

# New and unusual Pd-Tl-bearing mineralization in the Anomal'nyi deposit, Kondyor concentrically zoned complex, northern Khabarovskiy kray, Russia

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## ABSTRACT

New Pd-Tl-(Bi,As)-rich compounds are described from the Anomal'nyi Cu-PGE deposit, Kondyor alkaline ultramafic complex, northeastern Russia. They occur in vein-type settings associated with bodies of 'kosvite' (magnetite-rich clinopyroxenite) in the dunite-(peridotite) core, in pegmatitic and micaceous rocks. The ore zones are substantially enriched in phlogopite; they consist of diopside, disseminated titaniferous magnetite and fluorapatite (Sr-bearing). The observed assemblages of ore minerals include sulfides of the chalcopyrite-bornite-(secondary chalcocite) association and various species of platinum-group minerals (PGM) [isomertieite or arsenopalladinite rich in Sb, mertieite-II, mertieite-I, sobolevskite, kotulskite, merenskyite, zvyagintsevite, palarstanide, paalovite, sperrylite, maslovite or moncheite, hollingworthite and unnamed species of PGM] and a Ag-Au alloy. The oxides [Pd<sub>4</sub>(Bi,Te,Tl)O<sub>6</sub> and Pd<sub>4</sub>(Tl,Bi,Te)O<sub>6</sub>] probably formed *in situ* by oxidation reactions at the expense of the associated PGM intergrowths. These involve palladium bismuthide-thallide phases, Pd<sub>5</sub>(Tl,As,Bi) and Pd<sub>5</sub>(As,Tl,Bi), which are documented here for the first time. A fairly evolved environment, enriched in Cu, Pd, Te, Bi, Pb and volatile components, is indicated for the vein-type deposit at Anomal'nyi.

**KEYWORDS:** platinum-group elements, platinum-group minerals, Anomal'nyi PGE deposit, concentrically zoned complex, alkali-enriched ultramafic complex, Kondyor, Khabarovskiy kray, Russia.

## Introduction

THE zoned Kondyor ('Konder') alkaline ultramafic complex (Fig. 1a–e) is a well-known example of a platform analogue of the Uralian-Alaskan-type complexes. It is situated in far-eastern Russia, in northern Khabarovskiy kray, at the eastern margin of the Aldan Shield. Its host rocks consist of metamorphic and metasedimentary lithologies of

Archean and Late Proterozoic age, respectively. The complex displays a perfectly circular and zonal structure (Fig. 1a), with a dunite-(peridotite) core (~6 km in diameter), which accounts for about 90% of the complex. The core is surrounded by concentric zones of olivine clinopyroxenite, clinopyroxenite free of olivine, clinopyroxenite enriched in titaniferous magnetite, and melanocratic gabbro (e.g. Cabri and Laflamme, 1997; Nekrasov *et al.*, 2005, and references therein). The biotite in cross-cutting veins in dunite and in a dyke of 'kosvite' yielded identical <sup>40</sup>Ar/<sup>39</sup>Ar ages of 120 ± 1 Ma (Cabri *et al.*, 1998), which is inconsistent with an

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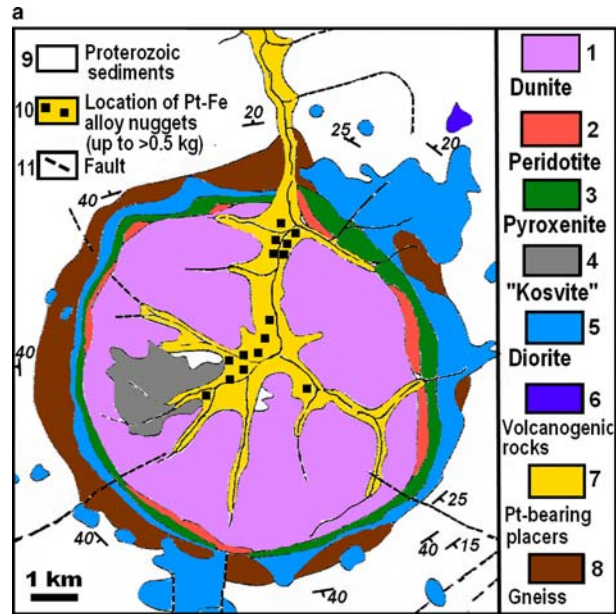


FIG. 1. (a) Geological sketch map of the Kondyor complex (after Cabri and Laflamme, 1997, and references therein). The 'kosvite' (or 'koswite') zone is a variety of magnetite-rich clinopyroxenite. This zone is, in fact, highly heterogeneous, sandwich-structured and is represented by a complex interlayering of 'kosvite' with the host dunite-(peridotite), and with the micaceous pegmatite-like mineralized rocks rich in phlogopite and apatite (see Fig. 1b). (b) A schematic geological cross-section of the Anomal'nyi area (after these data and observations made by A.A. Polonyankin, D.M. Gurevich and coworkers), which is based on a detailed investigation by borehole drilling (the location of borehole traverses is shown in Fig. 2d,e). (c–e) The location of the Kondyor complex in Russia (Fig. 1c) and of the Anomal'nyi PGE deposit associated with the 'kosvite' zone' within the dunite-(peridotite) core (Fig. 1d: 3D view map after NASA/GSFC/METI/ERSDAC/JAROS and U.S./Japan ASTER Science Team). Figure 1e shows the orientation of borehole traverses made in the Anomal'nyi area (after A.A. Polonyankin, D.M. Gurevich and coworkers).

upper Riphean (Proterozoic) age claimed for the dunite core (*cf.* Karetnikov, 2006).

In the Kondyor complex, the platinum-group element (PGE) mineralization is mostly associated *in situ* with segregations of chromian spinel. In addition, grains and unusually large nuggets of platinum-group minerals (PGM), some of which exceed 1.5 kg, occur in placers, eluvial and alluvial, related to this complex (e.g. Cabri and Laflamme, 1997; Shcheka *et al.*, 2004; Nekrasov *et al.*, 2005, and references therein). Several species of PGM were first discovered in the complex (Rudashevsky *et al.*, 1984, 1985, 1998; Mochalov *et al.*, 2007), and it remains a promising target for the discovery of new species or varieties.

Our aims in the present article are (1) to describe a newly discovered PGE deposit *in situ* at Anomal'nyi ('Anomalous') in the dunite core of the Kondyor complex and (2) to discuss the implications of the latest geological observations

and our mineralogical data obtained at the Anomal'nyi PGE deposit. The pattern of mineralization there involves unnamed phases of arsenide-bismuthide-thallide compositions and oxides of Pd, Bi, Te and Tl, which are hitherto unreported. This deposit differs strikingly from other PGE deposits associated with Kondyor and related complexes.

### Geological background in the Anomal'nyi area

Results of detailed borehole traverses, made recently in the Anomal'nyi area, are summarized in Fig. 1b; the location sketch-map is given in Fig. 1e. These data indicate that (1) the 'kosvite' zone, recognized within the dunite-(peridotite) core by previous investigators (Fig. 1a), is, in fact, highly heterogeneous. It is composed of complexly interlayered bodies of 'kosvite', which are partially discordant, have large dip angles, and are hosted by

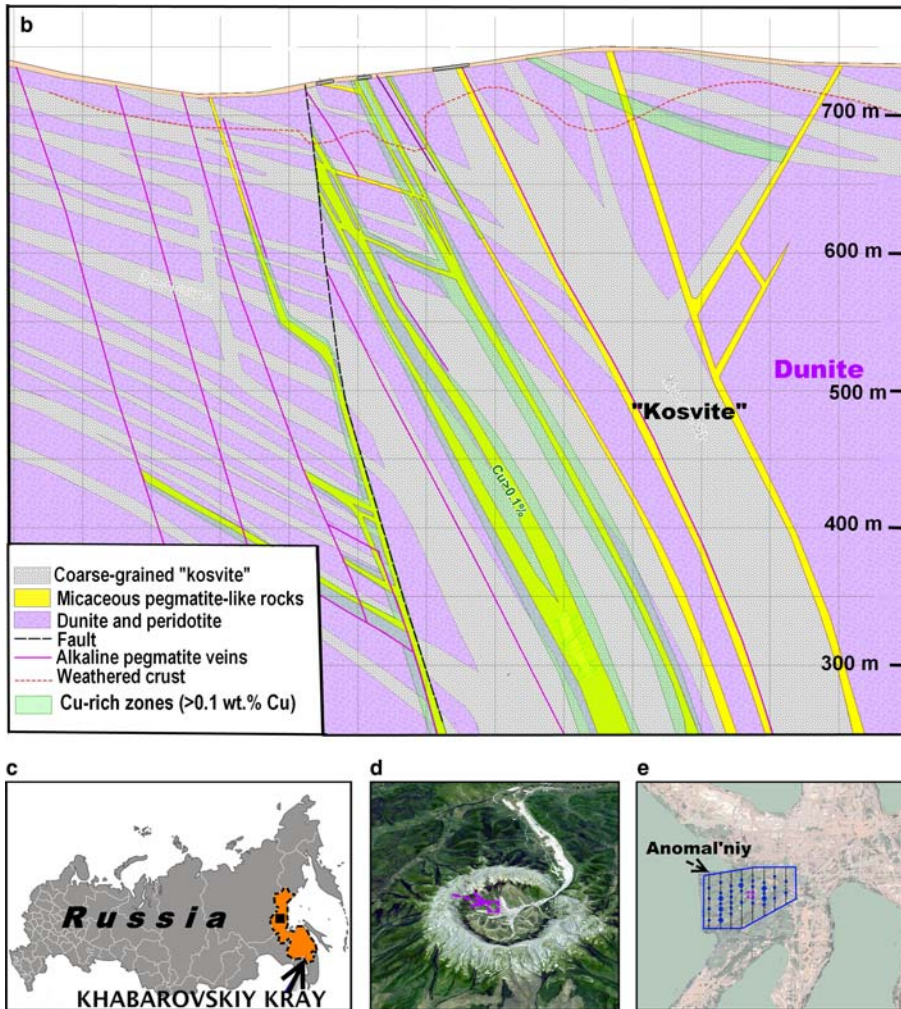


FIG. 1. Continued.

dunite that varies to peridotite. The name 'kovsite' (or 'kosvite'), after the Kos'vinskiy Kamen' complex in the northern Urals, pertains to a specific variety of magnetite-rich clinopyroxenite, or olivine-bearing clinopyroxenite (Duparc and Pearce, 1901). (2) The 'kovsite' rock commonly displays coarse-grained to pegmatitic grain-sizes. The 'kovsite' bodies are associated closely with a vein-like system of unusual orebodies; they are highly micaceous, up to ~20 m thick (Fig. 1b). The mineralized rock is coarse-grained to pegmatitic, anomalously rich in phlogopite, with a high content of apatite. The micaceous veins are especially rich in Cu, Pd and Pt; they consist of grains of base-metal sulfides (BMS), together with a variety of

PGM. (3) Veins of alkaline pegmatite also are present in the documented unit. Locally, these display discordant relations with the host, although they generally conform to the observed pattern of sandwich-structured interlayering of 'kovsite' with the phlogopite-rich orebodies and veins (Fig. 1b).

#### Mineral association observed at the Anomal'nyi Cu-PGE deposit

As noted, the presently discovered mineralization is developed within the dunite-(peridotite) core, in specific vein-type settings and zones associated with pegmatitic and micaceous mafic rocks

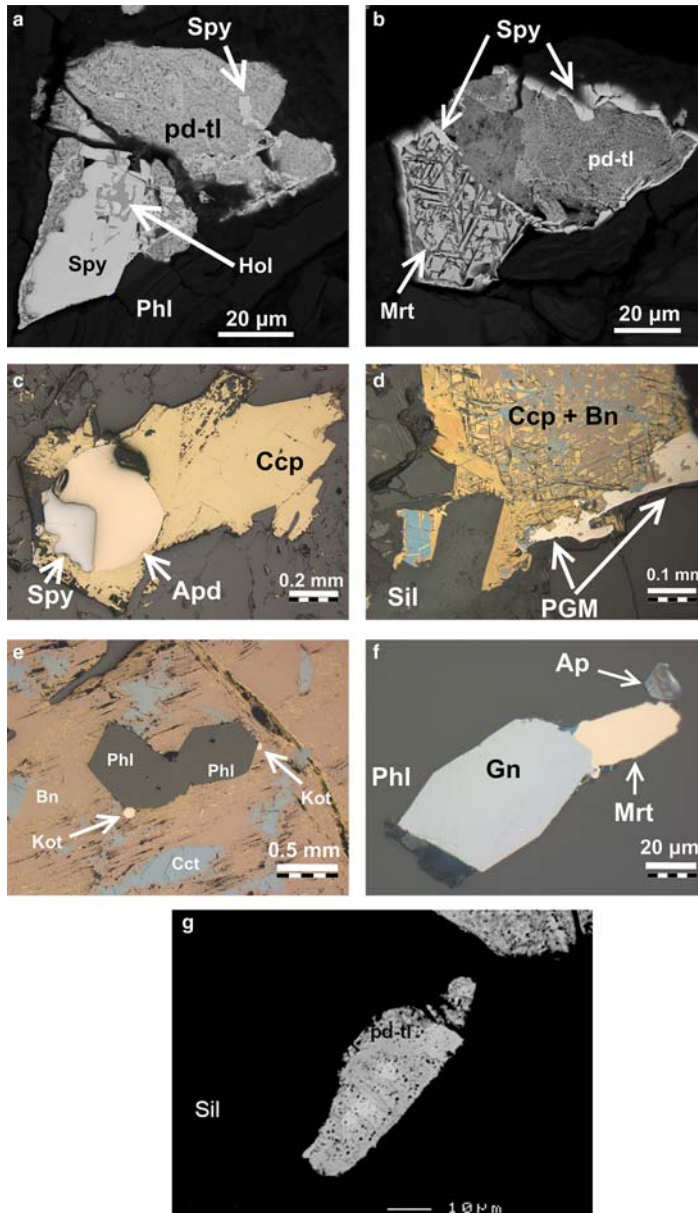


FIG. 2. (*a–f*). Characteristic textures and associations of PGM in the Anomal'nyi PGE deposit. (*a* and *b*) Back-scattered electron images of grains of oxides of Pd, Bi, Te and Tl (labelled pd-tl) are associated with sperrylite (Spy), hollingworthite (Hol) and mertieite-II (Mrt). Phl is host phlogopite. (*c–f*) Reflected-light microphotographs: (*c*) a roundish inclusion of isomertieite or Sb-rich arsenopalladinite (Apd) and sperrylite (Spy) is hosted by chalcopyrite (Ccp); (*d*) a rim-like grain of PGM (mostly zvyagintsevite) is developed along the boundary of a composite grain of chalcopyrite (Ccp) and bornite (Bn); (*e*) micrograins of kotulskite (Kot) are located at the contact of phlogopite (Phl) with bornite (Bn); (*f*) a micro-intergrowth of mertieite-II (Mrt), galena (Gn) and apatite (Ap) is hosted by phlogopite (Phl). The label 'Cct' and 'Sil' pertain to a secondary chalcocite and a silicate, respectively. (*g*) A back-scattered electron image showing a grain of arsenide-bismuthide-thallide phases (labelled pd-tl) hosted by a hydrous silicate mineral, sil, and probably phlogopite. The bright zones observed in the core are rich in Bi and Tl, and are relatively poor in As.

(Fig. 1b). The ore zones are invariably enriched in phlogopite. Various species of PGM are documented on the basis of detailed studies of samples acquired at the Anomal'nyi PGE deposit using scanning electron microscopy and quantitative energy-dispersive spectrometry (SEM-EDS; Table 1). These ore-bearing zones consist of variable amounts of diopside, which is moderately magnesian and enriched locally in the aegirine end-member ( $\text{Wo}_{40.9}\text{En}_{33.3}\text{Fs}_{15.7}\text{Ae}_{10.1}$ ). The latter pyroxene crystallized presumably from an evolved melt, inconsistent with equilibrium crystallization with phlogopite in a closed system. Deuteric clinocllore formed at the expense of primary mafic silicate. Titaniferous magnetite and fluorapatite (Sr-bearing) are common accessories.

In general, the mineralized zones are enriched substantially in Cu (up to 4%), as is shown by the abundance of sulfides of the chalcopyrite-bornite (secondary chalcocite) association; fletcherite is minor. Various species and varieties of PGM were identified on the basis of quantitative SEM/EDS: isomertieite or arsenopalladinite (Sb-rich), sobolevskite, kotulskite, Pb-enriched kotulskite, merenskyite, sperrylite, maslovite or moncheite,

mertieite-I, mertieite-II, zvyagintsevite, palarstanide, paolovite, hollingworthite, and Pd-rich phases of arsenide-bismuthide-thallide compositions and oxides of Pd, Bi, Te and Tl. The Tl-rich PGM were analysed by wavelength-dispersive spectroscopy (WDS) (Tables 2 and 3).

Grains of PGM typically occur as inclusions in BMS near their rim (Fig. 2c,d), located at grain boundaries of phlogopite with BMS (Fig. 2e), or intergrown with apatite hosted by phlogopite (Fig. 2f). Some of these textures are consistent with deposition from a sulfide melt enriched in Cu, nearly simultaneously or after the associated BMS. However, strong positive correlations are not observed invariably between Cu and the PGE (Pd + Pt). This fact agrees well with our observations that many grains of PGM are enclosed entirely within hydrous silicates, commonly in phlogopite, or, occasionally, in titaniferous magnetite. Such grains probably precipitated as separate phases (*cf.* Kamenetsky *et al.*, 2015) directly from microvolumes of a late-stage fluid rich in noble metals and metalloids at a postmagmatic-hydrothermal stage of crystallization. A compositionally diverse assemblage of ore minerals is recognized, which

TABLE 1. Mineral associations observed in the Anomal'nyi deposit, Kondyor complex, northeastern Russia.\*

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Clinopyroxene [(Ca<sub>0.82</sub>Na<sub>0.20</sub>)<sub>Σ1.02</sub>(Mg<sub>0.67</sub>Fe<sup>2+</sup><sub>0.12</sub>Fe<sup>3+</sup><sub>0.20</sub>Al<sub>0.05</sub>)<sub>Σ1.04</sub>Si<sub>2.03</sub>O<sub>6</sub>, or Wo<sub>40.9</sub>En<sub>33.3</sub>Fs<sub>15.7</sub>Ae<sub>10.1</sub>],  
 [Ca<sub>0.92</sub>Na<sub>0.03</sub>]<sub>Σ0.95</sub>(Mg<sub>0.84</sub>Fe<sup>2+</sup><sub>0.12</sub>Fe<sup>3+</sup><sub>0.07</sub>)<sub>Σ1.03</sub>(Si<sub>1.93</sub>Al<sub>0.07</sub>Ti<sub>0.02</sub>)<sub>Σ2.02</sub>O<sub>6</sub>, or Wo<sub>48.2</sub>En<sub>44.0</sub>Fs<sub>6.3</sub>Ae<sub>1.6</sub>]  
 Phlogopite [(K<sub>1.60-1.78</sub>Na<sub>0.18-0.34</sub>)(Mg<sub>4.75-5.41</sub>Fe<sub>0.75-1.17</sub>Ti<sub>0.09-0.14</sub>)Si<sub>5.94-5.95</sub>Al<sub>1.84-1.96</sub>O<sub>20</sub>(OH)<sub>4</sub>]  
 Clinocllore [(Mg<sub>3.41</sub>Fe<sub>1.46</sub>)<sub>Σ4.87</sub>Al(Si<sub>2.70</sub>Al<sub>1.50</sub>)<sub>Σ4.20</sub>O<sub>10</sub>(OH)<sub>8</sub>]  
 Magnetite (titaniferous; Cr-free)  
 Fluorapatite [(Ca<sub>9.44</sub>Sr<sub>0.16</sub>Fe<sub>0.05</sub>)<sub>Σ9.65</sub>(PO<sub>4</sub>)<sub>5.86</sub>(F<sub>1.43</sub>(OH)<sub>0.57</sub>)]  
 Chalcopyrite (Cu<sub>0.98</sub>Fe<sub>1.00</sub>S<sub>2.03</sub>), Bornite (Cu<sub>4.94</sub>Fe<sub>1.03</sub>S<sub>4.03</sub>), Chalcocite [Cu<sub>1.93</sub>Fe<sub>0.04</sub>S<sub>1.04</sub>]  
 Fletcherite [Cu<sub>0.99</sub>(Ni<sub>1.29</sub>Co<sub>0.85</sub>Fe<sub>0.20</sub>)S<sub>3.67</sub>], Galena (Pb<sub>1.00</sub>S<sub>1.00</sub>)  
 Silver [Ag<sub>78.8</sub>Au<sub>16.8</sub>Cu<sub>4.3</sub>]  
 Platinum-group minerals  
 Arsenopalladinite [(Pd<sub>7.76</sub>Cu<sub>0.29</sub>)<sub>Σ8.05</sub>(As<sub>1.37</sub>Sb<sub>1.30</sub>Te<sub>0.28</sub>)<sub>Σ2.95</sub>] or isomertieite  
 [Pd<sub>10.58</sub>Cu<sub>0.40</sub>]<sub>Σ10.98</sub> As<sub>1.87</sub>(Sb<sub>1.77</sub>Te<sub>0.38</sub>)<sub>Σ2.15</sub>, Sobolevskite [Pd<sub>1.00</sub>(Bi<sub>0.56</sub>Te<sub>0.44</sub>)]  
 Kotulskite [Pd<sub>1.03</sub>(Te<sub>0.52</sub>Bi<sub>0.45</sub>)], Pb-enriched kotulskite [Pd<sub>1.01</sub>(Te<sub>0.61</sub>Bi<sub>0.27</sub>Pb<sub>0.11</sub>)]  
 Merenskyite [Pd<sub>0.96</sub>(Te<sub>1.92</sub>Bi<sub>0.12</sub>)<sub>Σ2.04</sub>], Mertieite-I [(Pd<sub>10.28</sub>Cu<sub>0.72</sub>)<sub>Σ11.00</sub>(Sb<sub>2.14</sub>As<sub>1.87</sub>)<sub>Σ4.01</sub>]  
 Zvyagintsevite [Pd<sub>3.05</sub>(Pb<sub>0.70</sub>Sn<sub>0.25</sub>)<sub>Σ0.95</sub>]  
 Mertieite-II [(Pd<sub>7.56</sub>Cu<sub>0.49</sub>)<sub>Σ8.05</sub>(Sb<sub>1.54</sub>As<sub>1.41</sub>)<sub>Σ2.95</sub>], Palarstanide [Pd<sub>4.74</sub>(Sn<sub>1.79</sub>As<sub>0.47</sub>)]  
 Paolovite [Pd<sub>2.03</sub>(Sn<sub>0.88</sub>As<sub>0.09</sub>)], Sperrylite [(Pt<sub>0.94</sub>Rh<sub>0.08</sub>)<sub>Σ1.02</sub>(As<sub>1.83</sub>S<sub>0.15</sub>)<sub>Σ1.98</sub>]  
 Maslovite or moncheite [(Pt<sub>0.98</sub>Cu<sub>0.04</sub>)<sub>Σ1.02</sub>(Te<sub>1.25</sub>Bi<sub>0.73</sub>)<sub>Σ1.98</sub>]  
 Hollingworthite [(Rh<sub>0.91</sub>Pt<sub>0.10</sub>)<sub>Σ1.01</sub>As<sub>0.99</sub>S<sub>1.01</sub>], Unnamed Pd<sub>5</sub>(Tl, As, Bi)  
 Unnamed Pd<sub>5</sub>(As, Tl, Bi), Unnamed Pd<sub>4</sub>(Tl, Bi, Te)O<sub>6</sub>, Unnamed Pd<sub>4</sub>(Bi, Te, Tl)O<sub>6</sub>

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\*These data were acquired using SEM-EDS using the system MIRA 3 LMU (Tescan Ltd.), combined with an INCA Energy 450+ XMax 80 instrument (Oxford Instruments Ltd.) at Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia.

TABLE 2. Compositions (wt.%) of arsenide-bismuthide-thallide phases of Pd from the Anomal'nyi deposit, Kondyor complex.\*

	Pd	Pt	Cu	Tl	As	Bi	Te	Pb	Sb	S	Total	
1	76.87	0.24	0.61	9.53	4.44	5.52	1.15	0.50	0.17	0.50	99.53	
2	74.26	0.14	0.47	13.97	2.09	5.96	0.89	0.75	0.10	0.48	99.12	
3	73.70	0.09	0.48	13.30	2.45	5.64	0.90	0.63	0.02	0.52	97.73	
4	72.77	0.23	0.35	9.93	1.57	8.95	1.19	0.53	0	0.71	96.22	
5	72.28	0.18	0.30	12.07	1.73	8.47	0.95	0.37	0.17	0.50	97.02	
Atoms per formula unit (based on 6 atoms of oxygen)												
	Pd	Pt	Cu	ΣM	Tl	As	Bi	Te	Pb	Sb	S	Σ
1	4.85	0.008	0.06	4.92	0.31	0.40	0.18	0.06	0.02	0.009	0.11	1.08
2	4.88	0.005	0.05	4.94	0.48	0.20	0.20	0.05	0.03	0.006	0.11	1.06
3	4.88	0.003	0.05	4.93	0.46	0.23	0.19	0.05	0.02	0.001	0.11	1.07
4	4.90	0.008	0.04	4.95	0.35	0.15	0.31	0.07	0.02	0	0.16	1.05
5	4.89	0.007	0.03	4.93	0.43	0.17	0.29	0.05	0.01	0.010	0.11	1.07

\*These results listed in were acquired with a JEOL JXA-8900 electron microprobe, at McGill University, by a means of WDS, at 20 kV and 30 nA with a beam of 10 μm, employing the *Phi-Rho-Z* correction method and using the following set of standards (and lines): synthetic TlS<sub>2</sub> for Tl (*Mα*), CoNiAs for As (*Lα*), pure elements: Pd (*Lα*), Pt (*Mβ*), Te (*Lα*), Bi (*Mβ*), Sb (*Lβ*), CuFeS<sub>2</sub> for Cu and S (*Kα*) and synthetic PbCrO<sub>4</sub> for Pb (*Mα*). Values of the limit of detection are: 0.13 wt.% (Pt and Tl), 0.12% (Bi and Sb), 0.11% (Pb), 0.09% (Pd), 0.06% (Te), 0.04% (Cu and As) and 0.02% (S). Values of 0 = not detected.

includes PGM and Au-bearing silver (Ag<sub>78.8</sub>Au<sub>16.8</sub>Cu<sub>4.3</sub>). In general, the enrichment in Te, Bi and Pb is characteristic. Thallium accompanies Bi in the form of constituents of the Tl-Bi-rich PGM.

There are arseno-antimonides among the investigated species of PGM, i.e. isomertieite or intermediate phases in the arsenopalladinite–mertieite-II series with formula: (Pd<sub>7.56–7.76</sub>Cu<sub>0.29–0.49</sub>)Σ<sub>8.05</sub>(As<sub>1.37–1.41</sub>Sb<sub>1.30–1.54</sub>Te<sub>0–0.28</sub>)Σ<sub>2.95</sub>.

A typical composition in this series contains: Pd 71.6, Cu 1.6, Sb 13.7, As 8.9, Te 3.1, total 98.9 wt.%, corresponding to (Pd<sub>7.76</sub>Cu<sub>0.29</sub>)Σ<sub>8.05</sub>(As<sub>1.37</sub>Sb<sub>1.30</sub>Te<sub>0.28</sub>)Σ<sub>2.95</sub>, or to [Pd<sub>10.58</sub>Cu<sub>0.40</sub>]Σ<sub>10.98</sub>As<sub>1.87</sub>(Sb<sub>1.77</sub>Te<sub>0.38</sub>)Σ<sub>2.15</sub> (basis: Σ atoms = 11 and 15 atoms per formula unit (apfu), respectively). The latter formula is consistent with a substantial extent of a Sb-for-As substitution in isomertieite. These phases thus require an X-ray diffraction study. In addition, arsenopalladinite, triclinic Pd<sub>8</sub>(As,Sb)<sub>3</sub>,

TABLE 3. Compositions of oxides (wt.%) of Pd, Bi, Te and Tl from the Anomal'nyi deposit, Kondyor complex.\*

	PdO	PtO	CuO	Tl <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	Bi <sub>2</sub> O <sub>3</sub>	TeO <sub>2</sub>	PbO	Sb <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Total	
1	62.11	0	0.14	2.52	0	17.43	6.52	0.03	0	0.22	89.0	
2	61.44	0.05	0.18	2.70	0	17.68	5.78	0.13	0.09	0.25	88.3	
3	61.30	0	0.18	2.93	0	18.49	5.44	0.09	0	0.24	88.7	
4	60.27	0.08	0.71	10.05	0.32	6.30	1.31	0.48	0.04	0.94	80.5	
Atoms per formula unit (based on 6 atoms of oxygen)												
	Pd	Cu	Pt	ΣM	Bi	Te	Tl	As	Pb	S	Sb	Σ
1	4.18	0.01	0	4.20	0.62	0.34	0.09	0	0.001	0.02	0	1.07
2	4.18	0.02	0.002	4.21	0.63	0.30	0.10	0	0.005	0.03	0.004	1.07
3	4.18	0.02	0	4.20	0.66	0.28	0.11	0	0.003	0.03	0	1.08
4	4.41	0.08	0.003	4.49	0.24	0.07	0.39	0.03	0.019	0.11	0.002	0.86

\*These results from WDS analyses were acquired with a JEOL JXA-8900 electron microprobe at McGill University; see Table 2 for analytical conditions and details.

and mertieite-II, hexagonal Pd<sub>8</sub>(Sb,As)<sub>3</sub>, typically contain ≤0.5 apfu Sb and ≤0.5 apfu As, respectively (Cabri *et al.*, 1975; Cabri, 2002, and references therein).

### New arsenide-bismuthide-thallide phases and oxides of Pd, Bi, Te and Tl

The Tl-bearing PGM occur as composite grains or intergrowths, <0.05 to <0.1 mm across, which are hosted by phlogopite (Fig. 2a,b,g). Their WDS compositions (Tables 2 and 3) are consistent with two types of compounds: solid solutions of palladium arsenide-bismuthide-thallide and oxides of Pd, Bi, Te and Tl, which are presumably secondary and formed at the expense of primary PGM in intergrowths involving a thallide-rich phase.

The arsenide-bismuthide-thallide compounds show strong covariations in contents of As, Bi and Tl, because of their mutual substitutions. The WDS results obtained yield an atomic Pd : (As + Bi + Tl) ratio of 5:1 (Table 2). The As-dominant composition corresponds to: Pd<sub>5</sub>(As<sub>0.40</sub>Tl<sub>0.31</sub>Bi<sub>0.18</sub>S<sub>0.11</sub>Te<sub>0.06</sub>), or Pd<sub>5</sub>(As,Tl,Bi). It is probably a new species of PGM, related to synthetic Pd<sub>5</sub>As, which is known in the system Pd–As (Saini *et al.*, 1964; Kohlmann *et al.*, 2016). There are no A<sub>5</sub>B-type phases known in the systems Pd–Bi and Pd–Tl.

The Tl-dominant phase documented at Anomal'nyi is rich in Bi and As and corresponds to Pd<sub>5</sub>(Tl<sub>0.48</sub>As<sub>0.20</sub>Bi<sub>0.20</sub>S<sub>0.11</sub>Te<sub>0.05</sub>) (Table 2). It appears to be the first reported example of unnamed Pd<sub>5</sub>(Tl,As,Bi). Previously, another phase of a high-Pd thallide, Pd<sub>5</sub>Tl, was reported from layered intrusions (Holwell *et al.*, 2006; Grokhovskaya *et al.*, 2009; Groshev *et al.*, 2012). Two polymorphs of Pd<sub>5</sub>Tl have been documented in the system Pd–Tl (Bhan *et al.*, 1968; Kurtzemann and Kohlmann, 2010).

The observed WDS compositions of the Pd-rich oxides gave low totals (Table 3), which could be a consequence of the high porosity of these grains (Fig. 2a,b). Oxygen is clearly observed in their EDS spectra. In addition, the presence of (OH) cannot be excluded. Our compositions are consistent with the formulae Pd<sub>4</sub>(Bi,Te,Tl)O<sub>6</sub> and Pd<sub>4</sub>(Tl,Bi,Te)O<sub>6</sub> (Table 3). These oxides are somewhat similar to the associated arsenide-bismuthide-thallide phases; they all are rich in Bi and Tl, which covary in their compositions, and have high values of their Pd : (Tl + Bi + As + Te) ratio, ~5 vs. 4. In contrast, As is not essential in these oxides.

Various PGE-rich oxides have been reported (Augé and Legendre, 1994; McDonald *et al.*, 1999; Shcheka *et al.*, 2005), including Pd-rich ones: a Pd-Bi-Sb oxide from the Chiney complex, Russia (Tolstykh *et al.*, 2000) and Pd<sub>7</sub>PbO<sub>8</sub> from the Penikat intrusion, Finland (Barkov *et al.*, 1999, 2005). However, the oxide phases reported here, Pd<sub>4</sub>(Bi,Te,Tl)O<sub>6</sub> and Pd<sub>4</sub>(Tl,Bi,Te)O<sub>6</sub>, as well as the other natural PGE-rich oxides, require a special study to confirm that they are single-phase materials. X-ray absorption spectroscopy scans reveal that Pt is mostly in the metallic state and not bonded with O or OH<sup>-</sup> in O-bearing Pt-Fe grains from New Caledonia (Hattori *et al.*, 2010).

## Discussion

### Genetic interpretation

On the basis of our results, we infer that the Anomal'nyi Pd-Pt deposit contrasts with the previously known occurrences of PGM in the Kondyor complex and other zoned complexes, where Pt-Fe and Os-Ir-Ru alloys predominate, in association with segregations of chromian spinel (e.g. Nekrasov *et al.*, 2005). We suggest that fractional crystallization of a magma exerted the major control to form the Anomal'nyi Cu-PGE deposit. The following comagmatic series of rocks developed sequentially in the core of this complex: chromite-bearing dunite (+peridotite) → coarse-grained 'kosvite' (clinopyroxenite rich in magnetite) → vein-like pegmatitic mafic rocks of the Anomal'nyi deposit, which are anomalously rich in phlogopite, apatite, Cu-rich BMS, and contain the Pd-based species of PGM. Finally, alkali-enriched mafic pegmatite veins were emplaced into the sandwich-structured system (Fig. 1b).

Crystallization of the complex began with a high-Fo olivine and magnesiochromite-chromite (disseminated and podiform) in the dunite core. We presume that the 'kosvite zone' (Fig. 1a), which is highly heterogeneous (Fig. 1b), formed from the batch of notably fractionated magma, relatively rich in Fe, Cu, alkalis and volatiles, remaining after the crystallization of >90% of the dunite-peridotite core. The inferred buildup in levels of oxygen fugacity in the remaining volume of magma caused the deposition of abundant magnetite in the 'kosvite' zone. An evolved character of the crystallizing melt at Anomal'nyi also is indicated by: (1) the pyroxene composition enriched in the Fs and Ae components (Table 1), which is inconsistent with a closed-system crystallization with

phlogopite; and (2) a depletion in Cr and Ni, which is generally characteristic of Anomal'nyi. In addition, diopside, having a more magnesian composition, crystallized at an earlier stage, compared with the Ae-rich pyroxene (Table 1). (3) The enrichment in Pd, observed at Anomal'nyi, contrasts with the Pt-Os-Ir-Ru-rich character in the mineralized dunites of the core.

The pegmatitic textures of the mineralized area imply the presence of elevated levels of volatile components, accumulated in the 'kosvite zone' during formation of the vein-type Pd-Pt deposit at Anomal'nyi. In addition, the buildup in S and Cu, leading to the deposition of droplets of Cu-enriched sulfide melt, probably occurred during crystallization of the fractionated magma in the 'kosvite zone' late in the crystallization history of the core of the complex. Further, we infer that the ore-forming system remained relatively open, causing events of recrystallization and metasomatic activity (manifested by pegmatitic alkaline veins: Fig. 1*b*) at late magmatic and subsolidus stages in the 'kosvite zone' of the Anomal'nyi area. The abundance of phlogopite at Anomal'nyi may well be a reflection of an influx into the local system of aqueous fluid that is related genetically with the ultramafic core of the complex. In a similar situation, nearly Fe-free phlogopite has formed as a result of metasomatic activity during fenitization of pre-existing mafic megaxenoliths of the Khibina complex, Kola Peninsula (*cf.* Barkov *et al.*, 1997).

### Concluding comments

The 'kosvite zone' is heterogeneous (Fig. 1*b*) and hosts the newly discovered lode deposit of Pd, Pt and Cu, at Anomal'nyi, in the dunite core of the Kondyor complex. This deposit probably formed by the crystallization of a batch of notably fractionated magma relatively rich in Fe, Cu, alkalis and volatile components following the crystallization of the dunite-peridotite core. The observed event of metasomatic activity at Anomal'nyi follows an early-stage closed-system evolution of the complex, fluid saturation and, we believe, late open-system behaviour.

The strong enrichment in Cu, coupled with a general depletion in Ni in the observed sulfide association, are consistent with the alkali-rich character of the Kondyor complex. The investigated PGM (Tables 1–3) probably formed in a Cr-(Ni)-depleted environment, rich in volatiles, relatively late in the crystallization history of the complex.

Presumably, they typically deposited from portions of residual sulfide melt enriched in Cu and S, as well as in other metals (Bi, Pb, Tl) and metalloids (Sb, Te, As). The grains of newly recognized oxides [Pd<sub>4</sub>(Bi,Te,Tl)O<sub>6</sub> and Pd<sub>4</sub>(Tl,Bi,Te)O<sub>6</sub>] formed as a result of the late oxidation of the associated intergrowths of bismuthide-thallide PGM related to Pd<sub>5</sub>(Tl,As,Bi). The inferred presence of elevated levels of Bi and other fluxing components implies that droplets of that late melt remained at temperatures even below the solidus of the mafic assemblage, at a postmagmatic stage in the system. The enrichment in Bi, Te and Pb resulted in the abundance of ore species rich in these elements (Table 1). We hypothesize that macrocrystals of some PGM (e.g. zvyagintsevite), reported from a placer at Kondyor (Cabri and Laflamme, 1997), could well be derived from the ore veins of an Anomal'nyi-type deposit. The huge grain-size and well-formed faces of such crystals, found in placers, might well be a reflection of growth in a flux-rich pegmatitic environment enriched in PGE and metalloids.

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