(Ru) alloys representing the primary PGM assemblage at Verkh-Neivinsk) is indicative of a sub-chondritic source of sulfur. This conclusion is consistent with the osmium isotope data obtained for Os-bearing PGM from the Verkh-Neivinsk massif (Middle Urals). The considerable range of the sub-chondritic 187Os/188Os values in Ru-Os sulfides (0.11728–0.12788, n = 19, Figure 11) and Ru-Os-Ir alloys (0.11619–0.12270, n = 34, Figure 11) are clearly indicative of derivation from a sub-chondritic source. This wide 187Os/188Os range, with rare exceptions [35,63], is similar to that of the PGM from podiform chromitites within the mantle sections of dunite-harzburgite massifs and associated placer deposits (Figure 11, see also Figure 11 in Reference [36]). On the other hand, the osmium isotope data display a restricted range of sub-chondritic 187Os/188Os values for intimately intergrown laurite type 2 and Os-rich alloy pairs that form the primary PGM assemblage (Figure 9a,b). In such pairs, the Os-isotope signature of the adjacent phases is indistinguishable. This is consistent with similar findings for PGM from Witwatersrand, South Africa [42], Shetland, Scotland [35], and Hochgrossoen, Eastern Alps, Austria [49].

A single value of 187Os/188Os = 0.13459 ± 0.00002 identified in the erlichmanite indicates derivation from the source that evolved with long-term supra-chondritic Re/Os. This feature can be interpreted as evidence of a radiogenic crustal component, which was introduced during a subduction-related event or alternatively as an indication of an enriched mantle source. Consequently, supra-chondritic 187Os/188Os values (>0.12810), which have also been identified in detrital Os-Ir-(Ru) alloy grains [30,58,94,95], may indicate derivation from a distinct source, which is different from that of residual dunite-harzburgite sequences of an ophiolite complex. Distinct sources of HSE have recently been confirmed for Os-rich alloys derived from different lithologies (i.e., chromitite and clinopyroxenite) of the Kondyor massif [66] that was advocated to have trans-lithospheric mantle origin [96,97].
The time of formation of the oceanic crust in the Uralian ophiolites is usually ascribed to Early Devonian to Middle Ordovician (about 390 to 470 Ma) by Sm-Nd mineral and whole-rock isochrons on ultramafic rocks and gabbros from the Kempirsai massif [98,99] and by U-Pb dating of zircon from rock lithologies of the Vostochny Tagil (Middle Urals) and Nurali (South Urals) ultramafic complexes [100,101]. With the exception of two outliers (samples 160 and 161), the obtained T_{RD} ages of Ru-Os sulfides at Verkh-Neivinsk imply that the mantle domain under Middle Urals experienced melt extraction between 1525 and 435 Ma (Table 4, Figure 12). The Os isotopic compositions of these PGM indicate that they record much older melting events than it would be expected from a single-melting model of un-depleted mantle around 440 Ma. One of the explanations of this phenomenon is that after their formation, Ru-Os sulfides remained isolated from the convecting upper mantle. In this case, ultramafic rocks of the Verkh-Neivinsk massif do not represent a simple residue after partial melting at a mid-ocean ridge setting or evolved back-arc system in the Early Paleozoic. Instead, they may represent a mixture of (1) refractory isolated lithospheric blocks that retain much older ages and (2) ultramafic rocks formed during a partial melting episode in the Early Paleozoic. A similar scenario has been advocated by Parkinson et al. [102] and Snow and Schmidt [103] for the Izu-Bonina-Mariana and Zabargad peridotites, respectively. Osmium isotope systematics suggest that melt depletion events recorded by un-radiogenic $^{187}\text{Os}/^{188}\text{Os}$ at Verkh-Neivinsk (Figure 11) and some other peridotite occurrences worldwide, e.g., References [59,62,102,103], etc., are significantly older than the time of their emplacement into crustal levels. This observation is similar to the phenomenon recorded by Re-Os isotopes in sulfide inclusions in diamonds [104]. Variations in the T_{RD} ages of PGM at Verkh-Neivinsk point to prolonged melt-extraction processes and likely multi-stage evolution of HSE within the upper mantle. This is consistent with statistically significant data for Ru-Os-Ir alloys from the dunite-harzburgite massifs of the Urals [39] that show several stages of PGM formation with an average cycle of 150–200 Ma. This variability is likely to be due to discrete mantle melting events, which are probably controlled by deep mantle geodynamic processes [105]. The observed coincidence between the T_{RD} ages of PGM and U-Pb ages of zircon recovered from the ultramafic massifs of the Urals [39,59,98,106-109] provides a feasible evidence of close relationships between magmatic and ore-forming processes.

**Figure 11.** Os-isotopic composition of Ru-Os sulfides and Ru-Os-Ir alloys of dunite-harzburgite massifs. Os-isotopic data for Ru-Os sulfides of the Kraubath and Hochgrossen massifs (Eastern Alps) and Ru-Os-Ir alloys from the Timan, Polar, and Middle Urals according to References [39,49,56]. Present-day enstatite chondrite reservoir after Reference [74].
geochemical and isotopic analysis, provided a new set of mineralogical and S-Os isotope-geochemical constraints on the origin of detrital Ru-Os sulfides from primary PGM assemblage of the Verkh-Neivinsk ophiolite-type massif.

2. Ru-Os sulfides are recognized within two morphological types, including (i) solitary Ru-Os sulfide grains that have sizes from 0.5 to 1.5 mm and a wide compositional range for the laurite (RuS2)–erlichmanite (OsS2) solid solution series, and (ii) tiny euhedral inclusions of laurite hosted by Os-Ir(Ru) alloys. The primary nature of Ru-Os sulfides is supported by the occurrence of euhedral inclusions of high-Mg olivine (Fo82–94) that fall within the compositional range of mantle (primitive) olivine (Fo88–93).

3. The δ34S values in solitary Ru-Os sulfide grains of type 1 have a narrow range from 0.3 to 2.8‰, with a mean of 1.82 ± 0.83‰ (n = 14), corresponding, within an error, to that for laurite inclusions of type 2 characterized by δ34S variations ranging from 1.5 to 3.3‰ and a slightly higher δ34S mean of 2.66 ± 0.73‰ (n = 5). The similar sub-chondritic δ34S values reported for the detrital Ru-Os sulfides of the oceanic mantle origin [24,51] is consistent with derivation of sulfur from a sub-chondritic source.

4. The osmium isotope results identified two distinct sources of HSE for Ru-Os sulfides. A considerable range of the sub-chondritic 187Os/188Os values in Ru-Os sulfides (0.1173–0.1278, n = 18 [50], this study) and Ru-Os-Ir alloys (0.1162–0.1227, n = 34 [49], this study) clearly indicate a common near-chondritic source for the HSE.

5. The osmium isotope data display a restricted range of sub-chondritic 187Os/188Os values for intimately intergrown laurite type 2 and Os-rich alloy pairs that form the primary PGM assemblage. This is consistent with similar findings for PGM from Witwatersrand, South Africa [42], Shetland, Scotland [35], and Hochgrossen, Austria [49].

6. A single value of 187Os/188Os = 0.13459 ± 0.00002 identified in the erlichmanite indicated derivation from the source that evolved with a long-term supra-chondritic Re/Os. This feature may be interpreted as evidence of a radiogenic crustal component, which was introduced during a subduction-related event or an indication of an enriched mantle source. Consequently, supra-chondritic 187Os/188Os values (>0.12810) may indicate derivation from a distinct source other than residual dunite–harzburgite sequences of an ophiolite complex.

7. With the exception of two outliers (samples 160 and 161), the obtained TRD ages of Ru-Os sulfides at Verkh-Neivinsk imply that the mantle domain under Middle Urals

![Figure 12. Histogram of mantle-depletion (TRD) ages of Ru-Os sulfides at Verkh-Neivinsk.](image-url)
experienced melt extraction between 1525 and 435 Ma, and they record much older melting events than would be expected from a single-melting model of un-depleted mantle around 440 Ma. We suggest that variations in the $T_{RD}$ ages of the Verkh-Neivinsk PGM point to prolonged melt-extraction processes and likely multi-stage evolution of HSE within the upper mantle.

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