AN UNUSUAL ASSOCIATION OF HYDROTHERMAL PLATINUM-GROUP MINERALS FROM THE IMANDRA LAYERED COMPLEX, KOLA PENINSULA, NORTHWESTERN RUSSIA

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ABSTRACT

An unusual association of platinum-group minerals (PGM) is observed in a chromitite layer of the Mount Bol’shaya Varaka deposit, Imandra layered complex, Kola Peninsula, Russia. The PGM typically occur as cluster-like or chain-like micro-aggregates, and as separate minute grains located in contact with chromite along grain boundaries. The PGM are enclosed in magnesiohornblende, edenite, talc, or phlogopite, and may transect the host hydrous silicates; they include sperrylite, laurite–erlichmanite, unnamed Cu2(Ni,Co)Pt3S8, hollingworthite, pyrite rich in the platinum-group elements (Ru 10.96, Os 0.98, and Ir 0.54 wt.%), nickelian platarsite(?), (Pt0.71Ni0.26Co0.05)H90181.02As1.10S0.88, daomanite, and cooperite. Concentrations of Rh and S in the rhodian sulfurian sperrylite vary from 1.0 and 0.8 to 6.6 and 4.9 wt.%, respectively, and the composition most enriched in Rh and S is (Pt0.71Rh0.29)H90181.01(As1.53S0.47)H90182.00. The correlations Pt–Rh (correlation coefficient R = –0.99), Pt–As (R = 0.98), Pt–S (R = –0.99), Rh–As (R = –0.97), Rh–S (R = 0.97), and As–S (R = –1.00) are important and consistent with the existence of a new series of solid solution, extending from PtAs2 toward the pyrite-type Rh1–xS2 (“Rh2S5”). Most of the PGM precipitated during deuteric alteration at a postmagmatic-hydrothermal stage of crystallization of the chromitite. The majority of the laurite–erlichmanite grains display a close textural relationship with the hydrous silicates and form part of the hydrothermal mineralization at Imandra.

Keywords: platinum-group elements, platinum-group minerals, substitutions, hydrothermal mineralization, chromitite layer, layered intrusion, mafic rocks, Mount Bol’shaya Varaka, Imandra complex, Baltic Shield, Russia.

Nous avons découvert une association inhabituelle de minéraux du groupe du platine (MGP) dans un niveau de chromitite du gisement du Mont Bol’shaya Varaka, complexe stratiforme d’Imandra, péninsule de Kola, en Russie. Les MGP se présentent généralement en micro-agrégats ou en chaînes, et en grains isolés de taille infime au contact avec la chromite le long des grains. Les MGP sont inclus dans la magnésiohornblende, l’édérite, le talc ou la phlogopite, et peuvent même recouper les silicates hydratés qui les renferment. Parmi les MGP se trouvent sperrylite, laurite–erlichmanite, Cu2(Ni,Co)Pt3S8 sans nom, hollingworthite, pyrite riche en éléments du groupe du platine (Ru 10.96, Os 0.98, et Ir 0.54%, poids), platarsite nickelifère (?), (Pt0.71Rh0.29)H90181.01(As1.53S0.47)H90182.00, daomanite, et cooperite. La concentration de Rh et S dans la sperrylite varie de 1.0 et 0.8 à 6.6 et 4.9% (poids), respectivement, et la composition la plus enrichie en Rh et S est (Pt0.71Rh0.29)H90181.01(As1.53S0.47)H90182.00. Les corrélations Pt–Rh (coefficient de corrélation R = –0.99), Pt–As (R = 0.98), Pt–S (R = –0.99), Rh–As (R = –0.97), Rh–S (R = 0.97), et As–S (R = –1.00) sont importantes et semblent indiquer l’existence d’une solution solide entre PtAs2 et Rh1–xS2 (“Rh2S5”). La plupart des MGP se sont formés au cours d’une altération deutérique à un stade postmagmatique hydrothermal de la cristallisation de la chromitite. La majorité des grains de laurite–erlichmanite démontrent un lien textural étroit avec les silicates hydratés et font partie de l’événement d’altération hydrothermale à Imandra.


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INTRODUCTION

The Imandra mafic complex in the Kola Peninsula, northwestern Russia, has an Early Proterozoic age (U–Pb dating of zircon) of 2395 ± 30 Ma (Balashov et al. 1990) and 2441 ± 1.6 Ma (Amelin et al. 1995). This is one of several related layered intrusions in the Baltic (Fennoscandian) Shield (Fig. 1) that host various depos-
its of chromite, base-metal sulfides and platinum-group elements, PGE (e.g., Dokuchaeva et al. 1985, Barkov et al. 1997).

In this paper, we provide a detailed description of an unusual association of platinum-group minerals (PGM) from the Mount Bol’shaya Varaka (“Big Hill”) chromitite deposit in the Imandra layered complex, with emphasis on some uncommon or unique PGM and PGE-rich phases. The reported association and genetically indicative textures involving these PGM have important implications for the origin of PGE mineralization associated with chromitites.

GEOLoGICAL BACKGROUND

The Mount Bol’shaya Varaka, Umbarechensky, Mount Devich’ya and some other mafic intrusive bodies (a few to several tens of km across) are exposed in the Lake Imandra area, at the western and southwestern margins of the belt of the Imandra–Varzuga Supergroup of Proterozoic supracrustal rocks (Fig. 1). Dokuchaeva et al. (1982, 1985) noted that there is a general similarity in geological structure, geochemistry and mineral compositions among these bodies, and suggested that they are fragments of a pre-existing large lopolith (ca. 1500 km²) that was broken up by subsequent tectonic movements.

The layered series of the Imandra complex has been divided into four zones (Dokuchaeva et al. 1982, 1985): (1) The Lower Zone (ca. 0.15 km in thickness) composed of alternating layers of plagioclase-bearing pyroxenite, gabbronorite and norite; no olivine-rich cumulates were observed. (2) The Main Zone (ca. 2 km in thickness) of homogeneous mesocratic gabbronorite and subordinate melanocratic and leucocratic gabbro-norite. (3) The Upper Zone (ca. 0.3 km in thickness) of various layers of leucocratic gabbro and anorthosite. The main anorthosite layer (ca. 30 m in thickness) is located at the top of this zone. (4) The Uppermost Zone (ca. 0.5 km in thickness) of quartz-bearing gabbro and gabbrodiorite. The total thickness of the complex is approximately 3 km. Layers of vanadiferous magnetite occur in the upper zones, and several layers of chromitite are present at the lower stratigraphic levels of the complex (Kozlov et al. 1975, Dokuchaeva et al. 1985).

MINERALOGY OF THE PGE-BEARING CHROMITITE LAYER FROM THE MOUNT BOL’SHAYA VARAKA DEPOSIT

Chromite and plagioclase

The chromitite layer consists of up to 50 vol.% of chromite grains commonly less than 1 mm in diameter. The chromite grains are locally replaced by anhedral rutile (or another polymorph of TiO₂). The mean composition of three grains of chromite (WDS data) is TiO₂ 66.4%, Al₂O₃ 11.41%, Cr₂O₃ 30.56%, V₂O₃ 0.38%, FeO 28.67, Fe₂O₃ (calc.) 3.51, MnO 0.60, MgO 3.02, ZnO 0.16, for a total of 98.77 wt.%, corresponding to the formula (Fe²⁺0.82Mg0.16Mn0.02Zn0.01)Ti₄O₉(Al₄.09Fe³⁺0.09 Fe²⁺0.05Ti₂O₂V0.01)₂O₉.

Relict igneous plagioclase (probably intercumulus), present in the chromitite, is relatively enriched in the albite component: An₅₂.₆–₆₀.₄Ab₃₉.₄–₄₇.₄Orₐ₉₉.₉–₀.₀₉-

Hydrous silicates

Calcic amphiboles (magnesiohornblende and edenite: Table 1) are the principal hydrous silicates in the chromitite layer. They display very high values of mg [i.e., 100 Mg/(Mg + Fe + Mn)], 90.8 to 94.7, and are invariably enriched in Cr (0.6–2.0 wt.% Cr₂O₃). These compositions imply a high-magnesium character for igneous pyroxene in the chromitite; it presumably was a precursor primary mineral for these amphiboles, but is not preserved, even in relics. The calcic amphiboles

| TABLE 1: COMPOSITIONS OF AMPHIBOLES FROM THE CHROMITITE LAYER OF THE IMANDRA COMPLEX, KOLA PENINSULA, RUSSIA |
|-----------|-----------|-----------|-----------|-----------|-----------|
|           | 1         | 2         | 3         | 4         | 5         | 6         |
| SiO₂, wt.%| 47.64     | 47.11     | 50.58     | 54.06     | 59.94     |
| TiO₂      | 0.36      | 0.21      | 0.23      | 0.18      | 0.22      | 0.11      |
| Al₂O₃     | 10.65     | 5.91      | 73.86     | 8.66      | 5.99      | 8.68      |
| Cr₂O₃     | 1.56      | 0.94      | 0.59      | 1.73      | 0.74      | 2.03      |
| FeO       | 2.99      | 2.12      | 3.22      | 3.42      | 2.78      | 3.39      |
| Fe₂O₃ (calc.) | 3.51   | 3.01      | 1.01      | 1.02      | 0.35      | 0.34      |
| MnO       | 0.37      | 0.07      | 0.02      | n.d.      | n.d.      | 0.16      |
| MgO       | 19.81     | 22.38     | 19.17     | 19.96     | 21.16     | 19.55     |
| Na₂O      | 0.30      | 0.30      | 12.25     | 11.88     | 12.38     | 12.70     |
| CaO       | 0.25      | 0.01      | 0.01      | 0.17      | 0.08      | 0.17      |
| K₂O       | 0.06      | 0.06      | n.d.      | n.d.      | n.d.      | n.d.      |
| Cl        | 0.06      | n.d.      | n.d.      | n.d.      | n.d.      | n.d.      |
| O+Cl      | 0.01      | -         | -         | -         | -         | -         |
| Total     | 97.56     | 96.84     | 97.94     | 97.53     | 98.45     | 98.70     |

Columns 1 to 3: results of WD3 electron-microprobe analyses (JEDL-733 microprobe) 4 to 6: results of quantitative SEM/EDS electron-microprobe analyses. Numbers 1 and 2: host for two grains of PGE-rich pyrite and associated PGM (Fig. 3). 4 and 5: host for a micro-aggregate of PGM (Figs. 2A–D). 6: amphibole that forms an intergrowth with plagiogogie: SiO₂ 41.38, TiO₂ 1.77, Al₂O₃ 18.49, Cr₂O₃ 7.10, FeO 2.50, MgO 24.17, Na₂O 0.65, and K₂O 8.51, Fe₂O₃ 25 wt.%; results of SEM/EDS analyses. These amphibole and plagiogogie are the host for a micro-aggregate of PGM, which consists of follication, chrosite, xenolyte, lausite, and plattlerite). All Fe is expressed as Fe₂O₃ (wt.%). F was not detected; n.d. not detected. The summation was calculated on the basis of O + 23. mg > 100 Mg/(Mg + Fe + Mn).
are devoid of Cl or contain only trace amounts of Cl (Table 1), consistent with the crystallochemical constraints of the Mg–Cl avoidance principle discussed in Oberti et al. (1993). Talc also seems to be a replacement product of pyroxene. It is associated with the calcic amphiboles and phlogopite, and has the composition (EDS data) SiO$_2$ 63.19, MgO 30.73, FeO 0.94, Al$_2$O$_3$ 0.59, and total 95.45 wt.%, corresponding to a formula of $(Mg_{2.90}Fe_{0.05})_{2.95}(Si_{3.99}Al_{0.04})_{4.03}O_{10}(OH)_2$. Phlogopite is common in the chromitite layer. Its composition is close to end-member phlogopite (MgO 24.0–24.4, FeO 2.0–2.5 wt.%), and is characterized by elevated contents of Cr (0.9–2.1 wt.% Cr$_2$O$_3$), Ti (1.1–1.2%), and Na (0.6–0.7% Na$_2$O).

**Cl-rich apatite**

Apatite is a common accessory mineral in the chromitite. It is interstitial with respect to chromite, typically occurring as subhedral to anhedral grains up to 0.1–0.2 mm in maximum dimension, and invariably containing elevated levels of Cl. A grain of Cl-rich apatite is present in the same polished section as a microaggregate of PGM (Figs. 2A–D), and contains up to 3.45 wt.% Cl (i.e., 0.49 Cl atoms per formula unit, apfu).

**Baddeleyite and zircon**

Accessory baddeleyite (up to ca. 0.2 mm in length) is enclosed by hydrous silicates and mantled by a nar-
row rim of zircon, which is likely a consequence of the build-up of SiO$_2$ in the interstitial fluid, resulting in a reaction of the type ZrO$_2$ + SiO$_2$ = ZrSiO$_4$. The baddeleyite contains up to 2.0% HfO$_2$ and 0.6% TiO$_2$.

**Base-metal sulfides**

Chalcopyrite, bornite, millerite, pyrite, and pentlandite form single grains (typically up to 50 μm) or mutual intergrowths. These sulfides are scarce and typically enclosed by hydrous silicates, but they are occasionally present as inclusions within chromite. Two grains of chalcopyrite contain Cu 33.67 and 33.92, Fe 31.05 and 30.71, S 34.62 and 34.86, and total 99.34 and 99.49 wt.%, with formulae represented by Cu$_{0.98}$Fe$_{1.01-1.03}$S$_{1.99-2.00}$, and thus are more consistent with chalcopyrite than with any of the known chalcopyrite-derivative minerals: mooihoekite, talnakhite or putoranite. A representative composition of bornite is Cu 61.74, Fe 10.55, S 26.09, and total 98.38 wt.%, with a formula Cu$_{4.92}$Fe$_{0.96}$S$_{4.12}$. The composition of millerite is Ni 63.88, Fe 0.66, S 36.17, and total 100.71 wt.%, with a formula (Ni$_{0.98}$Fe$_{0.01}$)$_{0.99}$S$_{1.01}$. Pyrite contains minor amounts of Ni or Co; compositions of two grains are Fe 46.17 and 46.14, Ni 0.83 and 0.0, Co 0.0 and 0.81, S 53.87 and 53.05, and total 100.87 and 100.0 wt.%, corresponding to formulae in the range (Fe$_{0.98-0.99}$Ni$_{0.02-0.0}$Co$_{0.0-0.02}$)$_{1.00-1.01}$S$_{2.00-1.99}$, respectively. Pentlandite is strongly enriched in Ni: Fe 23.45, Ni 43.72, S 33.41, total 100.58 wt.%, with a formula (Ni$_{0.74}$Fe$_{3.24}$)$_{38.98}$S$_{8.03}$.

**Platinum-group minerals from the chromitite layer**

The compositions of laurite–erlichmanite in the chromitite vary from (Ru$_{0.90}$Os$_{0.06}$Ir$_{0.03}$)$_{0.99}$S$_2$ to (Os$_{0.63}$Ru$_{0.23}$Ir$_{0.08}$)$_{2.0}$S$_2$. Members of the laurite–erlichmanite series occur in two distinct textural associations: (1) they are dominantly located at the contact of chromite grains with the hydrous silicates or are enclosed within these hydrous silicates. The largest grain of laurite, which is euhedral and ca. 20 μm in size, occurs at the outer contact of chromite and displays compositional zoning: Ru is enriched in the core and Os at the edge of the grain. (2) Micro-inclusions of laurite–erlichmanite in chromite are also quite common, but these are less abundant than the laurite grains associated with the hydrous silicates.

Submicrometric laurite (less than 0.5 μm in size) occurs in close association with ruthenian pyrite (Fig. 3), and these PGM are enclosed by magnesiohornblende (anal. 2, Table 1). Laurite in this association was recognized on the basis of results of SEM/EDS analyses,
which are useful in spite of their low totals; such grains yielded a laurite-type formula (e.g., Ru$_{0.93}$S$_{2.07}$). The submicrometric laurite–erlichmanite also forms part of cluster-like micro-aggregates of the PGM in the Mg-rich calcic amphiboles, and is closely associated with hollingworthite, sperrylite, unnamed Cu$_2$(Ni,Co)Pt$_3$S$_8$, and chalcopyrite.

**Rhodian sulfurian sperrylite**

Sperrylite is relatively common and occurs as submicrometric grains closely associated with the other PGM and with the hydrous silicates. For example, four grains of sperrylite are present in the micro-aggregate shown in Figure 2B. Occurrences of submicrometric PtAs$_2$ are known in other Mg-rich environments, e.g., in komatiitic basalts of the Abitibi greenstone belt, Canada (Stone et al. 1996).

The rhodian sulfurian variety of sperrylite is very rare; only a few grains were observed. Results of a detailed study (SEM/EDS) of the largest of these grains, enclosed within talc (Fig. 4) that is homogenous and devoid of inclusions. Thus, Rh and S are believed to be present in solid solution. These compositions are in excellent agreement with the sperrylite-type formula (Pt,Rh)(As,S)$_2$, and display covariations in Pt, Rh, As and S (Table 2). The amount of Pt correlates

![Fig. 4. Anhedral grain of rhodian sulfurian sperrylite (Spy), which is enclosed within talc (Sil), near its contact with a magnesiohornblende (anal. 5, Table 1). Back-scattered electron image.](image-url)
strongly and negatively with that of Rh (correlation coefficient $R = -0.99$; Fig. 5A) and positively with As ($R = 0.98$: Fig. 5B). The Pt–S correlation is strong and negative: $R = -0.99$ (Fig. 5C). In contrast, the amount of Rh correlates negatively with that of As ($R = -0.97$: Fig. 5D) and positively with S ($R = 0.97$: Fig. 5E). The As–S correlation is inverse: $R = -1.00$ (Fig. 5F). These variations (Figs. 5A–F) are quite distinct from those observed in the sperrylite–hollingworthite series from the Nomgon complex, Mongolia (Izokh & Mayorova 1990). In addition, a strong grain-to-grain variation in the amount of Rh and S was observed in the sperrylite–hollingworthite; in contrast, individual grains of these sulfarsenides at Nomgon are not zoned and contain uniform levels of Rh and S (Izokh & Mayorova 1990). These observations imply that Rh and S occur in solid solution.

**Unnamed Cu$_2$(Ni,Co)Pt$_3$S$_8$**

An average composition of this complex chalcogenide can be recalculated to the formula Cu$_2$(Ni,Co)Pt$_3$S$_8$ (Table 3). This phase occurs as tiny grains (up to 7 \(\mu\)m in longest dimension), both anhedral and subhedral, enclosed by magnesian calcic amphibole(s) or located at the contact of chromite and hydrous silicate grains. In addition, unnamed Cu$_2$(Ni,Co)Pt$_3$S$_8$ is

![Fig. 5. (A–F). Correlation of Pt and Rh (A), Pt and As (B), Pt and S (C), Rh and As (D), Rh and S (E), and of As and S (F) (in atoms per formula unit, apfu: \(\Sigma\) atoms = 3) in EMPA compositions of rhodian sulfurian sperrylite from the Imandra complex (filled symbol: this study). Compositions of the sperrylite–hollingworthite series from the Nomgon complex, Mongolia, also are plotted for comparison [open symbol: compositions after Izokh & Mayorova (1990). The trends, regressions and values of correlation coefficients $R$ shown on these plots: this study].](image-url)
present in micro-aggregates among the other PGM (e.g., Figs. 2B, C).

**PGE-rich pyrite**

The average composition of PGE-rich pyrite (Fig. 3) is Fe 35.74, Ru 10.96, Os 0.98, Ir 0.54, S 51.71, for a total of 99.93 wt.%, which corresponds to the formula \((\text{Fe}_{0.81}\text{Ru}_{0.14}\text{Os}_{0.007}\text{Ir}_{0.004})/\text{H}_{0.96}\text{S}_{2.04}\) (WDS data; JEOL–733 microprobe: this study). Pt and As were not detected (minimum detection-limits: \(\leq 0.1\) wt.%).

**Hollingworthite**

Hollingworthite commonly occurs as submicrometric grains (less than 5 \(\mu\)m) among cluster- and chain-like micro-aggregates of PGM enclosed in hydrous silicates. Typically, it is close to stoichiometric RhAsS in composition: e.g., Rh 47.84, Pt 0.49, Ir not detected, As 36.15, S 15.52, and total 100.0 wt.%, with a formula \((\text{Rh}_{0.97}\text{Pt}<0.01)/\text{H}_{0.97}\text{As}_{1.01}\text{S}_{1.01}\).

**Nickelian platarsite (?)**

Tiny grains (up to 15 \(\mu\)m long) of a Pt–Ni sulfarsenide occur at the contact of chromite with hydrous silicates or are enclosed within them. Such grains may contain unidentified micro-inclusions, and there are signs of a late alteration of these grains along their contact with the host silicates. A part of such grain, which is 3 × 2 \(\mu\)m in size, was analyzed (SEM/EDS). This area appears quite homogeneous in back-scattered electron imaging and consists of a secondary Pt–Ni sulfarsenide, probably nickelian platarsite of composition Pt 52.51, Ni 5.75, Co 1.10, S 10.66, As 31.34, and total 101.36 wt.%. The corresponding formula is \((\text{Pt}_{0.71}\text{Ni}_{0.26}\text{Co}_{0.05})/\text{H}_{1.02}\text{As}_{1.10}\text{S}_{0.88}\), which implies the existence of a solid solution between platarsite \((\text{PtAsS})\) and gersdorffite–cobaltite \((\text{Ni,Co})\text{AsS}\). An excess in As is observed in this phase, relative to the As:S ratio of 1.00, and is consistent with the presence of a minor component of NiAs2 (rammelsbergorite or pararammelsbergorite), which is quite common in natural and synthetic gersdorffite. Alternatively, this increase in the As:S ratio points to the presence of the sperrylite \((\text{PtAs}_2)\) component.

**Daomanite**

Daomanite is present as rare submicrometric subhedral grains enclosed by hydrous silicates (Fig. 2D). Its composition agrees very well with the ideal formula \(\text{PtCuAsS}_2\), and is consistent with the existence of a minor substitution of Pt for Cu (Table 4). This occurrence of daomanite at Imandra is the only reported locality outside China, where it occurs in Cu–Co–(Pt)-rich veins enriched in bornite and chalcopyrite associated with a garnet amphibole pyroxenite and olivine pyroxenite (Yu 1986, 2001, Tin et al. 1981). Yu et al. (1978) proposed that daomanite could have formed by the replacement of bornite. This mode of formation is very unlikely for the subhedral daomanite from Imandra (Fig. 2D).

**Cooperite**

A subhedral crystal of cooperite \((ca. 5 \mu\)m in the longest dimension) occurs at the contact of chrome with a hydrous silicate and has the composition Pt 82.78, Pd 1.31, Ni 0.53, S 14.76, and total 99.38 wt.%, corresponding to a formula of \((\text{Pt}_{0.94}\text{Pd}_{0.03}\text{Ni}_{0.02})/\text{H}_{0.99}\text{S}_{1.02}\).

**Isoferroplatinum or ferroan platinum**

A Pt3Fe-type alloy \(<5 \mu\)m in size), either isoferroplatinum or ferroan platinum, forms an intergrowth with laurite–erlichmanite, within grains of chromite. The composition of this alloy is Pt 88.88, Rh 1.92, Fe 9.20, for a total of 100.0 wt.% and the formula is \((\text{Pt}_{0.85}\text{Rh}_{0.12})/\text{H}_{2.97}\text{Fe}_{1.03}\). The identification requires powder X-ray-diffraction data (Cabri & Feather 1975), which could not be obtained owing to its small grain-size.

### Table 3. Average Composition of unnamed Cu,Ni,Co,Pt,S, from the Imandra Layered Complex, Kola Peninsula, Russia

<table>
<thead>
<tr>
<th>Element</th>
<th>Average Composition</th>
<th>Range</th>
<th>Atom proportions</th>
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<tbody>
<tr>
<td>Pt</td>
<td>53.56 (49.87–56.64)</td>
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<td>Cu: 0.05</td>
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<tr>
<td>Ru</td>
<td>1.85 (0–4.28)</td>
<td></td>
<td>Fe: 0.07</td>
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<tr>
<td>Ir</td>
<td>0.94 (0–2.43)</td>
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<tr>
<td>Co</td>
<td>12.10 (11.04–12.40)</td>
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</tr>
<tr>
<td>Ni</td>
<td>4.27 (3.47–4.91)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>25.19 (24.26–25.71)</td>
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</tr>
<tr>
<td>Total</td>
<td>99.74</td>
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### Table 4. Composition of Daomanite from the Imandra Complex, Kola Peninsula, Russia

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<th>Element</th>
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<td>19.30</td>
</tr>
</tbody>
</table>

1. Daomanite from the Imandra complex, Russia (this study).
2. Daomanite from the Yanshan region, China (Yu 1986).

Atom proportions are based on a total of 5 atoms per formula unit (apfu).
Rh2S5 was reported to be of a “pseudopyrite type” and...
**Unnamed Cu(Ni,Co)PtS₈ and related synthetic phases**

This complex chalcogenide is similar to thiospinels in composition (Table 3), and its formula might be written as $(\text{Cu}_0.93\text{Fe}_{0.07})_2\text{Pt}_4\text{S}_8$, which is monoclinic, space group $P2/n$ (Gross & Jansen 1994). This revision of the ideal formula is consistent with the following observations: (1) It is known that natural thiospinels of Cu and PGE form very broad ranges of mutual solid-solutions in the system $\text{CuRh}_2\text{S}_4–\text{CuIr}_2\text{S}_4–\text{CuPt}_2\text{S}_4$. However, thiospinels close to end-member $\text{CuPt}_2\text{S}_4$ are lacking (e.g., Barkov et al. 1997 and references therein). (2) No synthetic $\text{CuPt}_2\text{S}_4$ having a spinel-type structure has been reported; instead, monoclinic $\text{Cu}_2\text{Pt}_4\text{S}_8$ occurs at this ideal composition (Gross & Jansen 1994). In contrast, the thiospinels $\text{CuRh}_2\text{S}_4$ and $\text{CuIr}_2\text{S}_4$ have been synthesized and are characterized widely in the literature. Thus, a miscibility gap may exist close to $\text{CuPt}_2\text{S}_4$ in the system $\text{CuRh}_2\text{S}_4–\text{CuIr}_2\text{S}_4–\text{CuPt}_2\text{S}_4$. (3) The content of Pt in the unnamed phase at Imandra is 2.8 $\text{apfu}$ (Table 3), which is close to 3 $\text{Pt}^{4+} \text{apfu}$ in monoclinic $\text{Cu}_2\text{Pt}_4\text{S}_8$. This correspondence implies that Ni$^{2+}$ and Co$^{2+}$ substitute for Pt$^{2+}$ in the Imandra phase, and that the likely structural formula is $\text{Cu}_x\text{Ni}_y\text{Co}_z\text{Pt}_2\text{S}_8$.

In the absence of structural data, the reported synthetic phases $\text{CuPt}_2\text{S}_4$ (Evstigneeva 1994) and $\text{Cu}(\text{Pt},\text{Ni})_2\text{S}_4$ (Peregoedova & Ohnenstetter 2002) may be, in fact, monoclinic $\text{Cu}_2\text{Pt}_4\text{S}_8$ and $\text{Cu}_2\text{Pt}_2\text{Ni}_2\text{S}_8$, and related to the monoclinic copper thioplatinate of Gross & Jansen (1994). It is noteworthy that the composition of the PGM (two grains) in Peregoedova & Ohnenstetter (2002) is $(\text{Cu}_{0.74}\text{Fe}_{0.26})_2\text{Pt}_2\text{Ni}_{0.13}\text{Fe}_{0.87}\text{S}_8$, and $\text{Cu}_2\text{Pt}_2\text{Ni}_{0.47}\text{Fe}_{0.53}\text{S}_8$ (Tikhomirova et al. 1999a). Sperrylite has also been obtained from the Kirakajupitsepp deposit in the Penikat complex, Finland (Barkov et al. 1999a).

The textural observations indicate that most of the PGM (namely sperrylite, unnamed $\text{Cu}_2(\text{Ni,Co})\text{Pt}_3\text{S}_8$, rhodian sulfurian sperrylite, hollingworthite, nickelian platarsite, PGE-rich pyrite, daomanite, and cooperite) were deposited during deuteric alteration at a postmagmatic-hydrothermal stage of crystallization of the chromitite layer. The presence of $\text{Cl}$ in this environment is evident from the high levels of $\text{Cl}$ in apatite associated with the PGM (up to 3.45 wt.% $\text{Cl}$). The enrichment in volatile species presumably facilitated crystallization of the PGM. Though Pt-rich sulfides (cooperite and braggite) crystallize under dry conditions at submagmatic temperatures of $\leq 1000^\circ\text{C}$ (Cabri et al. 1978), a Pt-rich sulfide has been successfully synthesized from a low-temperature solution at $<100^\circ\text{C}$ (Tarkian et al. 1996). Sperrylite has also been obtained by hydrothermal synthesis at $300^\circ\text{C}$ (Tikhomirova & Chichagov 2000). Synthetic $\text{CuPt}_2\text{S}_4$ (monoclinic $\text{Cu}_2\text{Pt}_3\text{S}_8$), which may be related to unnamed $\text{Cu}_2(\text{Ni,Co})\text{Pt}_3\text{S}_8$ from Imandra, was found to precipitate from low-temperature solutions at $350^\circ\text{C}$, and to form a rim around synthetic cooperite, $\text{PtS}$ (Evstigneeva 1994).
Laurite–erlichmanite forms micro-inclusions in chromite at Bol’shaya Varaka, similarly to laurite from other chromitites in a variety of geological settings. However, these laurite inclusions are generally less abundant than the laurite–erlichmanite grains located in contact with chromite grain margins in hydrous silicates or enclosed within hydrous silicates. Also, the larger grains of laurite were observed at the chromite grain boundaries, but submicrometric laurite is also present in the cluster-like micro-aggregates of PGM within the Mg-rich hydrous silicates and in close association with in the late-stage sperrylite, hollingworthite, Ru–Os–Ir-rich Mg-rich hydrous silicates and in close association with boundaries, but submicrometric laurite is also present.

Hydrothermal laurite–erlichmanite

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APPENDIX 1. ANALYTICAL METHODS

Wavelength-dispersion (WDS) electron-microprobe analyses of hydrous silicates and chromite were carried out using a JEOL–733 electron microprobe. The operating conditions were 15 kV and 15 nA, and the following X-ray lines and standards were used: Si Kα (wollastonite), Ca Kα (periclase), Mg Kα (orthoclase), Na Kα (jadeite), Al Kα (synthetic Al2O3), Ti Kα (rutile), Fe Kα, Cr Kα, V Kα, Ni Kα, Mn Kα (pure elements), and Cl Kα (KCl).

The WDS analysis of a PGE-rich pyrite was made using a JEOL–733 instrument operated at 20 kV and 15 nA. A finely focused beam and the following lines and standards were used: Ru Lα, Pt Lα, Os Lα, Ir Lα (pure metals), Fe Kα, and SKα (FeS2). The raw data were ZAF-corrected on line.

Energy-dispersion (EDS) electron-microprobe analyses of hydrous silicates, base-metal sulfides and various PGM were carried out at 15 kV and 1.7 nA, using a JEOL JSM–6400 scanning-electron microscope (SEM) equipped with a LINK eXL energy-dispersion spectrometer. The Kα line and the following set of standards were used for hydrous silicates: SiO2, apatite, MgO, orthoclase, jadeite, Al2O3, KCl, and pure Ti, Fe, and Cr. Most of the reported compositional data are based on results of quantitative SEM/EDS analyses; the choice of this method was influenced by the very small grain-size of the PGM. The following set of standards was used for the PGM: Pt, Ru, Os, Ir, Pd (pure metals), Rh (synthetic RhSb), Co, Ni, Cu (pure metals), Fe, S (FeS2), and As (PtAs2). The M X-ray line was used for Pt and Ir. The L line was used for Ru, Rh, and As. The K line was used for Fe, Co, Ni, Cu, and S. The spectra were processed by a LINK ISIS on-line program. If the analyses of PGM gave a total higher than 102 wt.% or slightly lower than 98 wt.%, they were normalized to 100%. The counting periods were 100 s, and a finely focused beam (ca. 1 μm) was used in all of the EDS analyses.