## New data on associations of platinum-group minerals in placer deposits of British Columbia, Canada

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#### Summary

We have conducted electron microprobe (EMP) analysis of 158 grains of platinumgroup minerals (PGM; 0.1-1 mm in size) from 11 placer samples collected from Holocene fluvial placers and buried paleochannel placers at various localities in British Columbia. These grains principally comprise Pt-Fe-(Cu) alloy minerals: Fe-rich platinum  $[\Sigma PGE:(Fe + Cu + Ni) = 3.6-7.6]$ , Pt<sub>3</sub>Fe-type alloy (isoferroplatinum or Fe-rich platinum), subordinate "Pt<sub>2</sub>Fe"-type alloy (probably, a compositional variant of Fe-rich platinum) and the tulameenite-tetraferroplatinum series. Less-abundant are iridium [Ir-dominant Ir-Os-(Pt) alloy] and osmium [Os-dominant Os-Ir-(Pt) alloy]. Ruthenium [Ru-dominant Ru-Ir-Os alloy] occurs as a single grain. One of these Pt-Fe alloy grains is unusually zoned; its core zone is: Pt74.0Fe20.4Cu1.9Ir1.5Rh1.1Pd1.0Os0.08Ru0.01Ni0.01 (in at%) [ $\Sigma$ PGE:(Fe + Cu + Ni) = 3.5], and its rim zone is: Pt<sub>78.5</sub>Fe<sub>15.5</sub>Cu<sub>1.7</sub>Ir<sub>1.5</sub>Rh<sub>1.4</sub>  $Pd_{1,2}Ni_{0,15}Os_{0,06}Ru_{<0,01}$  [ $\Sigma PGE:(Fe + Cu + Ni) = 4.8$ ]. This zoning indicates late-stage removal of Fe and corresponding addition of Pt, probably as a result of interaction with a late fluid phase. Various combinations of minor elements: Ir-Rh, Rh-Pd, and Ir-Rh-Pd are observed in the analysed Pt-Fe-Cu alloys. However, the Ir-Pd pair appears to be prohibited because of crystallochemical factors. Minute PGM inclusions in Pt-Fe alloy grains, likely derived from the Tulameen complex, comprise: hongshiite (Pt<sub>1.04</sub>Pd<sub>0.02</sub>  $Cu_{0.93}$ ), sperrylite ( $Pt_{0.93}Ir_{0.03}$ ) $_{\Sigma 0.96}$ (As<sub>2.02</sub>Sb<sub>0.01</sub>) $_{\Sigma 2.03}$ , hollingworthite-platarsite (Rh<sub>0.74</sub>)  $Pt_{0.21}Fe_{0.02}Pd_{0.02}Ir_{0.01})_{\Sigma 1.00}S_{0.91}As_{1.10}, cuprorhodsite-malanite\ (Cu_{0.91}Fe_{0.03}Ni_{<0.01})_{\Sigma 0.95}$  $(Rh_{1.06}Pt_{0.89}Ir_{<0.01})_{\Sigma 1.95}S_{4.10}$ , a rare Te-rich isomertieite  $(Pd_{10.96}Fe_{0.03})_{\Sigma 10.99}(Sb_{1.13})_{\Sigma 10.99}(S$  $Te_{0.94}$ ) $\Sigma_{2.07}As_{1.93}$ , and an unusual Pt-Pd-Rh antimonide [(Pt + Pd + Rh):(Sb + As) =1.2–1.25], related to genkinite. This antimonide may exhibit a minor solid solution

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extending from genkinite toward stumpflite. In addition, 20 grains of diopside  $[Ca_{46,4-49,1}Mg_{42,8-48,2}Fe_{3,1-8,1}; \leq 0.59 \text{ wt\% } Cr_2O_3]$  and 20 grains of olivine  $[Fo_{86,8-91,5}Fa_{7,9-12,5}]$ , from a PGM-bearing placer located in the vicinity of the Tulameen complex, were analysed. The compositional ranges of these placer silicates are comparable to those of clinopyroxene and olivine in the olivine clinopyroxenite and dunite units of the Tulameen complex. The majority of the analysed placer PGM grains were probably derived from Alaskan-type source rocks, whereas an ophiolitic source, associated with the Atlin ophiolite complex, is suggested for the placer PGM deposits in the Atlin area, northern British Columbia.

#### Introduction

Placer deposits of gold and minerals of platinum-group elements (PGE) were first discovered in British Columbia, Canada, in the mid- to late 1800s. Of the 106 occurrences currently listed in the provincial MINFILE database, approximately half of them are placer deposits. Diverse assemblages of platinum-group minerals (PGM) have been documented in placer and lode deposits associated with the Tulameen Alaskan-type complex, British Columbia (Nixon et al., 1990). Recently, various Au-PGE-enriched placers in British Columbia were investigated to evaluate relationships to their source rocks on the basis of sedimentological, geochemical and mineralogical criteria (Levson and Morison, 1995; Levson et al., 2002). The PGM from five of these deposits, represented by 70 placer grains, were characterized by *Barkov* et al. (2005a). In the present study, we present new results of electron-microprobe (EMP) analyses and observations made on additional 158 placer grains and tiny nuggets of PGM in 11 samples of placer concentrate from various localities throughout British Columbia. We follow the IMA-accepted nomenclature for alloy minerals of Pt-Fe-(Cu) and Os-Ir-Ru (e.g., Cabri and Feather, 1975; Harris and Cabri, 1973, 1991; Cabri, 2002); however, the prefix "ferroan" and accordingly, the name "ferroan platinum" are avoided in the light of a recent recommendation approved by the IMA (Bayliss et al., 2005).

#### Geological setting and description of placer samples

The locations of placer concentrates examined in this study are shown in Fig. 1. These samples are derived from various tectonostratigraphic settings, including mainly oceanic terranes associated with serpentinite-ultramafic complexes (e.g., Cache Creek and Slide Mountain terranes), and Alaskan-type and ophiolitic complexes in accreted island-arc terranes (mainly Quesnellia). Tectonostratigraphic affiliations for each sample are as follows: VLE-2001-69a, 70b: Atlin ophiolite complex in the Cache Creek terrane; VLE-2001-67 and 7b: serpentinite-ultramafic complexes adjacent to the Slide Mountain terrane; VLE-2001-82: Tulameen Alaskan-type complex; VLE-2001-17b, 33, 44, 85b, 91b, and 93: serpentinite-ultramafic rocks in Quesnellia. The exact source-rocks for the placers are difficult to ascertain owing to a complex drainage history. For example, samples in the Quesnel region are located in the terrane identified as Quesnellia, but paleo-rivers there probably also drained Slide Mountain and possibly Cache Creek terranes (Fig. 1).



Fig. 1. Location map showing the tectonostratigraphic setting and distribution of potential source-rocks for PGM placer concentrates in British Columbia, Canada. We show serpentinite-ultramafic rocks in oceanic (ophiolitic) and island-arc terranes and known occurrences of Alaskan-type ultramafic-mafic complexes (e.g., Tulameen)

The samples of concentrate are derived from two main types of placer deposits: Holocene fluvial placers and buried paleochannel placers. Most samples (VLE-2001-17b, 33, 44, 67, 69a, 82, 85b, and 93) are of the latter type. They were recovered at shallow depths (<4 m below the surface) from low terraces or dry channels, within a few metres of the level of modern rivers. One exception is sample VLE-2001-85b, collected from a terrace 20 m above river level, which may be glaciofluvial in origin. The host sediments are typically moderately to well sorted, pebble to cobble gravels, commonly overlain by sands and silts. Cementation, oxidation and weathering of the gravels occurred locally, but are not common. The gravels generally overlie bedrock or till. Most samples were concentrated in sluice boxes followed by processing with gold wheels, jigs, and gold pans. Recovered gold from these placers is typically dominated by flat flakes with rounded edges. The buried-paleochannel type of placer deposits, from which samples VLE-2001-7b, 70b, and 91b were derived, is distinctive in that they are typically coarsegrained gravels (large pebble to boulder), dense, and overlain by glacial sediments. 12 A. Y. Barkov et al.: New data on associations of PGM in placers, British Columbia

They may occur at depths of 10 or more metres below surface. Iron oxidation and cementation are common. The orientations and locations of the paleochannels depart substantially from the modern valleys, and the bottoms of the old channels typically are incised into bedrock at least several metres below the level of the modern streams. Placer concentrations in the paleochannel deposits are generally much higher than in their modern equivalents, because of the longer periods of erosion during their formation. Recovered gold from paleochannel placers usually contains a high proportion of coarse nuggets.

Gangue minerals in each of the concentrate samples are as follows (type and location of placer are given in parentheses): sample VLE-2001-7b (deep buried channel placer on Slate Creek): galena, arsenopyrite and pyrite; sample VLE-2001-17b (shallow alluvial placer along the Swift River): almandine, chromite, staurolite, pyrite, diopside, scheelite and goethite; sample VLE-2001-33 (low terrace placer on Government Creek): hematite, almandine, epidote, staurolite, chromite, kyanite, scheelite, pyrite, rutile, galena, spinel and spessartine; sample VLE-2001-44 (low terrace placer along the Quesnel River): almandine, hematite, pyrite, barite, chromite, olivine, diopside, rutile, chalcopyrite, galena, goethite and spinel; sample VLE-2001-67 (low terrace placer on Rosella Creek): ilmenite, almandine, goethite, hematite, diopside, pyrite, barite, chromite and chalcopyrite; sample VLE-2001-69a (low terrace placer on Wilson Creek): goethite, chromite and epidote; sample VLE-2001-70b (deep paleochannel placer at Wright Creek): pyrite, chalcopyrite, magnetite; sample VLE-2001-82 (modern stream placer in the Tulameen River): hematite, ilmenite, diopside, pyrite, chromite, spessartine, olivine, galena, rutile, chalcopyrite, scheelite and goethite; sample VLE-2001-85b (high terrace placer along the Cottonwood River): pyrite, garnet; sample VLE-2001-91b (buried channel placer high above the Quesnel River): pyrite, chalcopyrite, magnetite; and sample VLE-2001-93 (low terrace placer along the lower Quesnel River): hematite, pyrite, epidote, spessartine, chalcopyrite, apatite, chromite, barite, spinel, rutile, malachite, scheelite and arsenopyrite.

#### Samples and analytical methods

A table concentrate was produced by Overburden Drilling Management Limited, Ontario, Canada, for each of the placer samples. This concentrate was then micropanned to recover fine-grained sediment, and the latter was processed through heavy liquid and ferromagnetic separations. The PGM grains were hand-picked, identified by SEM, and mounted and polished for analysis. These PGM grains comprise various species of alloy minerals of Pt-Fe-Cu (up to ~1 mm in size) and Os-Ir-Ru (0.1 to <0.5 mm) and display various degrees of preservation of their primary morphologies (e.g., Figs. 2A–F and 3A–F).

EMP analyses of the PGM were carried out using a JEOL JXA-8600 (University of Western Ontario: UWO) and a JEOL JXA-8900 electron microprobe (McGill University) in wavelength-dispersion spectrometry mode (WDS) at 25 kV and 30 nA, with a finely focused beam (<2  $\mu$ m) and CITZAF or ZAF (JEOL) on-line correction procedures. At UWO, the following X-ray lines (and standards) were used: NiK $\alpha$ , FeK $\alpha$ , CoK $\alpha$ , CuK $\alpha$ , IrL $\alpha$ , PtL $\alpha$ , OsL $\alpha$ , RuL $\alpha$ , PdL $\beta$  (pure metals), RhL $\alpha$  (synthetic Pt<sub>90</sub>Rh<sub>10</sub>), AsL $\alpha$  (FeAsS), and SK $\alpha$  (FeS). The PdL $\beta$  line was used in-



Fig. 2. (A-F) Back-scattered electron images of placer grains. (A) A euhedral grain of Pt-Fe alloy "Pt-Fe", isoferroplatinum or Fe-rich platinum: Pt71.5Fe18.9Cu5.7Pd2.6Rh1.0Os0.2Ru0.07  $Ir_{0.03}Ni_{0.03}$ , with a  $\Sigma PGE:(Fe + Cu + Ni)$  ratio of 3.05, from sample VLE-2001-82. (B) A round grain of Fe-rich platinum "Pt-Fe" [Pt<sub>79.1</sub>Fe<sub>15.9</sub>Cu<sub>2.0</sub>Rh<sub>1.2</sub>Os<sub>0.7</sub>Ir<sub>0.3</sub>Pd<sub>0.7</sub>Ni<sub>0.1</sub>; ΣPGE: (Fe + Cu + Ni) ratio is 4.53], from sample VLE-2001-85b. (C) A euhedral grain of Os-Ir-Ru alloy "Os-Ir-Ru": Ir-Ru-rich osmium [Os48.6Ir37.1Ru11.0Pt1.4Rh1.0Fe0.8Ni0.1] from sample VLE-2001-70b. (D) A small grain of Ir-rich osmium "Os-Ir": Os<sub>55.3</sub>Ir<sub>34.3</sub>Ru<sub>7.0</sub>Rh<sub>1.6</sub>Pt<sub>1.1</sub>Fe<sub>0.6</sub>, partially mantled by isoferroplatinum or Fe-rich platinum "Pt-Fe" [Pt<sub>69,2</sub>Fe<sub>22,6</sub>Ir<sub>3,5</sub>Ni<sub>1,6</sub>Rh<sub>1,5</sub>  $Cu_{1,3}Os_{0,4}$ ;  $\Sigma PGE:(Fe + Cu + Ni)$  ratio is 2.93] from sample VLE-2001-33. (E) Two subhedral grains of Pt-(Ir)-Fe alloys from sample VLE-2001-44. The grain at left ("Pt-Fe") is isoferroplatinum or Fe-rich platinum [Pt73.5Fe21.0Cu2.3Rh1.4Pd0.9Ir0.7Ru0.1Ni0.1Os0.07] with a  $\Sigma$ PGE:(Fe + Cu + Ni) ratio of 3.29. The grain at right, labelled "Pt-Ir-Fe", is Fe-rich platinum enriched in Ir (16.1 wt%): Pt<sub>66.1</sub>Ir<sub>15.2</sub>Fe<sub>11.3</sub>Os<sub>2.7</sub>Rh<sub>1.8</sub>Ru<sub>1.6</sub>Cu<sub>0.8</sub>Ni<sub>0.5</sub>Pd<sub>0.1</sub>. (F) Composite "droplet" inclusions (DI) of a K-rich alumosilicate, magnetite and bornite in a placer grain of isoferroplatinum or Fe-rich platinum  $[Pt_{73.1}Fe_{20.8}Cu_{3.1}Rh_{2.0}Pd_{0.6}Os_{0.3}Ru_{0.07}Ni_{0.02}]$  with a  $\Sigma$ PGE:(Fe + Cu + Ni) ratio of 3.18, from sample VLE-2001-44

stead of PdL $\alpha$  in order to eliminate overlap between emission lines of Rh and Pd. All possible peak-overlaps were examined and corrected during a careful analysis of relevant standards. The minimum detection-limits were as follows: Pt 0.14%, Ir and As 0.13%, Os 0.12%, S 0.09%, Rh 0.06%, Ru and Pd 0.05%, Sb 0.04%, Cu, Ni, Te 0.03%, and Co and Fe 0.02 wt%. At McGill, the PGM were also analysed using a finely focused beam (<2 µm) and the following X-ray lines and the set of standards: RhL $\alpha$ , PdL $\beta$ , IrL $\alpha$ , PtL $\alpha$  (pure metals), CoK $\beta$  [(Co, Ni)As], CuK $\beta$ , FeK $\beta$ , SK $\alpha$  (CuFeS<sub>2</sub>), and NiK $\alpha$  [(Fe, Ni, Co)<sub>9</sub>S<sub>8</sub>]. We also analysed the silicate minerals associated with the PGM using WDS analysis at 15 kV and 20 nA and a set of well-defined synthetic and natural mineral standards.



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#### **Results and discussion**

#### Extent of Fe substitution for Pt in Pt-Fe alloys

We have summarized our results (EMP) for various Pt-Fe-(Cu) alloys in Fig. 4. Values of atomic  $\Sigma PGE$ :(Fe + Cu + Ni) ratio range from 1 to  $\sim$ 8 in these composi-



Fig. 4. Plot of values of atomic  $\Sigma PGE:(Fe + Cu + Ni)$  ratio in compositions of various Pt-Fe-(Cu) alloys from placer deposits of British Columbia *versus* the number of electron-microprobe analyses. Results of a total of 234 analyses are plotted in order of increasing  $\Sigma PGE:(Fe + Cu + Ni)$  ratio

Fig. 3. (A-F). Back-scattered electron images of selected placer grains. (A) A rim of tulameenite "Pt-Fe-Cu" [Pt<sub>50,7</sub>Fe<sub>23,6</sub>Cu<sub>22,8</sub>Ir<sub>1,2</sub>Rh<sub>0,6</sub>Os<sub>0,6</sub>Ni<sub>0,3</sub>Pd<sub>0,2</sub>Ru<sub>0,07</sub>] around a grain of isoferroplatinum or Fe-rich platinum "Pt-Fe" [Pt<sub>65.8</sub>Fe<sub>24.1</sub>Cu<sub>3.7</sub>Ir<sub>2.1</sub>Os<sub>1.7</sub>Ru<sub>0.9</sub>Rh<sub>0.8</sub>Pd<sub>0.6</sub> Ni<sub>0.3</sub>], with a  $\Sigma PGE:(Fe + Cu + Ni)$  ratio of 2.56; sample VLE-2001-82. (B) A grain of isoferroplatinum or Fe-rich platinum "Pt-Fe": [Pt<sub>72.6</sub>Fe<sub>15.1</sub>Cu<sub>10.5</sub>Pd<sub>0.7</sub>Rh<sub>0.6</sub>Os<sub>0.4</sub>Ru<sub>0.1</sub>Ir<sub><0.01</sub>] having a  $\Sigma PGE:(Fe + Cu + Ni)$  ratio of 2.91, with a micro-inclusion of osmium "Os" [Os<sub>96,6</sub>Ir<sub>1.4</sub>Pt<sub>1.1</sub>Ru<sub>0.4</sub>Rh<sub>0.3</sub>] intergrown with hongshiite, Pt-Cu ("Pt-Cu": dark phase); sample VLE-2001-82. (C) A zoned grain of Pt-Fe alloy (Zoned "Pt-Fe") with a core of Pt<sub>74.0</sub>Fe<sub>20.4</sub>  $Cu_{1.9}Ir_{1.5}Rh_{1.1}Pd_{1.0}Os_{0.08}Ru_{0.01}Ni_{0.01}$  [ $\Sigma PGE:(Fe + Cu + Ni) = 3.49$ ], and a rim-like zone of  $Pt_{78.5}Fe_{15.5}Cu_{1.7}Ir_{1.5}Rh_{1.4}Pd_{1.2}Ni_{0.2}Os_{0.06}Ru_{<0.01}$  with a  $\Sigma PGE:(Fe + Cu + Ni)$  ratio of 4.75; sample VLE-2001-33. (D) Minute grains of Te-rich isomertieite ("Ism") and cuprorhodsitemalanite ("Cpr"), hosted by a placer grain of isoferroplatinum or Fe-rich platinum "Pt-Fe":  $[Pt_{73,3}Fe_{21,0}Cu_{3,1}Pd_{1,5}Os_{0,7}Rh_{0,2}Ru_{0,1}Ni_{0,02}]$ , with a  $\Sigma PGE:(Fe + Cu + Ni)$  ratio of 3.15; sample VLE-2001-82. (E) A subhedral grain of isoferroplatinum or Fe-rich platinum "Pt-Fe''  $[Pt_{71,2-74,0}Fe_{23,8-26,7}Cu_{1,6-1,7}Ni_{0,2-0,3}Os_{0,2}Ru_{0,01-0,1}]$  with a  $\Sigma PGE:(Fe + Cu + Ni)$  ratio of 2.5–2.9. The grain hosts fine exsolution-induced lamellae of a Pt-Pd-Sb phase, probably genkinite ("Pt-Pd-Sb"), which are "crystallographically" oriented and subparallel to the edge. Minute black inclusions in this "Pt-Fe" grain are sperrylite; sample VLE-2001-82. (F) Magnification of lower portion of the Pt-Fe alloy grain shown in Fig. 3E; exsolution lamellae of Pt-Pd-Sb phase ("Pt-Pd-Sb"), corresponding to genkinite in composition, are hosted by isoferroplatinum or Fe-rich platinum "Pt-Fe". The symbol "Spy" refers to sperrylite

tions. Interestingly, a miscibility gap between the PtFe- and "Pt<sub>2</sub>Fe"-type alloys is clearly observed (shown by arrow in Fig. 4); in contrast, there is no evidence for the existence of a miscibility gap between "Pt<sub>2</sub>Fe" and Pt<sub>3</sub>Fe (isoferroplatinum or Fe-rich platinum). "Pt<sub>2</sub>Fe" is not reported in the system Pt-Fe, in which three alloy species are known (*Cabri* and *Feather*, 1975): (1) alloy with a disordered structure (*fcc*), space group *Fm3m*, is Fe-rich platinum, (2) isoferroplatinum, ideally Pt<sub>3</sub>Fe, has an ordered primitive cubic (*pc*) structure of Cu<sub>3</sub>Au type, space group *Pm3m*,

Table 1. Compositions of various Pt-Fe-(Cu) alloys from Au-PGE placer deposits, BritishColumbia, Canada

No.	Cu	Fe	Ni	Pt		Ir	Os	Pd	Rh	Ru	Total
1	0.27	3.58	0.13	74	.72	16.14	2.71	n.d.	0.97	0.87	99.39
2	0.45	3.94	n.d.	93	.91	0.05	0.15	0.59	0.31	n.d.	99.40
3	0.47	5.07	0.05	88	.85	0.04	0.86	0.48	3.46	0.24	99.52
4	0.60	5.34	0.22	91	.13	0.45	0.71	0.34	0.29	0.14	99.22
5	0.76	6.18	0.11	89	.60	n.d.	0.36	0.70	1.85	0.11	99.67
6	0.60	7.70	0.08	88	.21	1.39	0.40	0.09	1.43	0.05	99.95
7	2.29	6.63	n.d.	87	.63	0.04	0.23	1.71	0.61	0.04	99.18
8	0.57	8.21	n.d.	88	.89	1.16	0.30	n.d.	0.19	n.d.	99.32
9	1.07	8.01	n.d.	89	.15	0.30	n.d.	0.92	0.20	n.d.	99.65
10	0.39	9.08	n.d.	89	.02	0.10	0.08	0.71	0.76	n.d.	100.14
11	0.68	9.57	0.10	89	.26	n.d.	0.29	n.d.	n.d.	n.d.	99.90
12	0.38	9.87	2.67	81	.10	3.40	0.07	0.07	1.45	0.33	99.34
13	8.89	11.93	0.41	76	.82	n.d.	0.17	0.10	0.11	0.04	98.47
14	11.78	9.05	0.11	73	.59	1.66	0.87	0.15	0.51	0.07	97.79
Atom	ic propo	rtions									
No.	Pt	Ir	Os	Rh	Pd	Ru	Fe	Cu	Ni	$\Sigma PG$ Cu +	E/(Fe + Ni)
1	67.19	14.73	2.50	1.66	_	1.51	11.25	0.74	0.40	7.07	
2	84.65	0.05	0.14	0.53	0.97	_	12.41	1.23	_	6.33	
3	75.94	0.03	0.75	5.61	0.75	0.40	15.14	1.23	0.14	5.05	
4	79.27	0.40	0.63	0.48	0.54	0.23	16.23	1.59	0.63	4.42	
5	75.13	_	0.31	2.94	1.07	0.18	18.10	1.95	0.31	3.91	
6	72.30	1.15	0.33	2.22	0.14	0.08	22.05	1.52	0.21	3.21	
7	71.53	0.03	0.19	0.95	2.56	0.07	18.90	5.74	_	3.05	
8	73.36	0.97	0.25	0.29	_	_	23.67	1.45	_	2.98	
9	72.59	0.25	_	0.31	1.37	_	22.78	2.68	_	2.93	
10	71.28	0.08	0.07	1.15	1.04	· _	25.40	0.96	_	2.79	
11	71.15	_	0.23	_	_	_	26.65	1.65	0.28	2.50	
12	61.14	2.60	0.06	2.07	0.09	0.48	25.99	0.89	6.69	1.98	
13	51.99	_	0.12	0.15	0.12	0.05	28.20	18.47	0.91	1.10	
14	50.51	1.16	0.61	0.67	0.19	0.10	21.70	24.82	0.24	1.14	

Results of WDS electron-microprobe analyses; Co is not detected (<0.05 wt%). The analysed PGE alloy grains refer to the following placer samples: VLE 2001-44 (analyses 1, 6), VLE 2001-91b (no. 5), VLE 2001-82 (no. 7, 11, 13, 14), VLE 2001-85b (no. 2, 8), VLE 2001-33 (no. 4, 9, 12), and VLE 2001-17b (no. 3, 10)

and (3) tetraferroplatinum (PtFe) is tetragonal, space group P4/mmm, and forms a solid solution with tulameenite, Pt<sub>2</sub>FeCu (Nixon et al., 1990; Bowles, 1990). Our compositions (Table 1 and *Barkov* et al., 2005a) suggest that the tetraferroplatinumtulameenite series from British Columbia is somewhat nonstoichiometric, extending toward (Pt, PGE)<sub>1+x</sub>(Fe, Cu, Ni)<sub>1-x</sub>, not (Pt, PGE) (Fe, Cu, Ni). However, natural examples of "Pt<sub>2</sub>Fe"-type alloys were reported from several localities (Johan et al., 1989; Oberthür et al., 2002; Barkov et al., 2005a; Melcher et al., 2005), and  $Pt_{2,5}$  (Fe, Ni, Cu)<sub>1,5</sub> was reported from the Tulameen complex, Canada (*Nixon* et al., 1990) and Uralian-type complexes, Urals, Russia (Garuti et al., 2002). In addition, Malitch and Thalhammer (2002) have described "homogeneous Pt<sub>2</sub>Fe" with a disordered *fcc* structure. Thus, the latter alloy is structurally related to Ferich platinum. We suggest that "Pt<sub>2</sub>Fe"-type alloy from British Columbia and other localities is unlikely to be a new species of alloy; this alloy probably is a compositional variant of Fe-rich platinum, so that its "stoichiometric" composition could be rather serendipitous, and its value of  $\Sigma PGE:(Fe + Cu + Ni)$  ratio of  $\sim 2$ (Fig. 4) could reflect a lower limit of Pt content, possible in the mineral platinum (or isoferroplatinum, as a less probable alternative).

#### Unusual zoning in a placer Pt-Fe alloy grain

A zoned grain of Pt-Fe alloy, found in sample VLE-2001-33, consists of a corelike zone:  $Pt_{74.0}Fe_{20.4}Cu_{1.9}Ir_{1.5}Rh_{1.1}Pd_{1.0}Os_{0.08}Ru_{0.01}Ni_{0.01}$  (at%) with a  $\Sigma PGE$ : (Fe + Cu + Ni) ratio of 3.5 (i.e., darker zone in BSE image), and a rim-like zone:  $Pt_{78.5}Fe_{15.5}Cu_{1.7}Ir_{1.5}Rh_{1.4}Pd_{1.2}Ni_{0.15}Os_{0.06}Ru_{<0.01}$  with a  $\Sigma PGE:(Fe + Cu + Ni)$  ratio of 4.8 (i.e., brighter zone in BSE image: Fig. 3C). This compositional zoning is highly unusual, and provides evidence for a late enrichment in Pt and removal of Fe, which would be anomalous for a magmatic Pt-Fe alloy phase. Recently, similar zoning was described in a placer Pt-Fe alloy grain from another locality in British Columbia (*Barkov* et al., 2005a), where an original alloy (i.e.,  $Pt_{73,2}$ ) Rh<sub>2.3</sub>Os<sub>1.6</sub>Ir<sub>1.3</sub>Pd<sub>0.6</sub>Ru<sub>0.4</sub>Fe<sub>15.2</sub>Cu<sub>5.0</sub>Ni<sub>0.3</sub>) is clearly rimmed and replaced by a veinlet-forming alloy phase: Pt<sub>81.7</sub>Rh<sub>2.4</sub>Os<sub>1.8</sub>Ir<sub>1.6</sub>Pd<sub>0.5</sub>Ru<sub>0.4</sub>Fe<sub>6.0</sub>Cu<sub>5.5</sub>Ni<sub>0.1</sub>. Thus, the primary alloy and the alloy developed in zones of alteration are quite uniform in terms of their contents of Rh, Os, Ir, Pd, Ru, and Cu, and they are notably distinct in contents of Pt and Fe. Also, the  $\Sigma PGE:(Fe + Cu + Ni)$  ratio of the alteration-induced alloy phase (7.6) is much greater than that of the original alloy before alteration (3.9).

These rim- and veinlet-forming zones richer in Pt and poorer in Fe probably formed as a result of interaction of the original Pt-Fe alloy with a low-temperature fluid, resulting in a selective removal of Fe and simultaneous addition of Pt. Iron and Pt were thus remobilized and redistributed on the scale of this grain of alloy; in contrast, the other elements remained essentially immobile (*Barkov* et al., 2005a). The zoning shown in Fig. 3C appears to be of the same origin, also implying a late-stage removal of Fe and corresponding addition of Pt to the peripheral zone, owing to interaction of the original alloy (i.e., core phase; Fig. 3C) with a low-temperature fluid. Similar patterns of zoning were described in Pt-Fe-(Cu) alloy minerals (e.g., *Nixon* et al., 1990; *Melcher* et al., 2005).



Fig. 5. Contents of minor Ir, Rh and Pd (at%) in various Pt-Fe-(Cu) alloys from placer deposits of British Columbia, Canada. A total of 234 WDS electron-microprobe analyses (n = 234) are plotted. (1) Pt<sub>3</sub>Fe-type alloy(s) with a  $\Sigma$ PGE:(Fe + Cu + Ni) ratio ranging from 2.5 to 3.5, corresponding to isoferroplatinum or Fe-rich platinum (n = 88). (2) Fe-rich platinum with a  $\Sigma$ PGE:(Fe + Cu + Ni) ratio of 3.6–7.6 (n = 111). (3) "Pt<sub>2</sub>Fe"-type alloy(s) with a  $\Sigma$ PGE:(Fe + Cu + Ni) ratio of 1.8–2.5 (n = 17). (4) Members of the tetraferroplatinum-tulameenite series with a  $\Sigma$ PGE:(Fe + Cu + Ni) ratio of  $\sim 1$  (n = 18)

#### Minor Ir, Rh, and Pd in various Pt-Fe-Cu alloys

Contents of the minor elements Ir, Rh and Pd in the Pt-Fe-(Cu) alloys from the placer deposits are examined in Fig. 5; a broad compositional spectrum is observed, and it is important to note that the Ir-Pd join is clearly avoided, consistent with previous observations (Barkov et al., 2005a). In terms of the Ir-Rh-Pd diagram, the latter authors noted a curvilinear trend for minor Ir, Rh and Pd in various Pt-Fe-Cu alloys from British Columbia, extending from the Ir apex toward Rh and then curving toward Pd. A similar trend, observed for Pt<sub>3</sub>Fe-type alloys, was interpreted to reflect a compositional change with decreasing temperature (Tolstykh et al., 2002, and references therein). Indeed, the existing differences in melting points of Ir (2454 °C), Rh (1967 °C), and Pd (1555 °C) could presumably result in a relative decrease in amounts of Ir (and Rh) and increase in Pd with decreasing temperature of primary crystallization of Pt-Fe-Cu alloys. However, the total absence of compositions along the Ir-Pd join in Fig. 5 is not a function of temperature of crystallization, but rather occurs for a crystal-chemical reason. It is known that crystallochemical factors can be crucial in controlling the incorporation of various admixtures of components in alloys. For example, W + Mo abundances in a W-rich Os-Ir alloy grain from California are controlled by Ir and incorporated via the scheme:  $[(W + Mo) + Ir] \leftrightarrow Os$  (*Barkov* et al., 2006). Thus, various combinations of minor elements (Ir-Rh, Rh-Pd, and Ir-Rh-Pd) may be readily incorporated in the



Fig. 6. The Os-Ir-Ru diagram (at%) showing compositions of Ir-, Os-, and Ru-dominant alloys from the placer deposits examined in British Columbia. The dashed lines show the miscibility gap of *Harris* and *Cabri* (1991) and *Cabri* et al. (1996); RUIROS is the compositional field of rutheniridosmine. Open circles (1) are individual grains of Ir-Os-(Ru)-rich alloys, or Ir-Os-(Ru)-rich alloys in mutual intergrowth with Pt-Fe alloy. Filled circles (2) are micro-inclusions or lamellae of Os-dominant alloys enclosed by Pt-Fe alloy. Filled squares (3) are micro-inclusions or lamellae of Ir-dominant alloy enclosed in Pt-Fe alloy.

Pt-Fe-Cu alloys; however, a "forbidden zone" appears to exist along and close to the Ir-Pd join (Fig. 5).

#### Ruthenium and Ru-rich alloys of Os and Ir

Typically, placer grains of Os- or Ir-dominant alloys (<0.5 mm in size) contain minor amounts of Ru ( $\leq$ 5 at%), as shown in Fig. 6. However, several Ru-rich alloy grains were encountered. One such grain (0.2 mm in length) in sample VLE-2001-33 has a Ru-dominant composition corresponding to the mineral ruthenium: Ru<sub>36.5</sub>Os<sub>31.0</sub>Ir<sub>26.5</sub>Pt<sub>3.6</sub>Rh<sub>2.2</sub>Fe<sub>0.2</sub> (anal. 6, Table 2, Fig. 6), and encloses an elongate inclusion of Pt-Fe alloy [ $\Sigma$ PGE:(Fe + Cu + Ni) = 2.49]. The other alloy grains, also enriched in Ru, have the following compositions: Os<sub>36.7</sub>Ir<sub>31.1</sub>Ru<sub>29.9</sub>Pt<sub>1.4</sub>Rh<sub>0.7</sub> (VLE-2001-44); Os<sub>48.3</sub>Ir<sub>37.1</sub>Ru<sub>11.6</sub>Pt<sub>1.4</sub>Rh<sub>1.0</sub>Fe<sub>0.5</sub> (VLE-2001-67); Os<sub>48.5-58.0</sub>Ir<sub>24.9-37.1</sub>Ru<sub>11.0-11.2</sub>Pt<sub>1.4-4.4</sub>Rh<sub>0.5-1.0</sub>Fe<sub>0.8</sub> (two grains; VLE-2001-70b); Os<sub>35.9</sub>Ir<sub>31.8</sub>Ru<sub>25.9</sub> Fe<sub>4.2</sub>Ni<sub>1.2</sub>Pt<sub>0.3</sub> (VLE-2001-33); and Ir<sub>72.1</sub>Ru<sub>13.0</sub>Pt<sub>7.2</sub>Os<sub>3.3</sub>Rh<sub>2.3</sub>Fe<sub>1.8</sub> (VLE-2001-7b).

#### Exsolution-induced Ir- and Os-dominant alloys in Pt-Fe alloys

The compositions of fine exsolution-induced lamellae of Ir-dominant alloys in Pt-Fe alloys plot in the same compositional field as the placer grains of Ir-(Os)-rich alloy; in contrast, the Os-rich exsolution-induced phase displays extreme Os enrichment (Fig. 6). In addition, the Os lamellae are generally more abundant than

No.	Fe	Ni	Pt	Ir	Os	Pd	Rh	Ru	Total
1	0.11	n.d.	0.92	35.46	62.11	n.d.	0.37	1.14	100.11
2	0.17	0.05	8.43	53.58	33.96	n.d.	1.47	2.13	99.79
3	0.05	n.d.	0.57	40.67	54.67	n.d.	0.49	3.74	100.22
4	0.16	n.d.	1.47	39.82	51.21	n.d.	0.58	6.55	99.79
5	0.08	n.d.	1.65	36.46	42.51	n.d.	0.46	18.39	99.55
6	0.08	n.d.	4.51	32.63	37.76	n.d.	1.42	23.63	100.03
7	1.46	0.08	8.99	80.27	4.67	n.d.	2.32	1.30	99.09
8	0.12	n.d.	3.09	1.98	92.87	n.d.	0.45	0.63	99.14
Atomic	proport	tions							
1	0.38	_	0.89	34.61	61.27	_	0.67	2.12	100
2	0.57	0.15	8.01	51.64	33.08	_	2.64	3.91	100
3	0.17	_	0.54	38.85	52.78	_	0.87	6.79	100
4	0.51	_	1.35	37.14	48.27	_	1.01	11.62	100
5	0.23	_	1.39	31.11	36.66	_	0.74	29.85	100
6	0.21	0.05	3.61	26.49	30.98	_	2.16	36.49	100
7	4.75	0.25	8.34	75.61	4.45	_	4.08	2.33	100
8	0.40	_	3.00	1.95	92.58	_	0.83	1.18	100

Table 2. Compositions of various Ir-Os-Ru alloys from Au-PGE placer deposits, British Columbia, Canada

Results of WDS electron-microprobe analyses; Co and Cu are not detected (<0.05 wt%). The analysed PGE alloy grains refer to the following placer samples: VLE 2001-85b (analysis no. 1, 7, 8), VLE 2001-33 (no. 2, 6), VLE 2001-70b (no. 3), VLE 2001-67 (no. 4), and VLE 2001-44 (no. 5)

the Ir lamellae. These distinctions may reflect crystallochemical differences of Ir and Os, which are evident in the contrasting behaviour of these elements: a high amount of Ir can enter a Pt-Fe alloy, as reflected in the existence of chengdeite, the Ir-dominant analogue of isoferroplatinum from the Luanhe River placer, China ( $Y_u$ , 1995), and of a Pt-Fe alloy with 23 wt% Ir from the Saskatchewan River placer, Alberta, Canada (*Cabri* et al., 1996). In contrast, rather limited amounts of Os are reported in Pt-Fe alloys. For example, in our suite, the maximum content of Ir, in a grain of Pt-Fe alloy from sample VLE-2001-44, is 16.1 wt% (14.7 at%), whereas the maximum Os content attains 3 wt% only (Table 1). This content of Ir even surpasses the amount reported in a grain of Pt<sub>3</sub>Fe-type alloy from the Salmon River placer in Alaska (15.4 wt%: Tolstykh et al., 2002). We suggest that crystallochemical factors probably control the limited incorporation of Os in Pt-Fe alloys, thus resulting in the extreme accumulation of Os in the Os-rich exsolution products. In contrast, Ir can be readily incorporated in a Pt-Fe alloy host, and, consequently, extremely high levels of Ir are not characteristic of the Ir-dominant exsolution phases, and the latter are thus relatively less common.

#### Hongshiite, sperrylite, and hollingworthite-platarsite

A grain of  $Pt_3Fe$ -type alloy (sample VLE-2001-82) contains hongshiite ( $Pt_{1.04}$   $Pd_{0.02}Cu_{0.93}$ ), a rare intermetallic compound of Pt and Cu, which occurs as a nar-

No.	Cu	Fe	Ni	Pt	Ir	Rh	Pd	S	As	Sb	Te	Total
Wt%												
1	22.01	0.09	n.d.	75.29	n.d.	n.d.	0.87	n.d.	n.d.	n.d.	n.d.	99.69
2	n.d.	n.d.	n.d.	54.32	1.80	n.d.	n.d.	n.d.	45.27	0.47	n.d.	101.86
3	n.d.	0.41	n.d.	17.44	0.79	32.72	0.86	12.47	35.25	0.07	n.d.	100.0
4	12.23	0.38	0.03	36.45	0.07	23.09	n.d.	27.75	n.d.	n.d.	n.d.	100.0
5	n.d.	0.12	n.d.	n.d.	n.d.	n.d.	73.97	n.d.	9.16	8.73	7.64	99.62
6	n.d.	0.11	n.d.	51.36	n.d.	3.24	8.04	n.d.	0.97	36.29	n.d.	100.0
7	n.d.	0.13	n.d.	50.27	n.d.	3.51	8.71	n.d.	0.10	36.08	n.d.	99.06
apfu												
No.	Cu	Fe	Ni	Pt	Ir	Rh	Pd	$\Sigma$ Me	S	As	Sb	Te
1	0.93	< 0.01	_	1.04	_	_	0.02	_	_	_	_	_
2	_	_	_	0.93	0.03	3 —	_	0.96	_	2.02	0.01	_
3	_	0.02	_	0.21	0.01	0.74	0.02	1.00	0.91	1.10	< 0.01	_
4	0.91	0.03	< 0.01	0.89	< 0.01	1.06	_	2.90	4.10	_	_	_
5	_	0.03	_	_	_	_	10.96	10.99	_	1.93	1.13	0.94
6	_	0.02	_	2.70	_	0.32	0.77	3.81	_	0.13	3.05	_
7	_	0.02	_	2.67	_	0.35	0.85	3.89	_	0.01	3.07	_

Table 3. Electron-microprobe data on hongshiite, sperrylite, hollingworthite-platarsite, cuprorhodsite-malanite,Te-rich isomertieite, and genkinite from British Columbia, Canada

Analysis: *I* hongshiite, *no.* 2 sperrylite, *no.* 3 hollingworthite-platarsite, *no.* 4 cuprorhodsite-malanite, *no.* 5 Te-rich isomertieite, and *no.* 6, 7 genkinite. Analyses 6 and 7 are mean of 5 and 7 analyses, respectively. These results of WDS analyses pertain to PGM from sample VLE-2001-82 (see Fig. 1 for location). Ru, Os, Co, and Bi were not detected (n.d.). The atomic proportions are based on a total of 2 atoms per formula unit, *apfu* (no. 1), 3 *apfu* (no. 2,3), 7 *apfu* (no. 4, 6, 7), and 15 *apfu* (no. 5). The total in analysis 1 includes 1.43 wt% Os, ascribed to secondary fluorescence from an associated osmium grain. The total in analysis 7 includes 0.26 wt% Sn (0.02 *apfu*)

row rim-like grain in intergrowth with native Os (Fig. 3B). Its Pd content is minor (anal. 1, Table 3), indicating the insignificance of the skaergaardite component; skaergaardite, PdCu, is a newly reported PGM species discovered in the Skaergaard intrusion, East Greenland (*Rudashevsky* et al., 2004). A member of the skaergaardite-hongshiite solid-solution series  $[(Pd_{0.92}Pt_{0.10})_{\Sigma 1.02}Cu_{0.98}]$  has been reported from the Penikat complex, Finland (*Barkov* et al., 2005b).

Sperrylite is present as tiny grains (e.g., Fig. 3F) and fine exsolution-lamellae hosted by a  $Pt_3Fe$ -type alloy (sample VLE-2001-82). Its composition,  $(Pt_{0.93} Ir_{0.03})_{\Sigma 0.96}(As_{2.02}Sb_{0.01})_{\Sigma 2.03}$  (anal. 2, Table 3), is close to being stoichiometric. It differs from that of a metal-rich and S-bearing sperrylite  $(Pt,Rh,Fe)(As,S)_{2-x}$  reported from another placer locality in British Columbia (*Barkov* et al., 2005a). The latter formula may also apply to a "Pt<sub>2</sub>As<sub>3</sub>" phase, which is probably related, from the Konder alkaline-ultramafic complex, Aldan Shield, Russia (*Nekrasov* et al., 2005).

Hollingworthite forms minute and irregular inclusions ( $\sim 5 \,\mu$ m) in a Pt<sub>3</sub>Fetype alloy grain (sample VLE-2001-82). A representative composition of hollingworthite, (Rh<sub>0.74</sub>Pt<sub>0.21</sub>Fe<sub>0.02</sub>Pd<sub>0.02</sub>Ir<sub>0.01</sub>)<sub> $\Sigma 1.00$ </sub>S<sub>0.91</sub>As<sub>1.10</sub> (anal. 3, Table 3), is a solid solution toward platarsite, with an excess in As relative to the As:S ratio of 1

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in ideal RhAsS (*Stumpfl* and *Clark*, 1965). This departure implies the presence of a minor diarsenide component (As<sub>2</sub>). Platarsite has the ideal formula PtAsS (*Cabri* et al., 1977a; *Cabri*, 2002), and apparently is a mixed-valence compound:  $Pt^{4+}_{0.5}$   $Pt^{2+}_{0.5}$ [AsS]<sup>3-</sup> (*Barkov* and *Fleet*, 2004). The naturally occurring platarsite and platarsite-type phases typically have As-excess compositions (e.g., *Cabri* and *Laflamme*, 1981). The excess of As in hollingworthite grains, analyzed in this study, likely reflects the presence of a platarsite component, and implies a corresponding increase in  $Pt^{4+}$  relative to  $Pt^{2+}$  in its composition in order to maintain charge balance.

#### Cuprorhodsite-malanite, Te-rich isomertieite and genkinite

A minute grain of PGE thiospinel, found as an inclusion in a Pt-Fe alloy (sample VLE-2001-82; Fig. 3D), corresponds to an intermediate member of the cuprorhodsite-malanite series, poor in cuproiridsite and ferrorhodsite components: (Cu<sub>0.91</sub>  $Fe_{0.03}Ni_{<0.01})_{\Sigma 0.95}(Rh_{1.06}Pt_{0.89}Ir_{<0.01})_{\Sigma 1.95}S_{4.10}$  (anal. 4, Table 3). This formula is close to  $Cu^+(Rh^{3+}Pt^{4+})S^{2-}_4$ , which suggests that all Pt occurs as  $Pt^{4+}$  in this thiospinel phase. Members of the cuprorhodsite-(ferrorhodsite)-malanite series, displaying extensive coupled substitutions, were reported from the Penikat layered complex, Finland (Barkov et al., 2000); various PGE-rich thiospinels occur in Uralian-type complexes (Melcher, 2000, and references therein). In another placer from British Columbia, a Ni-rich cuproiridsite-(cuprorhodsite-malanite)  $[(Cu_{0.58}Ni_{0.26}Fe_{0.12})_{\Sigma 0.97}(Ir_{1.11}Rh_{0.45}Pt_{0.36}Co_{<0.01})_{\Sigma 1.92}S_{4.12}; Barkov et al., 2005a]$ displays the same degree of nonstoichiometry (4.1 S apfu) as the cuprorhodsitemalanite grain analysed in this study. This deviation is consistent with experimental data (e.g., Somasundaram et al., 1997). A relative deficit at the Rh-(Ir) site, which is characteristic of these two examples of thiospinel PGM from British Columbia, is indicated by the analytical data obtained using two different EMP facilities.

A rarely encountered variant of isomertieite  $[(Pd_{10.96}Fe_{0.03})_{\Sigma10.99}(Sb_{1.13} Te_{0.94})_{\Sigma2.07}As_{1.93}]$ , enriched in Te (anal. 5, Table 3), occurs in close association with the cuprorhodsite-malanite grain (Fig. 3D). The Te likely substitutes for Sb, and the atomic Te:Sb ratio is high (0.83), implying the existence of a Te-dominant analogue of isomertieite. Indeed, Te-rich isomertieite was described from the Chindwin River area in Burma (*Hagen* et al., 1990; *Cabri* et al., 1996). We note that one composition reported from Burma in fact corresponds to a Te-dominant (unnamed) analogue of isomertieite:  $(Pd_{10.44}Pt_{0.55})_{\Sigma10.99}(Te_{1.08}Sb_{0.86})_{\Sigma1.94}As_{2.08}$ . Phases of the  $Pd_{11}(Te,Sb)_2As_2$  type were also reported from placers of Finnish Lapland (*Törnroos* et al., 1996) and of the Bushveld complex (*Oberthür* et al., 2004).

An unusual Pt-Pd-Rh antimonide, related to genkinite, occurs as fine exsolution-induced lamellae developed near the centre of a subhedral grain of  $Pt_3Fe$  alloy (sample VLE-2001-82). These lamellae are subparallel to edges of the host grain (Figs. 3E, F). Two sets of WDS analyses of this phase, made on twelve lamellar grains, gave narrow compositional ranges within each of these sets. The average compositions (anal. 6 and 7, Table 3) are somewhat metal-deficient and nonstoichiometric relative to the ideal proportions of genkinite [(Pt,Pd,Rh)<sub>4</sub>Sb<sub>3</sub>] from the Bushveld complex, South Africa, and Ethiopia (*Cabri* et al., 1977b; *Cabri* and



Fig. 7. Back-scattered electron images showing a subhedral to euhedral morphology of fine-grained clinopyroxene (Cpx: A) and olivine (Oliv: B) from placer sample VLE-2001-82

*Laflamme*, 1981). The values of the (Pt + Pd + Rh):(Sb + As) ratio, observed for this phase, are 1.2 (JEOL-8600 microprobe) and 1.25 (JEOL-8900 microprobe); this value should be 1.33 in ideal  $(Pt,Pd,Rh)_4Sb_3$ . Thus, the compositions of this Pt-Pd antimonide from British Columbia may imply the existence of a limited solid-solution extending from genkinite toward stumpflite (PtSb; *Johan* and *Picot*, 1972). The elevated content of Pd in this phase is indicative of a solid solution with ungavaite, Pd<sub>4</sub>Sb<sub>3</sub>, a new PGM species from the Mesamax Northwest deposit, Quebec, Canada (*McDonald* et al., 2005).

#### Clinopyroxene and olivine

Twenty placer grains (n = 20) of clinopyroxene, associated with PGM in sample VLE-2001-82, are typically euhedral (Fig. 7A), and exhibit the following compositional ranges (wt%): SiO<sub>2</sub> 52.20–54.45, TiO<sub>2</sub> 0.08–0.30, Al<sub>2</sub>O<sub>3</sub> 1.14–2.77, Cr<sub>2</sub>O<sub>3</sub> 0.09–0.59 (with a mean of 0.3 wt%), FeO 2.00–5.21, MnO 0.02–0.17, MgO 15.44–17.63, CaO 22.95–24.66, Na<sub>2</sub>O 0.20–0.62 (K<sub>2</sub>O not detected). Thus, this clinopyroxene has a diopside composition: Ca<sub>46.4–49.1</sub>Mg<sub>42.8–48.2</sub>Fe<sub>3.1–8.1</sub>, with very high values of mg [84.1 < 100 Mg:(Mg + Fe + Mn) < 93.9], and is compositionally similar to diopside from olivine clinopyroxenite of the Tulameen complex. The most magnesian diopside grain observed in this placer deposit is Ca<sub>49.1</sub>Mg<sub>47.7</sub>Fe<sub>3.1</sub> (mg 93.9; 0.59 wt% Cr<sub>2</sub>O<sub>3</sub>), which is close to Ca<sub>49.6</sub>Mg<sub>47.2</sub>Fe<sub>3.2</sub> (mg 93.6; 0.44 wt% Cr<sub>2</sub>O<sub>3</sub>), representative of diopside from the olivine clinopyroxenite unit of the Tulameen complex (*Nixon* et al., 1990).

The ranges observed for twenty grains of placer olivine (sample VLE-2001-82; Fig. 7B) are the following (wt%): SiO<sub>2</sub> 40.33–41.32, FeO 7.89–12.25, MnO 0.13–0.27, MgO 47.78–51.39, CaO 0.04–0.58, and NiO 0.04–0.31, corresponding to Fo<sub>86.8–91.5</sub>Fa<sub>7.9–12.5</sub>. Interestingly, the overall compositional range (Fo<sub>87–92</sub>) observed for these olivine grains corresponds closely to the range Fo<sub>88–91</sub>, characteristic of the dunite core of the Tulameen complex (*Nixon* et al., 1990). Therefore, these olivine and clinopyroxene placer grains were likely derived from the dunite and olivine clinopyroxenite units of the nearby Tulameen complex (Fig. 1).

Canada											
Mineral or phase	Numbe	r of PG	M grain	is analys	sed in th	uis study	(per sa	mple)			
	VLE 2001	VLE 2001	VLE 2001	VLE 2001	VLE 2001	VLE 2001	VLE 2001	VLE 2001	VLE 2001	VLE 2001	VLE 2001
	17b	44	91b	93	33	85b	7b	67	69a	70b	82
Fe-rich platinum [ $\Sigma$ PGE /(Fe + Cu + Ni) = 3.6–7.6]	9	17	8	8	25	18	0	0	0	1	1
Pt <sub>3</sub> Fe-type alloy [ $\Sigma$ PGE /(Fe + Cu + Ni) = 2.5–3.5]	5	6	1	1	10	S	5	1	0	0	13
"Pt <sub>2</sub> Fe"-type alloy [ $\Sigma$ PGE /(Fe + Cu + Ni) = 1.8–2.5]	0	0	0	0	б	0	0	0	0	0	0
Tulameenite-tetraferroplatinum series [DPGE/	0	0	0	0	0	0	0	0	0	0	б
(Fe + Cu + Ni) = ca. 1											
Iridium [Ir-dominant Ir-Os-(Pt) alloy]	0	0	0	0	٢	4	1	0	1	0	0
Osmium [Os-dominant Os-Ir-(Pt) alloy]	0	1	0	0	0	1	0	0	0	4	0
Ruthenium [Ru-dominant Ru-Ir-Os alloy]	0	0	0	0	1	0	0	0	0	0	0
Sperrylite <sup>§</sup>	0	0	0	0	0	0	0	0	0	0	0
Hollingworthite-platarsite <sup>§</sup>	0	0	0	0	0	0	0	0	0	0	0
Cuprorhodsite-malanite <sup>§</sup>	0	0	0	0	0	0	0	0	0	0	1
Isomertieite <sup>§</sup>	0	0	0	0	0	0	0	0	0	0	1
Genkinite <sup>§</sup>	0	0	0	0	0	0	0	0	0	0	12
Hongshiite <sup>§</sup>	0	0	0	0	0	0	0	0	0	0	1
$PtAs_{1-x}S_{1+x}$	0	0	1	0	0	0	0	0	0	0	0
<i>Note</i> : The location and terrane affinities for these samples	are shov	vn in Fig	g. 1. The	admun :	rs of PG	M grain	s listed	in Table	4 includ	le single	placer
grains and various PGM and PGE-rich phases, which occur	r in com	oosite gr	ains or 1	nutual i	ntergrow	/ths, exc	ept for 1	nicro-in	clusions	and exse	olution
lamellae of Os- and Ir-dominant alloys in Pt-Fe-(Cu) alloy	grains, v	which ar	e not in	cluded h	ere. The	: Pt <sub>3</sub> Fe-t	ype allo	y is isofé	erroplati	num or H	e-rich
platinum. <sup>5</sup> These PGM occur in trace or minor amounts, Composition of the $PtAs_{1-x}S_{1+x}$ phase was reported by	typically Barkov	y as tuny et al. (2	7 inclusi 2005a)	ons or 1	amellae	enclose	uniw da	n placer	grains c	ir Pt-Fe	alloys.

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#### Droplet inclusions in Pt-Fe alloy

Several droplet-shaped inclusions, presumably formed from microdroplets of trapped liquid, are observed in a placer grain of isoferroplatinum or Fe-rich platinum from sample VLE-2001-44 (Fig. 2F). These inclusions are mineralogically heterogeneous and comprise a complex mixture of unidentified K-rich aluminosilicate, Ti-bearing magnetite (?) and bornite ( $Cu_{4.8}Fe_{0.9}S_4$ : EMP data). Silicateglass inclusions, which also are rich in K, and are hosted by isoferroplatinum, possibly derived from an Alaskan-type intrusion, were described from the Durance River alluvium, France (*Johan* et al., 1990). Similarly, some of the silicate inclusions enclosed within grains of Pt-Fe alloy from British Columbia have K-rich compositions, e.g., a potassian sodic-calcic amphibole like richterite occurs in intimate intergrowth with native Os (*Barkov* et al., 2005a). The K-rich compositions of these micro-inclusions in Pt-Fe alloy imply that they have crystallized from a late-stage melt.

# *Terrane affinities and mineralogical implications for primary sources of placer PGM*

The terrane affinities shown in Fig. 1 and mineralogical characteristics of the placer PGM grains provide information pertaining to their potential source-rocks. The mineral species of the analyzed PGM are summarized in Table 4. The PGE alloys are the principal PGM in these placer deposits; any S-(As-Sb-Te)-bearing species are very rare, consistent with the low-S magmatic environment that is characteristic of Alaskan-type and ophiolite complexes.

The association of placer PGM in sample VLE-2001-82 exhibits the following characteristics: (1) Pt-Fe alloys are the principal PGM, and no Os-, Ir-, or Ru-rich alloys are observed (Table 4); (2) interestingly, in contrast to most of the other placer samples, grains of a Pt<sub>3</sub>Fe-type alloy are strongly dominant; (3) grains of Cu-rich Pt-Fe alloys of the tulameenite-tetraferroplatinum series (and hongshiite, PtCu) are present only in this sample; (4) this sample is characterized by the greatest diversity of PGM species (Table 4), including a rare Pt-Pd antimonide related to genkinite (Pt-Pd antimonides have been reported from the Tulameen complex; *St Louis* et al., 1986; *Nixon* et al., 1990); (5) the PGM are associated with highly magnesian diopside containing elevated Cr and with Fo-rich olivine, consistent with dunite and olivine clinopyroxenite source-rocks within the Tulameen complex; (6) the faceted morphologies of the placer PGM, diopside and olivine grains (Figs. 2A, 7A and B) indicate a short distance of transport from their source. All of these observations are consistent with provenance from an Alaskan-type complex, namely, the Tulameen complex.

The associated PGM grains in sample VLE-2001-7b also are characterized by a high proportion of grains of  $Pt_3Fe$ -type alloy, similar to sample VLE-2001-82 (Table 4). This placer site lies within the island-arc terrane of Quesnellia (Fig. 1), and thus provenance from an Alaskan-type complex appears probable. A single grain of Ru-rich iridium (13 at% Ru) observed in this placer PGM association is not inconsistent with an Alaskan-type source. At sulfur fugacities below the Ru-RuS<sub>2</sub> buffer, Ru could presumably be incorporated in the Ir-(Os)-dominant alloy instead of a Ru-Os-Ir disulfide of the laurite-erlichmanite series. In addition, an

abundance of grains of Os-dominant alloy enriched in Ru and associated with subordinate Pt-Fe alloys (e.g., *Weiser* and *Bachmann*, 1999), rather than the presence of minor Ru-rich alloy(s), would point to an ophiolite source.

In contrast, the PGM in placer sample VLE-2001-70b are closely associated with the Cache Creek oceanic terrane in the Atlin area (Fig. 1), and Os-dominant alloy species enriched in Ru (6-11 at% Ru) are dominant in this sample (Table 4). Thus, the Atlin ophiolite complex is the most probable source for these PGM grains, which is consistent with findings at other occurrences of placer PGM in the Atlin area (*Cabri* et al., 1996; *Barkov* et al., 2005a). Only a few PGM grains were recovered from placer samples VLE-2001-69a (also located at Atlin) and 67 (Fig. 1). The latter sample contains two Os-dominant alloy grains (one with 11.6 wt% Ru), which also are consistent with an ophiolitic origin (Slide Mountain Terrane).

An ophiolitic origin also may be appropriate for at least some PGM from sample VLE-2001-33, which were collected in a complex tectonostratigraphic setting with potential influence by both island-arc (Quesnellia) and oceanic (Slide Mountain and possibly Cache Creek) terranes (Fig. 1). The PGM in this sample display the following distinctive features: (1) grains of Pt-Fe alloy with high values of their  $\Sigma$ PGE:(Fe + Cu + Ni) ratio dominate among the placer PGM (Table 4), and the presence of an unusually zoned Pt-Fe alloy grain is noteworthy (Fig. 3C), (2) grains of Ir-dominant alloys with variable amounts of Ru ( $\leq$ 5 to 25.9 at%) are relatively common, and (3) a placer grain of Ru-dominant alloy corresponds to the mineral ruthenium.

Samples VLE-2001-91b and 93, collected from the same placer locality (Fig. 1), show uniform relative abundances of Pt-Fe alloy grains. The grains which have high values of the  $\Sigma$ PGE:(Fe + Cu + Ni) ratio (3.6–7.6) are much more abundant than those of the Pt<sub>3</sub>Fe-type alloy, and the grains of Pt-Fe alloys occur to the exclusion of Os-, Ir-, or Ru-dominant alloys in both samples (Table 4). Similarly, samples VLE-2001-44 and 85 have abundant grains of Pt-Fe alloy, and the grains with high values of their  $\Sigma$ PGE:(Fe + Cu + Ni) ratio are most common. In addition, Pt-Fe alloy is the only species of PGM observed in sample VLE-2001-17b (Table 4).

Samples VLE-2001-91b, 93, 44, 17b, and 85b exhibit strong mineralogical affinities, in that they all contain principally grains of Pt-Fe alloy with high values of their  $\Sigma$ PGE:(Fe + Cu + Ni) ratio, consistent with a common provenance. The derivation of the PGM in these placers suggests an Alaskan-type source, even though no such complexes are presently known in this area (Fig. 1). The round shapes of Fe-rich platinum grains (e.g., Figs. 2B and 3C; samples VLE-2001-85b and 33) indicate significant distances of transport. The association of species of Pt- and Ir-dominant alloys observed in these samples (Table 4) may well reflect a relative enrichment in Pt and Ir in the mineralized host-rocks. It is interesting to note that this Pt-Ir association is consistent with a "M"-shaped chondrite-normalized abundance pattern, with peaks at Pt and Ir, typical of Alaskan-type PGE mineralization. However, the observed presence of Rudominant alloy in sample VLE-2001-33 is more consistent with an ophiolitic source and, thus, this placer deposit could have a mixed tectonostratigraphic heritage and provenance. In addition, our latest results obtained for detrial grains of

chrome spinels from a suite of chromitiferous placer deposits of British Columbia (*Barkov* et al., in prep.) suggest that grains of chrome spinels and associated PGM of potentially ophiolite provenance may be much more widespread than was previously recognized.

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