Palladosilicide, \( \text{Pd}_2\text{Si} \), a new mineral from the Kapalagulu Intrusion, Western Tanzania and the Bushveld Complex, South Africa

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ABSTRACT

Palladosilicide, \( \text{Pd}_2\text{Si} \), is a new mineral (IMA 2014-080) discovered in chromite-rich samples from the Kapalagulu intrusion, western Tanzania (30°03′51″E 5°53′16″S and 30°05′37″E 5°54′26″S) and from the UG-2 chromitite, Bushveld complex, South Africa. A total of 13 grains of palladosilicide, ranging in size from 0.7 to 39.1 μm (equivalent circle diameters), were found. Synthetic \( \text{Pd}_2\text{Si} \) is hexagonal, space group \( \text{P}6\overline{2}2\text{m} \), with \( a = 6.496(5) \), \( c = 3.433(4) \) Å, \( V = 125.5(1) \) Å\(^3\), \( c:a = 0.529 \) with \( Z = 3 \). The strongest lines calculated from the powder pattern (Anderko and Schubert, 1953) are \([d \text{ in Å} (I) (hkl)]\) 2.3658 100 (111); 2.1263 37 (120); 2.1808 34 (021); 3.240 20 (110); 1.8752 19 (030); 1.7265 12 (002); 1.3403 11 (122); 1.2089 10 (231). The calculated density for three analyses varies from 9.562 to 9.753 g cm\(^{-3}\). Palladosilicide is considered to be equivalent to synthetic \( \text{Pd}_2\text{Si} \) based on results from electron backscattered diffraction analyses. Reflectance data in air for the four Commission on Ore Mineralogy wavelengths are \([\lambda \text{ nm, } R_1(\%) R_2(\%)]\) 470 49.6 52.7; 546 51.2 53.8; 589 51.6 53.7; 650 51.7 53.3 and the mineral is bright creamy white against chromite, weakly bireflectant and displays no discernible pleochroism or twinning. It is weakly anisotropic, has weak extinction and rotation tints in shades of blue and olive green. Electron probe microanalyses of palladosilicide yield a simplified formula of \( \text{Pd}_2\text{Si} \).

KEYWORDS: new mineral, palladosilicide, silicide, platinum-group minerals, platinum-group elements, Kapalagulu intrusion, Tanzania, UG-2, Bushveld complex, South Africa, palladium-silicon binary.

Introduction

PALLADOSILICIDE (\( \text{Pd}_2\text{Si} \)) is a new mineral, discovered recently in two different localities. One was the Platinum-Group Element (PGE)-chromite horizon of the Kapalagulu Intrusion near the eastern shore of Lake Tanganyika, western Tanzania, with the mineral being discovered in diamond drill cores KPD 044 (30°03′51″E 5°53′16″S; sample D396) and KPD 024 (30°05′37″E 5°54′26″S; sample 10369), and from the UG-2 chromitite, Bushveld Complex, RSA. In both cases the mineral was discovered in heavy-mineral concentrates collected for detailed quantitative mineralogical investigations associated with mineral processing and optimization.

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of PGE recovery; details regarding these concentrates were reported by Cabri (2004) for the Tanzanian samples and from a flotation tailing for the UG-2 chromitite by Cabri et al. (2008).

Disseminated copper and nickel sulfide in harzburgite near the base of the Kapalagulu Intrusion has been known for over a century. The Kapalagulu Intrusion lies near the eastern shore of Lake Tanganyika in Western Tanzania and forms part of a series of mafic intrusions that include Musongati and Kabanga, known as the Central African Nickel Belt (Fig. 1). In the late 1990s, Broken Hill Proprietary found Pt-Pd mineralization associated with Ni-bearing lateritic regolith. During 2002 and 2003, Goldstream Mining, in partnership with Lonmin plc, identified sulfide-chromitite horizons in harzburgite below the lateritic regolith that contain PGE with grades of between 1 and 12 g/t PGE (Wilhelmij and Joseph, 2004). The PGE horizons are is located in the Lower Ultramafic Sequence of the Kapalagulu Intrusion that is preserved in a dyke-like extension to the Upper Mafic Sequence, known as the Lubalisi Zone (Fig. 2).

![Fig. 1. Location of the Kapalagulu Intrusion with respect to other intrusions of the Central African nickel belt (after Maier et al., 2008).](image-url)
The upper Critical Zone of the Bushveld Complex hosts the largest concentration of PGE in the world (Schouwstra et al., 2000). The UG-2 Reef is a PGE-bearing chromitite layer, usually 1 m thick but can vary from ~0.4 to 2.5 m, developed some 20–400 m below the better-known Merensky Reef (Schouwstra et al., 2000). A comprehensive review of the UG-2 may be found in Cawthorn (2002).

Mineral name and type material

The mineral is named after the two essential chemical components, palladium and silicon. The mineral and name were approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification on 3 December, 2014 (IMA 2014-080, Cabri et al., 2015). Part of the holotype has been deposited in the collections of the Canadian Museum of Nature, Gatineau, Québec, Canada, catalogue number CMNMC 86891.

Occurrence and associated minerals

Palladosilicide was found in samples from both localities in monolayer polished sections of high-grade gravity concentrates made with an early-model manual hydroseparator (HS-02) by one of us (NSR); see for example, Rudashevsky et al. (2004) and McDonald et al. (2015) who report a large number of platinum-group minerals (PGM) from the Coldwell complex (Ontario) found by using the newer computer-operated model hydroseparator (HS-11).

A total of 13 grains of palladosilicide were found, ranging in size from 0.7 to 39.1 μm (equivalent circle diameters, ECD), four of which, found in the Tanzanian samples, were imaged (Fig. 3). They came from two unoxidized samples, both 30 cm long: DDH KPD044 KPD024.
The mineralogical study of pristine sulfide-bearing samples as well as oxidized samples from the regolith will form part of a future publication (by Wilhelmij and Cabri).

Common heavy minerals in the samples include chromite, pentlandite, pyrrhotite/troilite; minor minerals were chalcopyrite and magnetite; and rare to trace minerals include gudmundite, arsenopyrite, zircon, galena and anglesite. Six of the palladinosilicide grains were free; the others were either attached to chromite (n = 5) or locked in chromite (n = 2). The total frequency of precious-metal minerals found in the three samples ranged from 93 for sample D396 to 137 for sample 10369, which included some found during image analysis of unconcentrated sample splits. Table 1 illustrates a typical range of precious-metal minerals found in heavy-mineral concentrates with their relative abundances for sample 10369.

The concentrates of the UG-2 tailing sample are dominated by chromite with a few PGM comprising free laurite (ideally RuS₂) particles, a graphic intergrowth of tetraferroplatinum (ideally PtFe) in pyrrhotite, isoperroplatinum (ideally Pt₃Fe) included in pentlandite, sobolevskite (ideally PdBi₂) attached to a larger particle of orthopyroxene, and a smaller (3.8 μm ECD) inclusion of kotulskite (ideally PdTe) included in an undefined Cu-Ag telluride (22.2 μm ECD), which is itself attached to a larger particle of chromite. A single free particle of palladinosilicide measuring 39.1 μm in size (ECD) with an unidentified Pd-Sn mineral (taimyrite?) 6.3 μm in size (ECD) and undetermined very small bright metallic inclusions (maximum width ~1 to 3 μm) were found after preparing additional concentrations.

Fig. 3. BSE images of four grains of the Pd silicide from the Kapalagulu intrusion.
Physical and optical properties

Palladosilicide appears bright creamy white in reflected light against the surrounding plastic, grains of chromite, and its inclusions of a Pd-(Cu)-Sn mineral (taimyrite?), unknown 1 (grey) and unknown 2 (bright white), as shown in Fig. 4. The two unknown inclusions are not visible on the earlier scanning electron microscopy-backscattered electron (SEM-BSE) image (Fig. 3) but appeared after repolishing, along with a larger area of the Pd-(Cu)-Sn mineral. Palladosilicide has an anhedral to subhedral habit, a metallic lustre, is weakly bireflectant and displays no discernible reflection pleochroism or twinning. It is weakly anisotropic, has a weak extinction and rotation tints in shades of light blue and olive green. Micro-indentation hardness could not be measured due to small grain size. Tenacity and streak were not determined, and cleavage, partings and fracture were not observed in reflected light.

Reflectance spectra were measured relative to a WTiC standard (Zeiss 314) on the grain from UG-2 in air and oil following the methodology of Stanley et al. (2002) and are shown in Fig. 5; the colour values are listed in Table 2 and reflectance data in Table 3. No internal reflections were noted.

Chemical composition

Chemical analyses were made using energy dispersive spectroscopy (EDS) and a Camscan Microspec-4DV SEM with a Link AN-10000 detector. The operating conditions included an accelerating beam voltage of 30 kV, a beam current of 1–2 nA, a beam diameter of 1 μm and

| Mineral                  | Frequency | Mass % | Volume % |
|--------------------------|-----------|--------|----------|
| Ag>Au alloy              | 1         | 0.0    | 0.0      |
| Atokite                  | 3         | 6.9    | 6.9      |
| “electrum”               | 5         | 20.7   | 16.1     |
| Genkinite                | 1         | 0.1    | 0.1      |
| Isoferroplatinum         | 1         | 0.4    | 0.2      |
| Keithconnite             | 3         | 0.1    | 0.1      |
| Kotulskite               | 3         | 4.2    | 4.6      |
| Mertieite-II             | 11        | 10.6   | 10.8     |
| Moncheite                | 42        | 14.4   | 16.1     |
| Palladium                | 2         | 0.7    | 0.5      |
| Palladosilicide          | 4         | 2.5    | 2.8      |
| Platinum                 | 2         | 0.1    | 0.2      |
| Sobolevskite             | 2         | 5.5    | 5.3      |
| Sperrylite               | 21        | 31.8   | 33.8     |
| Stibiopalladinite        | 19        | 0.8    | 0.8      |
| Sudburyite               | 1         | 1.3    | 1.6      |
| Vysotskite               | 2         | 0.0    | 0.0      |
| Total                    | 123       | 100    | 100      |

Table 1. Precious-metal minerals in heavy-mineral concentrates from Kapalagulu (sample 10369).

Fig. 4. Images of palladosilicide from UG-2: (a) BSE image of Pd silicide with inclusion of a Pd-(Cu)-Sn mineral and (b) reflected light photomicrograph of the same grain after re-polishing showing more inclusions (1 and 2), as well as the Pd-(Cu)-Sn mineral with a larger surface area.
counting times of 50–100 s. Standards used were Si, diopside CaMgSi$_2$O$_6$; As, InAs; other elements, pure metals.

The analyses of three grains from the Kapalagulu intrusion gave close to stoichiometric compositions (based on three atoms): (Pd$_{1.75}$Ni$_{0.20}$Cu$_{0.08}$Fe$_{0.01}$Sn$_{0.03}$Pt$_{0.02}$)$_{2.11}$ (Si$_{0.72}$As$_{0.16}$)$_{0.88}$ (shown in Fig. 3); (Pd$_{1.53}$Ni$_{0.23}$Pt$_{0.07}$Sn$_{0.07}$Cu$_{0.05}$Fe$_{0.03}$)$_{2.18}$ (Si$_{1.02}$) (shown in Fig. 3); and (Pd$_{1.62}$Ni$_{0.23}$Cu$_{0.05}$Pt$_{0.07}$)$_{2.21}$ (Si$_{0.96}$As$_{0.03}$)$_{0.99}$ (shown in Fig. 2), as well as on one grain from the UG-2 sample (Pd$_{1.61}$Ni$_{0.22}$Cu$_{0.08}$Sn$_{0.05}$Pt$_{0.03}$)$_{2.01}$ (Si$_{0.90}$As$_{0.12}$)$_{1.02}$ (shown in Fig. 4). Although Ag, Se, Sb, Te, Au, Pb and Bi were sought in sample 10369 (grains 6 and 18) and sample D396 (grain 21), these elements were not detected. For the UG-2 grain, Sb was sought and not detected.

Electron-microprobe analyses (wavelength dispersive spectroscopy mode) were later carried out on two grains with a JEOL 8900L electron microprobe at CANMET-MMSL in Ottawa (Table 4). Operating conditions were, 20 kV accelerating current, 40 nA beam current, 1 μm spot size, raw data were corrected using a ZAF matrix correction. The following standards and analytical lines were used: SiKα, Si metal; CrKα, chromite; PdLα, Pd metal; AgLβ, Au$_{60}$Ag$_{40}$; SKα, pyrite; SeLα, Se metal; NiKα, NiSb; TeLα, Te metal; PKα, apatite; SbLα, NiSb; AsLα, FeAs$_2$; FeKα, pyrite; PtMα, Pt metal; SnLα, Sn metal; PbMα, galena; CuKα, chalcopryte; RhLα, Rh metal. Counting times were 20 s peak and 10 s background on both sides, except for Pd and Pb which were measured for 50 s peak and 25 s

| Table 2. Colour values for palladosilicide (UG-2). |
| --- | --- | --- | --- |
| A illuminant | | | |
| $x$ | 0.451 | 0.448 | 0.451 | 0.449 |
| $y$ | 0.41 | 0.41 | 0.41 | 0.41 |
| $\gamma$% | 51.3 | 53.6 | 37.6 | 39.4 |
| $\lambda_d$ | 583 | 576 | 582 | 579 |
| $P_e$% | 3.9 | 2.1 | 4.2 | 3 |

| C illuminant | | | |
| --- | --- | --- | --- |
| $x$ | 0.315 | 0.312 | 0.315 | 0.313 |
| $y$ | 0.322 | 0.321 | 0.323 | 0.322 |
| $\gamma$% | 51.2 | 53.6 | 37.5 | 39.4 |
| $\lambda_d$ | 573 | 567 | 572 | 569 |
| $P_e$% | 2.8 | 1.8 | 3.2 | 2.4 |

300
The small grain size and the presence of inclusions precluded the analysis of palladosilicide by standard powder X-ray diffraction (XRD) methods. The crystallographic properties of the mineral were thus studied by electron backscattered diffraction (EBSD). Preliminary SEM-EDS analyses of the grain selected for EBSD analysis (Grain 6, 10369 45-1) confirm major Pd and Si, along with trace Ni, Pt, As and Sn. The grain studied was found to contain submillimeter inclusions, representing perhaps 5% of the total area, of an unidentified Sn-bearing Ag telluride.

**Table 4. Electron probe microanalyses (EPMA) results.**

| LOD (ppm) | Ideal wt.% | Kapalagulu (sample D395 45-75 1a) | UG-2 (Ct-2) |
|-----------|-------------|-----------------------------------|-------------|
| Si        | 204         | 11.66                             | n/a         |
| Pd        | 244         | 88.34                             | n/a         |
| Ag        | 1478        | 1.84                              | n/a         |
| Ni        | 384         | 4.70                              | n/a         |
| Te        | 456         | 0.47                              | n/a         |
| Sb        | 553         | 0.33                              | n/a         |
| As        | 652         | 3.66                              | n/a         |
| Fe        | 366         | 0.65                              | n/a         |
| Pt        | 753         | 1.85                              | n/a         |
| Sn        | 350         | 1.85                              | n/a         |
| Cu        | 525         | 2.02                              | n/a         |
| Rh        | 431         | 2.52                              | n/a         |

| Totals    | 100.00      | 98.44                             | 99.94       |

**Notes:**
- LOD: Limits of detection; St. dev: standard deviation.
- First analysis.
- Average of 8 analyses. After the first analysis the epoxy softened, the grain tilted and became covered with epoxy resulting in low totals.
The EBSD analyses were carried out on grain 6 (10369 45-1) from Kapalagulu with a JEOL 6400 SEM equipped with an HKL EBSD system (HKL Technology Inc., Oxford Instruments Group), an accelerating voltage of 20 kV, a beam current of 2.4 nA and a sample-to-camera working distance of 130 mm. The system was calibrated using a crystal of synthetic Si. Care was taken to avoid collecting EBSD (Kikuchi) patterns from those areas proximal to the Ag-Te inclusion (Fig. 6). Frames were collected for 20 ms, with 64 frames per image, both being selected so as to mitigate degradation of the epoxy surrounding the grain, this being found to be quite unstable under the electron beam. Channel5 software (Oxford Instruments; Day and Trimby, 2004) was used to collect Kikuchi (EBS) patterns along with pattern matching and interpretation (Fig. 7). Note that the Kikuchi patterns from three subareas were found to be near identical, indicating that all three areas are nearly identical in crystallographic orientation and thus that the grain being studied is presumably close to being single.

From each of the Kikuchi patterns obtained \((n = 3)\), seven strong bands were selected manually and used for matching purposes.

### Table 5. Atoms per formula unit for two grains analysed by EPMA.

|          | Kapalagulu (D395 45-75 1a) Anal #1 | UG-2 (Ct-2) |          |
|----------|-----------------------------------|-------------|----------|
|          | \(n = 8\)                         | \(n = 12\)  |          |
| Pd       | 1.636                             | 1.657       | 1.557    |
| Ni       | 0.199                             | 0.201       | 0.212    |
| Cu       | 0.079                             | 0.088       | 0.061    |
| Rh       | 0.061                             | 0.06        | 0.088    |
| Fe       | 0.029                             | 0.029       | 0.015    |
| Ag       | 0.042                             | 0.026       | 0.007    |
| Pt       | 0.024                             | 0.023       | 0.055    |
| Sn       | 0.039                             | 0.039       | 0.063    |
| Sum      | 2.109                             | 2.123       | 2.058    |
| Si       | 0.753                             | 0.728       | 0.869    |
| As       | 0.121                             | 0.136       | 0.07     |
| Sb       | 0.007                             | 0.008       | 0.002    |
| Te       | 0.009                             | 0.006       |          |
| Sum      | 0.890                             | 0.878       | 0.941    |
| 3 Atoms  | 2.999                             | 3.001       | 2.999    |
| \(D (g \text{ cm}^{-3})\) | 9.718                             | 9.753       | 9.562    |

**Fig. 6.** BSE images of grain 6 (sample 10369) and X-ray maps. a1 = BSE location map in hydroseparation concentrate; a2 = higher magnification BSE image of grain 6; the X-ray maps (b to j) are mirror images of a2. The Sn-bearing Ag-Te inclusion (bright areas in a2) shown in h, i and j has an approximate composition of \(\text{Ag}_{0.65}\text{Te}_{0.35}\), which corresponds to either hessite (\(\text{Ag}_2\text{Te}\)) or stützite (\(\text{Ag}_{5-\delta}\text{Te}_3\)).
Matching was accomplished through comparison with Kikuchi patterns calculated for synthetic Pd$_2$Si, along with those for a number of synthetic phases having similar stoichiometries, including (with the corresponding International Crystal Structure Database, ICSD, number) Pd$_2$B (ICSD 615207), Pd$_2$N (ICSD 96418), Pd$_2$As (ICSD 26279), Pt$_2$Si (ICSD 77973), Ni$_2$S (hexagonal, ICSD 105342) and Ni$_2$S (orthorhombic, ICSD 165257). Matches were evaluated on the basis of MAD (mean angular deviation), which is a measure of the misfit (in degrees) between observed and simulated Kikuchi bands. In general, MAD values <1 indicate reasonable matches between the Kikuchi patterns obtained for an unknown and that calculated for a material. Through the evaluation undertaken in this study, only the match with the Kikuchi pattern calculated for Pd$_2$Si was found to give a MAD value <1, in this case, 0.34. The MAD values for all other matches were found to be large (all being >1, most >2) and the phases from which they were calculated were disregarded. Given its stoichiometry and small MAD value, palladosilicide is thus considered to be isostructural with synthetic, metal-rich Pd$_2$Si and structurally, could be considered as the Pd-Si analogue of barringerite (Fe,Ni)$_2$P (Buseck, 1969).

The crystal structure of synthetic, metal-rich Pd$_2$Si (Fe$_2$P type) has been solved and refined to $R = 9.2\%$ (Nylund, 1966). It has Pd in the 3f and 3g positions, with Si in the 2c and 1b sites.

Calculated cell data based on synthetic, metal-rich Pd$_2$Si (Nylund, 1966) are as follows: Hexagonal, space group $P\bar{6}2m$, $a = 6.496(5)$ Å, $c = 3.433(4)$ Å, $V = 125.5(1)$ Å$^3$, $c:a = 0.529$. Calculated and measured powder XRD data for metal-rich Pd$_2$Si are listed in Table 6. The density could not be measured due to the small size of the grain being studied. Density (calc.) = 9.718 g cm$^{-3}$ [sample D395/6(1)], 9.753 g cm$^{-3}$ [D395/6(2)] and 9.562 g cm$^{-3}$ (sample Ct-2) using the derived empirical formulae; for sample numbers refer to Table 5.

**Synthesis**

The earliest account of the synthesis of Pd$_2$Si is by Buddery and Welsh (1951), which was subsequently determined to be isotypic with Fe$_2$P (C22 type) by Anderko and Schubert (1953). These findings were confirmed by Grigorev et al. (1952). The Pd$_2$Si phase is reported to melt congruently at 1330°C, based on thermal analyses (Hansen and Anderko, 1958). The crystal structure of metal-rich Pd$_2$Si (revised C22 type) was reported, refined, to be hexagonal, space group $P\bar{6}2m$, $a = 6.496$, $c = 3.433$ Å and that of Si-rich Pd$_2$Si to have a superstructure [$a = 15.05(5)$ $c = 27.49(0)$ Å] by Nylund (1966). However, Nylund’s study was undertaken before electron microprobes became readily available. Phase equilibrium investigations usually require detailed metallographic studies together with XRD analyses in order to determine phase boundaries, tie lines and related information (e.g. Cabri, 1965). Note that Nylund reported that it was extremely difficult to achieve thermodynamic equilibrium, but this aspect was not discussed further.
Classification and other occurrences of metal silicides

In the Nickel-Strunz classification, the mineral belongs to Elements, metallic carbides, silicides, nitrides and phosphides, 01.BB Silicides, 01.BB.36 palladosilicide Pd$_2$Si, P6$_2$m. In the Dana classification, palladosilicide belongs to Suessite Group silicides, 01.01.23.08, palladosilicide Pd$_2$Si, P6$_2$m;
suessite (Fe, Ni)₃Si, gupeiite Fe₂Si, linzhiite FeSi₂,
naquite FeSi, xifengite Fe₄Si₃, hapkeite Fe₅Si,
lubousaite Fe₀.₃₃Si₂, mavlyanovite Mn₃Si₃ and
brownleite MnSi.

Natural examples of metal silicides are rare, the
first (suessite) having been reported from extra-
terrestrial objects (an olivine pigeonite achondrite,
also known as ‘ureilite’). Gupeiite and xifengite
were found as cores of spheres 0.1–0.5 mm in
diameter, in placers from the Yanshan area, Hebei
Province, People’s Republic of China (Yu, 1984).
They were found as heterogeneous grains, with
outer shells consisting of magnetite, wüstite and
maghemite, an inner shell of kamacite and taenite,
and the cores being either gupeiite or xifengite.
The minerals present and the morphology of the
spheres were thought to be extraterrestrial in
origin.

Rudashevskii et al. (2001) gives the first
account of several PGE-bearing, Fe- and Cu-
silicides that were found in ferromanganese crusts
that formed on the ocean floor in areas that were
almost completely sediment-free. They ascribed
formation of the base- and precious-metal silicides
to be related to emanations of highly reducing
fluids that accompanied basalt formation.

Iron silicides have also been characterized as
new minerals from podiform ophiolitic chromitites
at Luobusha, Tibet (Bai et al., 2006; Li et al.
2012a, b). Two of these minerals were first
reported by Gevorkyan (1969) and Gevorkyan
et al. (1969) in heavy-mineral concentrates from
placers and drill-core samples in sandstones from
the Ukraine and described as two new alloy
minerals (FeSi and FeSi₂), but without approval
by the then named Commission on New Minerals
and Mineral Names. Owing to their chemical
properties and mineral assemblage, the Luobusha
Fe silicides were considered to be xenocrysts
from the mantle, transported to shallow depths by
a rising plume and then captured by the melts
from which the Luobusha chromitites crystallized
(Bai et al., 2000; Yang et al., 2014).

Silicides may also form due to very high
temperatures (e.g. 1800°C) such as in ‘fulgurites’,
formed as a result of lightning strikes (e.g. Myers
and Peck, 1925).

Genetic implications and discussion

In the case of palladosilicide, which appears to be
the first report of a PGM silicide, there are a few
cues regarding its origin based on mineral
associations. A few of the palladosilicide grains
had some chromite attached and two were included
within chromite, strongly suggestive that the
mineral crystallized in association with or within
chromite. The chemistry and zoning of the
chromite itself has not been studied in this work. The
effect of highly reducing fluids during formation of
mantle-derived ultramafic rocks was discussed by
Rudashevskiy (1983), Rudashevskii (1984) and
Rudashevskiy and Yertsseva (1987). The formation
and evolution of different chromitite deposits was
recently reviewed and discussed by Mungall (2014);
this includes the questioning by Spandler et al.
(2007) of the popular interpretation that anomalous melt inclusions represent samples of
unmodified mantle melts. In light of the ease with
which some chemical components can diffuse
through chromite at magmatic temperatures, it is
possible that chromite may serve as a semi-
permeable membrane allowing some constituents
of the melt inclusions, but not others, to reach
equilibrium with ambient conditions (James
Mungall, pers. comm., 2014). As chromite itself
contains both Fe³⁺ and Fe²⁺, diffusive exchanges
involving both of these species driven by counter-
fluxes of other cations might lead to extreme
perturbations in fO₂ within melt inclusions. Some
grains of palladosilicide were found associated
with, and others included in, chromite, suggesting
that the mineral is paragenetically earlier than
chromite, probably forming under conditions of
very low fO₂. Similarly extremely reducing mineral
assemblages including moissanite (SiC), Fe–Si and
Fe–C phases have been reported from other
chromitites (e.g. Bai et al., 2006; Yang et al., 2014).

We anticipate that this first report of a
palladium silicide found in chromitite-rich facies
of layered PGE-bearing intrusions will lead to
further studies focused on understanding the
chemical-physical and thermodynamic conditions
directed to constraining the specific conditions
under which such minerals crystallize. The
presence of inclusions of a Ag telluride in one
case and of a Pd–(Cu)-Sn mineral plus much
smaller unidentified minerals in a second grain
also call for a better understanding of phase
equilibria in the Pd–Si–Ag–Te, Pd–Si–Sn and
Pd–Si–As systems, as well as re-investigation of
the Pd–Si binary.

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