

## Compounds of Ru–Se–S, alloys of Os–Ir, framboidal Ru nanophases, and laurite–clinochlore intergrowths in the Pados-Tundra complex, Kola Peninsula, Russia

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**Abstract:** This is the first report of occurrences of platinum-group minerals (PGM) and unnamed phases of platinum-group elements (PGE) from the Pados-Tundra ultramafic complex of Paleoproterozoic age, Kola Peninsula. The PGM occur as individual inclusions or intergrowths ( $\leq 1\text{--}10\ \mu\text{m}$ ) hosted by cores of zoned grains of chromite–magnesiochromite (Chr) in chromitite of the Dunite block in the eastern portion of the complex. Osmium-poor laurite is abundant, commonly as intimate intergrowths with clinochlore ( $>80\%$  laurite grains), followed by Os- and Ir-dominant alloys (*i.e.*, the minerals osmium and iridium, respectively); unnamed phases of ruthenium selenide [RuSe<sub>2</sub>] and rhodium telluride [RhTe] are rare. Selenium-rich laurite, not reported previously, likely belongs to an inferred RuS<sub>2</sub>–RuSe<sub>2</sub> series. Native Ru forms micro-(nano)-spherules in framboid-type aggregates, in association with relict laurite, which are surrounded by a skeletal grain of clinochlore; the host is Chr. The framboidal texture of nanophases of ruthenium, hitherto unreported in PGE alloys, likely formed as a result of deposition from a H<sub>2</sub>-bearing fluid, involving a reaction of desulfurisation and reduction of laurite. A highly S-deficient environment is indicated; a low sulfur fugacity, presumably below the Os–OsS<sub>2</sub> buffer, caused the observed coexistence of a low-Os variety of laurite with Os-dominant alloy. An ultimate loss of total S is implied to have decreased the S/Se ratio, which resulted in the precipitation of Ru-dominant sulfoselenide–selenide phases, likely from an oxidizing fluid at a late stage of mineralization. We also infer that the laurite–clinochlore intergrowths crystallized relatively late, from microvolumes of an H<sub>2</sub>O-bearing fluid of contrasting composition, enriched in Ru, S, and lithophile elements.

**Key-words:** platinum-group elements; platinum-group minerals; ruthenium; alloy minerals; RuS<sub>2</sub>–RuSe<sub>2</sub> compounds; framboidal textures; chromitite; chromite–magnesiochromite; Pados-Tundra; Kola Peninsula; Russia.

### 1. Introduction

It is well known that platinum-group elements (PGE) of the Ir subgroup (Ru, Os, Ir: IPGE) are associated with chromian spinel in ophiolite, Alaskan-Uralian-type and stratiform (layered) complexes (*e.g.*, Cabri, 1981, 2002; Johan, 2006). The Cr-IPGE mineralization typically contains members of the laurite (RuS<sub>2</sub>)–erlichmanite (OsS<sub>2</sub>) series, which are common species of platinum-group minerals (PGM) in ultramafic complexes of different geotectonic settings. In this article, we document the first occurrence of PGM and PGE phases recognized in association with zones of chromite–magnesiochromite (Chr) in the Pados-Tundra complex, Kola Peninsula, northwestern Russia (Fig. 1a). Some of these phases are hitherto unreported; they are rich in Se and likely belong to

an inferred RuS<sub>2</sub>–RuSe<sub>2</sub> series. In addition, unusual microtextures and associations involving clinochlore, laurite and native Ru are reported, providing useful petrogenetic information.

The Pados-Tundra ultramafic complex ( $\sim 6 \times 1.5\text{--}2.1\ \text{km}$ ) is associated with a Paleoproterozoic upthrust in the Lapland granulite rocks of the Kola-Mezenskiy block, close to the contact with the Archean Belomorskiy block of granite and gneiss. It is a principal member of the Serpentinite belt, which includes the Notozerskiy (Notozero) suite (Murashov, 1958; Vinogradov, 1971; Zak, 1980). The complex has a Paleoproterozoic age:  $\sim 2.15\ \text{Ga}$  (Shapkin *et al.*, 2008; Shapkin & Bayanova, 2009). It consists of minor metagabbroic rocks (marginal series) and a series of dunite–harzburgite–orthopyroxenite rocks. The associated massif (Malyy Pados; Fig. 1c) is a satellite

intrusion (Mamontov & Dokuchaeva, 2005) or, more likely, a dislocated block detached from the Pados-Tundra complex (Barkov *et al.*, 2016).

Three stratiform layers of chromitite are accompanied by segregations and pipe-like bodies rich in Cr–Fe oxides, all hosted by the Dunite block (Fig. 1b). The presently reported occurrences of PGM and PGE-rich phases are related with chromitite developed in dunitic rock of this block. Mamontov & Dokuchaeva (2005) recognized four chromitite layers of subeconomic grade, with the  $Cr_1$  layer located in the “endocontact zone” of the northeastern flank, and  $Cr_2$ ,  $Cr_3$  and  $Cr_4$  developed in the Dunite block (Fig. 1b). The  $Cr_1$  ore zone, however, is more likely a contact-type deposit; consequently, the Main Chromitite Layer, MCL ( $Cr_2$  after Mamontov & Dokuchaeva, 2005) is defined as the main layer among the three Chr horizons (Fig. 1b).

## 2. Occurrences, specimens and analytical methods

Specimens of the Chr mineralization were collected from the MCL, which is not well exposed; nevertheless, specimens of chromitite, as we have observed, occur as disintegrated and fragmented pieces (<0.1 to 0.4–0.5 m across). In agreement with these observations, Mamontov & Dokuchaeva (2005) noted that the  $Cr_2$  layer (*i.e.*, the MCL; this study) has been intersected by two boreholes, as well as by stripping the covering sediments; it likely extends ~1.4 km, and is accompanied by numerous boulders (up to 0.6 m across) of chromitite along all of its extent. Presumably, this mode of occurrence is caused by epochs of intense orogeny known in the region. Cataclastic textures are observed in some of these specimens. We also sampled *in situ* segregations of Chr (up to 0.3–0.4 m in size) hosted by dunitic rock in the Dunite block, as well as zones of accessory mineralization, in which disseminated Chr locally exceeds 5–10 vol% in the dunite.

Ten samples of chromitite, represented by a total of fifty polished sections, were examined with a combination of reflected-light microscopy and manual scanning electron microscopy (SEM). All minerals were analysed in polished sections *in situ* at the Sobolev Institute of Geology and Mineralogy, SB RAS, Novosibirsk. Analyses of Chr (Table 1) were acquired at 20 kV and 50 nA, in wavelength-dispersive spectrometry mode (WDS), using a JEOL JXA-8230 microprobe (1–2- $\mu$ m beam). As V was sought, the Cr– $K\beta_1$  X-ray line was used for Cr. The  $K\alpha_1$  line was used for other elements. Magnesian chromite (for Cr, Fe, Mg, and Al), rutile (Ti), manganiferous garnet (Mn),  $NiFe_2O_4$  (Ni),  $ZnFe_2O_4$  (Zn), and  $V_2O_5$  (V) were used as standards. The results were processed with the corrections of a ZAF-type JEOL program. The minimum detection limits are: 0.01 wt% for Mg, Zn, Ni, Al, and 0.02 wt% for Ti, V and Mn.

Owing to very small grain sizes, the bulk of PGE-rich phases and associated clinocllore (Tables 2 and 3) were analysed at 20 kV and 1.6 nA by SEM (MIRA 3 LMU,

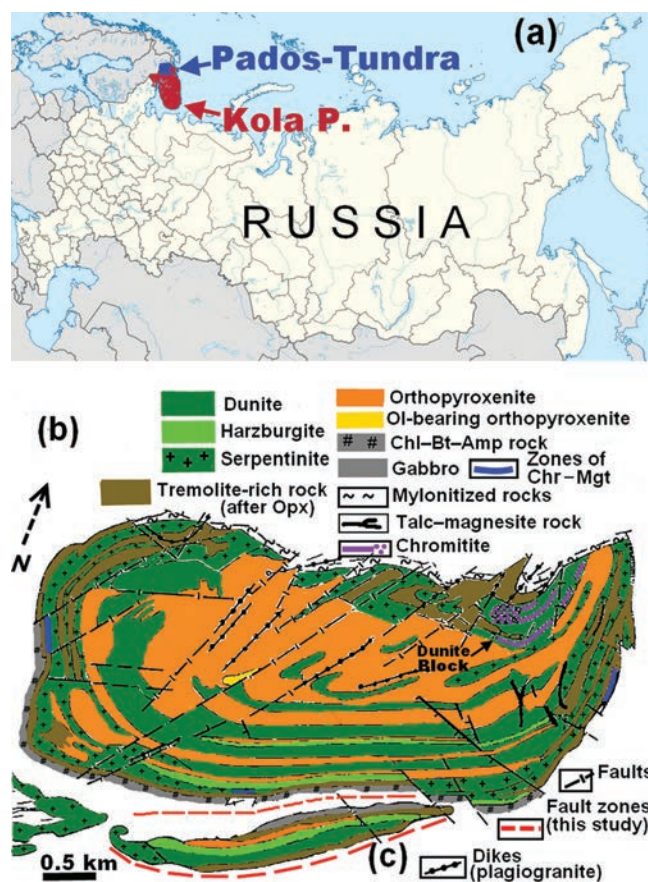


Fig. 1. (a–c) The location (in the Kola Peninsula; (a)) and geological map of the Pados-Tundra complex (b), and of the associated Maliy-Pados massif (c), slightly modified from Mamontov & Dokuchaeva (2005). Stratiform layers, segregations and pipe-like orebodies of chromitite are shown schematically and out of the scale in purple colour; these mineralized zones are hosted by the Dunite block. In addition, zones of mineralization rich in Chr are present at the outer contact; these are shown in blue (out of the scale).

Tescan Ltd.) in energy-dispersive spectrometry (EDS) mode (INCA Energy 450+ XMax 80, Oxford Instruments Ltd). The  $L$  lines and pure elements were used as standards for Ru, Os, Ir, Rh, and Se, along with  $FeS_2$  (for S),  $PtAs_2$  (As) and  $HgTe$  (Te). The  $K$  lines and diopside (for Mg and Ca), pure  $SiO_2$ ,  $Al_2O_3$ ,  $Cr_2O_3$ , and Fe were used to analyse clinocllore. The  $L$  lines, synthetic phosphates of the type  $REE(PO_4)$  and  $Ca_2P_2O_7$  were used to analyse monazite-(Ce). The XPP matrix correction scheme was applied in all cases.

The WDS analyses of sulfoselenide–selenide phases of Ru (Table 3) were carried out at 20 kV and 50 nA, using a JEOL JXA-8230 microprobe (~1- $\mu$ m beam). The following X-ray lines (and standards) were used: Ru– $L\alpha$ , Rh– $L\alpha$ , Os– $M\alpha$ , Ir– $M\alpha$  (pure metals), Se– $L\alpha$  ( $Bi_2Se_3$ ), Te– $L\alpha$  ( $PbTe$ ), As– $L\beta$  ( $InAs$ ), and S– $K\alpha$  ( $CuFeS_2$ ). These results were also processed with the corrections of a ZAF JEOL program. Detection limits are 0.05 wt% for all analysed elements. Accuracy and reproducibility of the analytical procedures were evaluated with special tests (Korolyuk *et al.*, 2009; Lavrent'yev *et al.*, 2015a and b).

Table 1. Mean results (and ranges) of electron-microprobe analyses (WDS) of zoned chromite–magnesiochromite from chromitite of the Pados-Tundra complex, Kola Peninsula.

|                                   | TiO <sub>2</sub>        | Al <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | V <sub>2</sub> O <sub>3</sub> | FeO(t)                     | FeO (calc.)         | Fe <sub>2</sub> O <sub>3</sub> (calc.) | MnO                     | MgO                       | NiO                     | ZnO                     | Total  |      |      |       |
|-----------------------------------|-------------------------|--------------------------------|--------------------------------|-------------------------------|----------------------------|---------------------|----------------------------------------|-------------------------|---------------------------|-------------------------|-------------------------|--------|------|------|-------|
| 1<br>(Core)                       | 0.37<br>(0.12–<br>1.87) | 10.41<br>(8.22–<br>11.92)      | 52.07<br>(50.47–<br>53.26)     | 0.10<br>(0.05–<br>0.15)       | 24.68<br>(21.24–<br>28.12) | <i>wt%</i><br>16.49 | 9.10                                   | 0.99<br>(0.80–<br>1.11) | 10.37<br>(9.17–<br>11.71) | 0.05<br>(0.02–<br>0.09) | 0.82<br>(0.64–<br>1.04) | 100.77 |      |      |       |
| 2<br>(Rim)                        | 0.26<br>(0.18–<br>0.38) | 1.51<br>(0.26–<br>3.55)        | 45.30<br>(27.29–<br>49.78)     | 0.05<br>(0.02–<br>0.09)       | 43.41<br>(35.24–<br>63.62) | 20.36               | 25.62                                  | 1.32<br>(0.91–<br>1.51) | 6.79<br>(5.29–<br>8.36)   | 0.31<br>(0.21–<br>0.61) | 0.45<br>(0.23–<br>0.59) | 101.97 |      |      |       |
| <i>Atomic proportions (O = 4)</i> |                         |                                |                                |                               |                            |                     |                                        |                         |                           |                         |                         |        |      |      |       |
|                                   | Cr                      | Al                             | Fe <sup>3+</sup>               | Ti                            | V                          | Σ                   | Mg                                     | Fe <sup>2+</sup>        | Mn                        | Zn                      | Ni                      | Σ      | mg#  | cr#  | fe3+# |
| 1                                 | 1.35                    | 0.40                           | 0.22                           | 0.009                         | 0.003                      | 1.98                | 0.51                                   | 0.45                    | 0.03                      | 0.02                    | 0.001                   | 1.01   | 0.50 | 0.77 | 0.11  |
| 2                                 | 1.25                    | 0.06                           | 0.67                           | 0.007                         | 0.001                      | 1.99                | 0.35                                   | 0.59                    | 0.04                      | 0.01                    | 0.009                   | 1.00   | 0.35 | 0.95 | 0.34  |

Note. Results of WDS analyses acquired with a JEOL JXA-8230 microprobe are quoted in wt%. Number 1 is the mean composition that pertains to cores; no. 2 pertains to rims in zoned grains of chromite–magnesiochromite. These specimens of chromitite were collected as fragmented pieces (0.1–0.4 m in size) in the area of development of the Main Chromitite Layer, Dunite block (Fig. 1b). Results of a total of 28 point-analyses are presented, which pertain to 14 zoned grains from 7 individual samples (Pds-201, 202, 203, 205, 207, 208, and 209). FeO(t) is all Fe as FeO. FeO(calc.) and Fe<sub>2</sub>O<sub>3</sub> (calc.) are values calculated on the basis of stoichiometry per four oxygen atoms. The index *mg#* is Mg/(Mg + Fe<sup>2+</sup> + Mn + Zn); *cr#* is Cr/(Cr + Al); and *fe3+#* is Fe<sup>3+</sup>/(Cr + Al + Fe<sup>3+</sup>).

### 3. Results and discussion

#### 3.1. Chromitite and zoning in chromian spinel in the Dunite block

The investigated specimens of chromitite contain ~60–90 vol% Cr–Fe–Mg oxides. Compositions of Chr (cores) in ore fragments associated with the MCL are notably more magnesian than those from segregations hosted *in situ* in dunite of the Dunite block. Gangue minerals are mostly clinocllore and serpentine; relics of olivine (Fo<sub>93</sub>) were observed in a dunite rich in disseminated Chr. This rock in the Chr segregation consists of ~0.2-mm grains of millerite [Ni<sub>1.03</sub>Fe<sub>0.01</sub>S<sub>0.96</sub>] and Co-bearing pentlandite [(Ni<sub>5.80</sub>Fe<sub>2.64</sub>Co<sub>0.46</sub>)Σ<sub>8.90</sub>S<sub>8.10</sub>]. The Ni content of the latter is close to the limit known for Ni in this species. So far, the most magnesian olivine (cumulus) is Fo<sub>91</sub> at Pados-Tundra (Barkov *et al.*, unpubl. data). Thus, the associated Fo<sub>93</sub> and Ni-rich pentlandite are presumably a reflection of low-temperature equilibration and exchange with the chromian spinel, which likely increased their Mg/Fe and Ni/Fe values.

A narrow rim is commonly present in grains of Chr in all varieties of the Cr-rich specimens (Fig. 2a and b). In chromitite associated with the MCL, the core zones are Mg-dominant and correspond to magnesiochromite. In terms of their *mg#* and *cr#* indexes (Table 1), the Chr phases are similar to cores reported from Chr deposits in layered intrusions (2.4–2.5 Ga in age) of the Fennoscandian Shield: Burakovsky (Lavrov *et al.*, 1987), Monchepluton, Russia (Chashchin *et al.*, 1999), and Kemi, Finland (Alapieti & Huhtelin, 2005). In contrast, grains of Chr at Pados-Tundra (MCL) generally differ in higher levels of Zn and Mn. The observed zoning (Table 1) is not

unusual. Contents of Fe<sup>2+</sup> and, especially, Fe<sup>3+</sup> (and *fe3+#* index) increase in the rim, followed by a corresponding decrease in Mg and Al, thus indicating a significant drop in temperature and build-up in oxygen fugacity in the late environment.

#### 3.2. PGE-rich phases and the inferred RuS<sub>2</sub>–RuSe<sub>2</sub> series

Grains of laurite and Os–Ir alloys were found in all types of Chr mineralization: disseminated Chr, segregations and chromitite associated with the MCL in the Dunite block. However, PGM are notably more abundant in the latter chromitite; they occur as ~1–10 μm inclusions in cores enriched in the magnesiochromite component (Table 1). Laurite is the major species of PGM in the chromitite, followed by Os- and Ir-dominant alloys (*i.e.*, the minerals osmium and iridium, respectively). Native ruthenium, unnamed RuSe<sub>2</sub> and RhTe are rare (Table 2). Results of the WDS analyses of native Ru and Os-dominant alloy [Os<sub>55.5</sub>Ir<sub>33.3</sub>Ru<sub>10.6</sub>Rh<sub>0.6</sub>; JEOL 8200] are consistent with the SEM-EDS data (Table 2). A single Pt-rich phase was encountered, but could not be analysed because of its small grain-size (<1 μm).

A total of fifty-five point analyses (SEM-EDS) of laurite gave the following ranges expressed in wt% (and values of atoms per formula unit, apfu): Os n.d.–12.6 (0.12 apfu); Ir n.d.–10.7 (0.10), Rh n.d.–2.0 (0.03), As n.d.–0.6 (0.01), and Se n.d.–12.7 wt% (0.30 apfu). These compositions are stoichiometric: ΣPGE in the range 1.97–2.03, and (S + Se + As) in the range 0.97–1.03 apfu. Thus, the extent of solid solution toward erlichmanite is very subordinate in this series. Pure OsS<sub>2</sub> is known to crystallize at a higher level of sulfur fugacity (*f*S<sub>2</sub>) than RuS<sub>2</sub> (*e.g.*, Stockman & Hlava, 1984). The low-Os

Table 2. Compositions (SEM/EDS) of platinum-group minerals and PGE-rich phases from the Pados-Tundra complex, Kola Peninsula.

| Sample |        |                   | Ru    | Os    | Ir    | Rh    | As   | Te    | Se    | S     | Total |
|--------|--------|-------------------|-------|-------|-------|-------|------|-------|-------|-------|-------|
| 1      | 207-3  | Laurite           | 51.07 | 5.69  | 4.40  | 0     | 0    | 0     | 0     | 36.05 | 97.2  |
| 2      | 205-2  | Laurite           | 45.13 | 11.04 | 5.41  | 1.16  | 0    | 0     | 0     | 35.05 | 97.8  |
| 3      | 203-4  | Selenoan laurite  | 52.88 | 0     | 1.19  | 0     | 0.57 | 0     | 12.72 | 28.43 | 95.8  |
| 4      | 203-4  | Laurite           | 51.83 | 5.73  | 6.27  | 0     | 0    | 0     | 0     | 36.71 | 100.5 |
| 5      | 201-1  | Laurite           | 48.65 | 8.01  | 5.96  | 0     | 0    | 0     | 0     | 35.74 | 98.4  |
| 6      | 202-3  | Laurite           | 50.76 | 4.88  | 7.23  | 1.09  | 0    | 0     | 0     | 36.70 | 100.7 |
| 7      | 202-3  | Laurite           | 50.62 | 4.78  | 6.71  | 2.00  | 0    | 0     | 0     | 36.51 | 100.6 |
| 8      | 207-5  | Laurite           | 51.12 | 4.92  | 6.53  | 1.08  | 0    | 0     | 0     | 36.54 | 100.2 |
| 9      | 202-1  | Laurite           | 43.08 | 12.37 | 10.68 | 1.30  | 0    | 0     | 0     | 34.67 | 102.1 |
| 10     | 203-1  | Laurite           | 49.37 | 6.78  | 7.42  | 0     | 0    | 0     | 0     | 36.44 | 100.0 |
| 11     | 209-2  | RuSe <sub>2</sub> | 32.81 | 0     | 2.53  | 5.16  | 3.17 | 0     | 47.23 | 4.04  | 94.9  |
| 12     | 209a-2 | RuSe <sub>2</sub> | 37.36 | 0     | 0     | 3.24  | 0    | 0     | 52.22 | 2.07  | 94.9  |
| 13     | 209a-2 | RhTe              | 2.49  | 6.51  | 5.13  | 33.71 | 0    | 51.55 | 0.62  | 0     | 100.0 |
| 14     | 216    | Osmium            | 5.72  | 54.50 | 39.51 | 0     | 0    | 0     | 0     | 0     | 99.7  |
| 15     | 216    | Osmium            | 6.00  | 54.44 | 39.49 | 0.75  | 0    | 0     | 0     | 0     | 100.7 |
| 16     | 208-2  | Iridium           | 1.12  | 43.83 | 52.62 | 3.04  | 0    | 0     | 0     | 0     | 100.6 |
| 17     | 202-4  | Osmium            | 3.58  | 59.49 | 39.97 | 0     | 0    | 0     | 0     | 0     | 103.0 |
| 18     | 203-5  | Ruthenium         | 77.86 | 9.76  | 13.17 | 0     | 0    | 0     | 0     | 0     | 100.8 |
| 19     | 203-5  | Ruthenium         | 73.71 | 10.05 | 11.99 | 1.55  | 0    | 0     | 0     | 0     | 97.3  |
| 20     | 207-3  | Ruthenium         | 70.64 | 13.54 | 10.03 | 0     | 0    | 0     | 0     | 0     | 97.7  |

| Atomic proportions |      |      |      |      |       |      |      |      |      |      |
|--------------------|------|------|------|------|-------|------|------|------|------|------|
|                    | Ru   | Os   | Ir   | Rh   | ΣM    | As   | Te   | Se   | S    | Σ    |
| 1                  | 0.90 | 0.05 | 0.04 | 0    | 1.00  | 0    | 0    | 0    | 2.00 | 2.00 |
| 2                  | 0.82 | 0.11 | 0.05 | 0.02 | 1.00  | 0    | 0    | 0    | 2.00 | 2.00 |
| 3                  | 0.99 | 0    | 0.01 | 0    | 1.00  | 0.01 | 0    | 0.30 | 1.68 | 2.00 |
| 4                  | 0.89 | 0.05 | 0.06 | 0    | 1.00  | 0    | 0    | 0    | 2.00 | 2.00 |
| 5                  | 0.87 | 0.08 | 0.06 | 0    | 1.00  | 0    | 0    | 0    | 2.00 | 2.00 |
| 6                  | 0.88 | 0.04 | 0.07 | 0.02 | 1.00  | 0    | 0    | 0    | 2.00 | 2.00 |
| 7                  | 0.87 | 0.04 | 0.06 | 0.03 | 1.01  | 0    | 0    | 0    | 1.99 | 1.99 |
| 8                  | 0.88 | 0.05 | 0.06 | 0.02 | 1.01  | 0    | 0    | 0    | 1.99 | 1.99 |
| 9                  | 0.78 | 0.12 | 0.10 | 0.02 | 1.02  | 0    | 0    | 0    | 1.98 | 1.98 |
| 10                 | 0.86 | 0.06 | 0.07 | 0    | 0.99  | 0    | 0    | 0    | 2.01 | 2.01 |
| 11                 | 0.84 | 0    | 0.03 | 0.13 | 1.01  | 0.11 | 0    | 1.55 | 0.33 | 1.99 |
| 12                 | 0.98 | 0    | 0.00 | 0.08 | 1.07  | 0    | 0    | 1.76 | 0.17 | 1.93 |
| 13                 | 0.06 | 0.08 | 0.06 | 0.79 | 1.00  | 0    | 0.98 | 0.02 | 0    | 1.00 |
| 14                 | 10.3 | 52.2 | 37.5 | 0.0  | 100.0 | —    | —    | —    | —    | —    |
| 15                 | 10.6 | 51.3 | 36.8 | 1.3  | 100.0 | —    | —    | —    | —    | —    |
| 16                 | 2.0  | 42.3 | 50.2 | 5.4  | 100.0 | —    | —    | —    | —    | —    |
| 17                 | 6.4  | 56.2 | 37.4 | 0.0  | 100.0 | —    | —    | —    | —    | —    |
| 18                 | 86.5 | 5.8  | 7.7  | 0.0  | 100.0 | —    | —    | —    | —    | —    |
| 19                 | 84.8 | 6.1  | 7.3  | 1.8  | 100.0 | —    | —    | —    | —    | —    |
| 20                 | 85.0 | 8.7  | 6.3  | 0.0  | 100.0 | —    | —    | —    | —    | —    |

Note. Numbers 1–19: results of SEM/EDS electron-microprobe analyses; no. 20: WDS analysis (JEOL JXA-8230 microprobe operated at 20 kV and 50 nA; beam size is ~1 μm; the standards are pure Ru, Os, Ir, and FeS<sub>2</sub>; XPP correction method was used). Samples nos. 201–209 are specimens of chromitite, which occurs as disintegrated fragments in the area of development of the Main Chromitite Layer, Dunite block (Fig. 1b). Sample no. 216 represents a mineralized dunite containing abundant grains of disseminated chromite in the Dunite block. Zero is not detected or not analyzed. Values of atomic proportions are calculated on the basis of a total of 3 (analyses 1–12) and 2 (no. 13) atoms per formula unit, or per a total of 100 at% (no. 14–20).

compositions of laurite (poor in OsS<sub>2</sub>) associated with native Os indicate that levels of fS<sub>2</sub> were below the Os–OsS<sub>2</sub> buffer. In addition, Ir and Os display slightly positive covariations (correlation coefficient  $R=0.7$ ), pointing to the substitution (Os + Ir) ↔ Ru.

The disulfide–diselenide phases of intermediate compositions are especially interesting; notably they are stoichiometric: [(Ru<sub>0.99</sub>Ir<sub>0.01</sub>)Σ<sub>1.00</sub>(S<sub>1.68</sub>Se<sub>0.30</sub>As<sub>0.01</sub>)Σ<sub>1.99</sub>] and [(Ru<sub>0.84</sub>Rh<sub>0.13</sub>Ir<sub>0.03</sub>)Σ<sub>1.01</sub>(Se<sub>1.55</sub>S<sub>0.33</sub>As<sub>0.11</sub>)Σ<sub>1.99</sub>] (an. 3 and 11, Table 2). The latter phase is strongly Se-dominant,

corresponding to RuSe<sub>2</sub>, which is a potentially new species of PGM. Results of WDS analyses of these compounds agree well with the SEM-EDS data (Table 3).

Synthetic RuSe<sub>2</sub> is isostructural with laurite and has a pyrite-type structure, space group *Pa3* (Lutz *et al.*, 1990). Thus, by analogy with pyrite-type compounds, the formal valences in the diselenide are Ru<sup>2+</sup>(Se<sub>2</sub>)<sup>2-</sup>, *i.e.*, the presence of the selenoan dianion is presumably inferred. The existence of a natural RuS<sub>2</sub>–RuSe<sub>2</sub> solid-solution is clearly implied by the phases at Pados-Tundra. Presum-

Table 3. Compositions (WDS) of phases of ruthenium disulfide–diselenide from the Pados-Tundra complex, Kola Peninsula.

|   | Ru    | Os   | Ir   | Rh   | As   | Te   | Se    | S     | Total |
|---|-------|------|------|------|------|------|-------|-------|-------|
| 1 | 52.20 | 1.29 | 2.16 | 0.84 | 0.15 | 0.03 | 16.03 | 27.72 | 100.4 |
| 2 | 51.66 | 0.61 | 1.98 | 0.86 | 0.20 | 0    | 15.68 | 27.59 | 98.6  |
| 3 | 51.35 | 1.00 | 2.71 | 0.86 | 0.24 | 0    | 13.76 | 27.61 | 97.5  |
| 4 | 50.07 | 1.95 | 3.70 | 0.85 | 0.26 | 0    | 12.70 | 27.46 | 97.0  |
| 5 | 51.60 | 0.71 | 1.90 | 0.90 | 0.20 | 0    | 15.85 | 27.57 | 98.7  |
| 6 | 32.36 | 0.76 | 3.52 | 5.83 | 0.96 | 0.90 | 51.40 | 4.27  | 100.0 |

| <i>Atoms per formula unit (per a total of 3 apfu)</i> |      |      |      |      |      |       |      |      |      |      |
|-------------------------------------------------------|------|------|------|------|------|-------|------|------|------|------|
|                                                       | Ru   | Os   | Ir   | Rh   | ΣM   | As    | Te   | Se   | S    | Σ    |
| 1                                                     | 0.96 | 0.01 | 0.02 | 0.02 | 1.01 | 0.004 | 0    | 0.38 | 1.61 | 1.99 |
| 2                                                     | 0.96 | 0.01 | 0.02 | 0.02 | 1.00 | 0.005 | 0    | 0.37 | 1.62 | 2.00 |
| 3                                                     | 0.97 | 0.01 | 0.03 | 0.02 | 1.02 | 0.006 | 0    | 0.33 | 1.64 | 1.98 |
| 4                                                     | 0.96 | 0.02 | 0.04 | 0.02 | 1.03 | 0.007 | 0    | 0.31 | 1.65 | 1.97 |
| 5                                                     | 0.96 | 0.01 | 0.02 | 0.02 | 1.00 | 0.005 | 0    | 0.38 | 1.62 | 2.00 |
| 6                                                     | 0.80 | 0.01 | 0.05 | 0.14 | 1.00 | 0.032 | 0.02 | 1.62 | 0.33 | 2.00 |

Note. These results of WDS analyses were acquired with a JEOL JXA-8230 microprobe. Zero is not detected or not analyzed. Analyses no. 1–5 pertain to sample Pds-203; no. 6 pertains to sample Pds-209, collected as fragmented peaces at the Main Chromitite Layer, Dunite block.

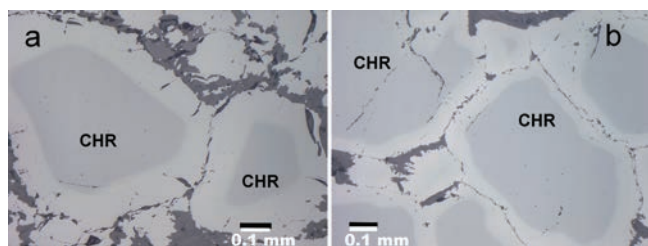


Fig. 2. (a and b) Reflected-light micrographs showing examples of zoned grains of chromite–magnesiochromite (Chr) from specimens of chromitite collected as fragments at the Main Chromitite Layer (a) and from a segregation *in situ* (b); Dunite block, Pados-Tundra complex.

ably, special conditions are required to incorporate Se into  $\text{RuS}_2$ . Normally, laurite is depleted in Se. Hattori *et al.* (2004) documented the presence of hundreds of ppm of Se in laurite from Borneo. In general, examples of compounds of Se and IPGE are extremely rare. Tolstykh *et al.* (1997) reported the unnamed phase  $\text{Ir}(\text{As}, \text{Se}, \text{S})_2$  with ~40% of the  $\text{IrSe}_2$  component from placers of the Zolotaya River, western Sayans, Russia.

In addition, a single grain of unnamed  $\text{RhTe}$  (an. 13, Table 2) was found. It seems to be analogous to the  $\text{RhTe}$  phase that forms peritectically in the system  $\text{Rh}-\text{Te}$  (Ding *et al.*, 1990).

### 3.3. Laurite–clinocllore intergrowths and their implications

Laurite typically forms intergrowths with clinocllore, which may display well-developed crystal faces (Fig. 3a) and commonly mantles the laurite crystals (Fig. 3b–e). Of a total of 25 grains of laurite found as inclusions in Chr, 21 grains (*i.e.*, >80%) are intimately intergrown with clinocllore. No grains of base-metal sulfides were observed in these specimens in the MCL; as noted, millerite and pentlandite occur only in chromitite

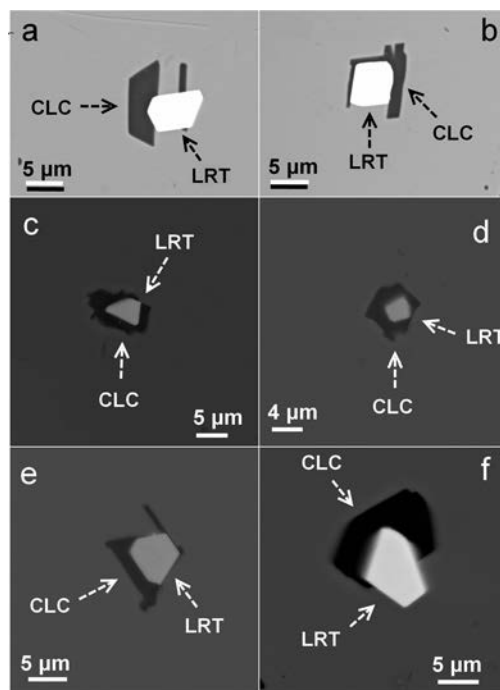


Fig. 3. (a–f) Examples of micro-intergrowths of laurite (Lrt) with clinocllore (Clc), hosted by chromite–magnesiochromite; SEM BSE images.

segregations. In spite of tiny grain sizes, clinocllore is well recognized in the SEM-EDS data (Table 4). It contains up to ~4 wt%  $\text{Cr}_2\text{O}_3$  in larger grains next to Chr, consistent with clinocllore from chromitite in other localities (*e.g.*, Zaccarini *et al.*, 2006).

The following compositional ranges were obtained for variously textured clinocllore, which is fairly abundant, including grains that do not have contacts with PGM: (1) A total of 12 grains in mutual intergrowths with laurite, hosted by Chr, yield a *mg#* value in the range 90.0–96.8, with a mean 94.9; (2) two representative (individual)

Table 4. Compositional data for clinochlore in intimate intergrowths with laurite in chromitite of the Pados-Tundra complex, Kola Peninsula.

|   | Sample | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | FeO  | MgO   | Total |
|---|--------|------------------|--------------------------------|--------------------------------|------|-------|-------|
| 1 | 207-3  | 27.77            | 15.59                          | 4.11                           | 1.90 | 31.47 | 80.8  |
| 2 | 203-2  | 26.89            | 10.56                          | 5.01                           | 3.23 | 28.57 | 74.3  |
| 3 | 202-2  | 25.16            | 12.30                          | 4.44                           | 3.09 | 28.21 | 73.2  |
| 4 | 202-3  | 30.19            | 11.53                          | 5.60                           | 3.06 | 33.63 | 84.0  |
| 5 | 207-1  | 31.58            | 17.91                          | 5.69                           | 2.06 | 34.81 | 92.1  |
| 6 | 203-4  | 32.00            | 11.47                          | 4.98                           | 2.17 | 34.28 | 84.9  |
| 7 | 207-1  | 30.34            | 15.15                          | 3.83                           | 1.38 | 33.28 | 84.0  |

| <i>Atomic proportions (per O = 14 apfu)</i> |      |      |      |     |      |      |      |     |      |
|---------------------------------------------|------|------|------|-----|------|------|------|-----|------|
|                                             | Si   | Al   | Cr   | Σ   | Al   | Mg   | Fe   | Σ   | mg#  |
| 1                                           | 2.85 | 0.82 | 0.33 | 4.0 | 1.06 | 4.81 | 0.16 | 5.0 | 96.7 |
| 2                                           | 3.04 | 0.51 | 0.45 | 4.0 | 0.90 | 4.82 | 0.31 | 5.1 | 94.0 |
| 3                                           | 2.89 | 0.71 | 0.40 | 4.0 | 0.95 | 4.83 | 0.30 | 5.1 | 94.2 |
| 4                                           | 3.02 | 0.54 | 0.44 | 4.0 | 0.82 | 5.01 | 0.26 | 5.3 | 95.1 |
| 5                                           | 2.84 | 0.75 | 0.41 | 4.0 | 1.15 | 4.68 | 0.16 | 4.8 | 96.8 |
| 6                                           | 3.13 | 0.48 | 0.39 | 4.0 | 0.84 | 5.00 | 0.18 | 5.2 | 96.6 |
| 7                                           | 2.98 | 0.72 | 0.30 | 4.0 | 1.03 | 4.87 | 0.11 | 5.0 | 97.7 |

*Note.* Results of SEM/EDS electron-microprobe analyses are listed in wt%. Analyses 1–5 pertain to grains of clinochlore which occur in intimate micro-intergrowths with laurite (*e.g.*, an. 2 refers to the grain shown in Fig. 3f). Analyses 6 and 7 refer to clinochlore grains associated with Se-bearing laurite (no. 6: Fig. 4a) and monazite-(Ce) (no. 7: Fig. 4d). Atomic proportions are based on 14 oxygen atoms per formula unit (apfu). The *mg#* index is Mg/(Mg + Fe).

inclusions in Chr gave 94.7 and 96.2 (mean 95.5); and (3) interstitial patches (two data points) yield *mg#* values of 96.6 and 97.6 (mean 97.1). These values are fairly consistent, and indicate that all of these varieties crystallized in equilibrium with a fluid. Clinochlore has a relatively high upper thermal stability limit (670–820 °C; Müller & Saxena, 2012).

The laurite–clinocllore intergrowths presumably crystallized from microvolumes of H<sub>2</sub>O-bearing fluid of multicomponent composition, enclosed by the Chr cores. Laurite is commonly interpreted to be a magmatic phase (*e.g.*, Brenan & Andrews, 2001; Andrews & Brenan, 2002). However, its deposition under hydrothermal conditions is inferred in the environments rich in volatiles associated with chromitite (Barkov & Fleet, 2004; Pushkarev *et al.*, 2015). The close association of PGM with clinochlore is characteristic of the Kirakkajupura deposit, Finland (Barkov *et al.*, 2004, 2005). Note that the phlogopite–orthopyroxene inclusions are commonly present in Chr of the Merensky Reef, Bushveld complex, South Africa (Li *et al.*, 2005).

In addition, monazite-(Ce) [(Ce<sub>0.47</sub>La<sub>0.38</sub>Nd<sub>0.10</sub>Pr<sub>0.03</sub>Sm<sub>0.01</sub>Ca<sub>0.01</sub>)Σ<sub>1.00</sub>P<sub>1.00</sub>O<sub>4</sub>], an unusual phase in chromitite, is associated with interstitial patches of clinochlore and magnesian Chr (Fig. 4d).

### 3.4. Framboidal micro-(nano)-spheres of native Ru

Figure 5 documents a highly unusual mode of occurrence. Micro- to nano-spheres or nanoparticles of native ruthenium (with Os and Ir in solid solution: an. 18, Table 2) fill a cavity having the shape of a skeletal clinochlore crystal in a magnesian Chr host. The observed morphology, hitherto unreported for a PGE alloy,

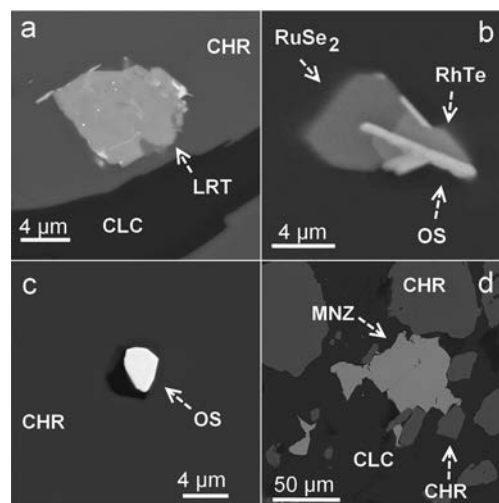


Fig. 4. (a) A grain of Se-bearing laurite (Lrt) near the boundary of chromite–magnesiochromite (Chr) and clinochlore (Clc). (b) The intergrowth of Os-dominant alloy (Os) with unnamed RuSe<sub>2</sub> and RhTe is hosted by a grain of Chr. (c) Inclusion of native osmium (Os) in Chr; (d) A grain of monazite-(Ce) (Mnz) is associated with chromite–magnesiochromite (Chr) and clinochlore (Clc); SEM BSE images.

resembles that known in framboidal pyrite or Fe oxide. A tiny grain of laurite is present, likely as a relic (Fig. 5). We interpret that it is a negative crystal of Chr filled with clinochlore, associated initially with laurite in the core, similar to the laurite–clinocllore intergrowths (Fig. 3a–f). The nanospherules were likely precipitated from a reducing fluid, in which laurite reacted with hydrogen (produced *via* serpentinisation) to form metallic ruthenium: RuS<sub>2</sub> + 2H<sub>2</sub> → Ru + 2H<sub>2</sub>S. Observations on catalysts in the literature agree well; after a hydrogen treatment (at

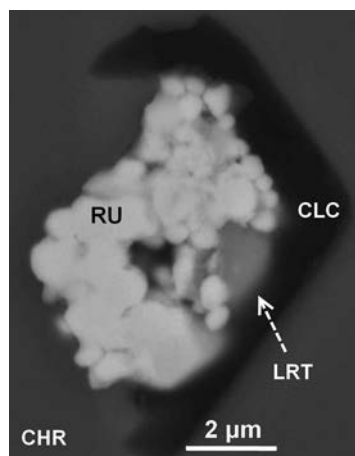


Fig. 5. A SEM BSE image showing framboidal spheres of native ruthenium (Ru) associated with laurite (Lrt); Clc is clinochlore, and Chr is the host grain of chromite–magniochromite.

$\geq 330$ – $400^\circ\text{C}$ ) nanometric particles of crystalline phases  $\text{RuS}_2 + \text{Ru}$  formed as a result of transformation of pyrite-type  $\text{RuS}_2$  (laurite analogue) into Ru metal (Guczi *et al.*, 1993). A Ru-rich alloy phase formed as a result of desulfurisation of laurite in chromitite of the Vourinos complex, Greece (Garuti & Zaccarini, 1997). In addition, nanophases of PGE were obtained by synthesis (Helmy *et al.*, 2013).

#### 4. Origin of IPGE-rich sulfoselenides and concluding comments

In chromitite at Pados-Tundra, unusual intergrowths of laurite and clinochlore are developed in the virtual absence of base-metal sulfides in this association. In fact, clinochlore represents the main phase coexisting with laurite; more than 80% of the grains of laurite typically occur as two-phase inclusions hosted by very magnesian cores of Chr. Uniform values of *mg*# are observed for variously textured grains of clinochlore in the micro-intergrowths, single inclusions and in grains that are interstitial with respect to Chr. Therefore, all of these varieties crystallized in equilibrium with an aqueous fluid in the ore-forming environment. This observation is consistent with that of Johan (2006) and Johan *et al.* (2017) that hypermagnesian compositions can reflect the effects of  $\text{H}_2\text{O}$  activity and low-temperature equilibration.

The laurite–clinochlore intergrowths (Fig. 3a–f) likely crystallized from portions of  $\text{H}_2\text{O}$ -bearing multicomponent fluid. This happened fairly late in the crystallization history of the chromitite, as reflection of a local build-up in the levels of excess and incompatible constituents (*e.g.*, Si, Ru and other PGE, S,  $\text{H}_2\text{O}$ ) remaining during the crystallization of the host Chr. These contrasting components thus accumulated in microvolumes of hydrous fluid; ruthenium and the other PGE, along with S, thus essentially partitioned into the fluid. The presence of  $\text{H}_2\text{O}$  could result in a delayed crystallization of the two-phase association, laurite + clinochlore, after the host Chr.

The observed arrangement of the laurite–clinochlore intergrowths, in which laurite is in the centre, suggests that laurite crystallized first. However, in other intergrowths, the observed faces of laurite are subparallel to those of clinochlore, implying a possibility of their near-simultaneous crystallization from the dispersed fluid.

A highly sulfide-deficient environment is indicated for the ore occurrences in chromitite of the Dunite block in the Pados-Tundra complex. Levels of  $f_{\text{S}_2}$  were presumably below the Os–Os $\text{S}_2$  buffer, thus resulting in the coexistence of a low-Os variety of laurite with Os-dominant alloy. The framboidal nanospheres of native ruthenium likely deposited from a  $\text{H}_2$ -bearing reducing fluid, involving the reduction of laurite associated with clinochlore.

The occurrences of sulfoselenide–selenide phases of Ru (with S/Se ratio  $\leq 6$ ), presently documented at Pados-Tundra, are unique. Indeed, they are fairly anomalous, because extremely low S/Se values are implied in the mineral-forming environment. The S/Se value of the mantle is estimated at 2850–4350, with a mean of  $\sim 3250$  (*e.g.*, Lorand *et al.*, 2003; Smith *et al.*, 2016), and the chondritic value of  $2500 \pm 270$  is consistent (Dreibus *et al.*, 1995). The lowest S/Se values (190–700) were documented in sulfide microdroplets of the Platinova Reef, Skaergaard layered complex, east Greenland (Holwell *et al.*, 2015). Thus, an IPGE-rich sulfoselenide would unlikely have crystallized as a primary magmatic phase, under normal conditions, from a melt associated with ultramafic rocks; pure sulfides would be stable instead. In addition, the IPGE–Se-rich phases could not have formed by magmatic contamination; normally, crustal rocks have higher S/Se values, ranging from 3500 to 100 000 (*e.g.*, Smith *et al.*, 2016).

We thus infer that the observed occurrences of IPGE phases of diselenide–disulfoselenide compositions likely reflect a process of ultimate S loss, causing a critical lowering of the S/Se ratio during a late-stage evolution of the  $\text{H}_2\text{O}$ -bearing fluid involved in the formation of laurite–clinochlore intergrowths at Pados-Tundra. An oxidizing character of this fluid is clearly implied, which appears to be essential to form selenide minerals (*i.e.*, close to the anglesite–galena buffer: Simon *et al.*, 1997). This suggestion is corroborated by the fact that S is, indeed, more mobile than Se in hydrothermal fluids, being preferentially incorporated into aqueous fluids (*e.g.*, Ewers, 1977; Howard, 1977). On the other hand, the presently documented IPGE–Se-rich compounds may represent phases of metastable crystallization, which would explain their unique compositions.

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