## Major- and trace-element composition of platinum group minerals and their inclusions from several Yukon placers

#### Yana Fedortchouk<sup>1</sup>

Department of Earth Sciences, Dalhousie University, Halifax, Canada

*William LeBarge<sup>2</sup>* Yukon Geological Survey, Whitehorse, Yukon, Canada

**Andrei Yu Barkov** Department of Earth and Planetary Sciences, McGill University, Montreal, Canada

> *Luca Fedele and Robert J. Bodnar* Department of Geosciences, Virginia Tech, Blacksburg, USA

Fedortchouk, Y., LeBarge, W., Barkov, A.Y., Fedele, L. and Bodnar, R.J., 2010. Major- and traceelement composition of platinum group minerals and their inclusions from several Yukon placers. *In:* Yukon Exploration and Geology 2009, K.E. MacFarlane, L.H. Weston and L.R. Blackburn (eds.), Yukon Geological Survey, p. 185-196.

#### ABSTRACT

Occurrences of placer platinum-group minerals (PGM) were reported in several gold placer deposits in Yukon. The source rock and the type of platinum mineralization are not known for these localities. We investigated five grains of Pt-Fe alloy from Burwash Creek (map area 115G and F), one grain from Scroggie Creek (map area 115O and N) and one grain from Wolverine Creek (map area 105C and D). Results of multiple electron microprobe analysis display elevated levels of Pd, Rh, Ir and Cu in these Pt-Fe alloy grains. The grains host micro-inclusions of various species of PGMs and silicatemelt inclusions with diopside, albite and sodic-calcic amphiboles. Trace element composition of the silicate inclusions determined using laser ablation ICP-MS shows a notable enrichment in large ion lithophile elements. We infer that the reported association of PGM and the trace element composition of silicate-melt inclusions observed in the studied grains are likely derived from a subduction-related Alaskan-type mineralization.

<sup>1</sup>yana@dal.ca <sup>2</sup>bill.lebarge@gov.yk.ca

#### **INTRODUCTION**

Many gold placer deposits in Yukon historically report placer occurrences of platinum-group minerals (PGM). Only very few of these occurrences were confirmed analytically, while the source rocks of the placer PGMs is not well known. Platinum mineralization can be associated with several types of mafic and ultramafic intrusive rocks, including Alpine-type peridotites or ophiolites, subduction-related Alaskan-type complexes and continental mafic-ultramafic intrusive rocks, such as Triassic Kluane sills, which are associated with continental rifting events. The Alaskan-type, concentrically zoned ultramafic-mafic complexes, are a recognized source of placer platinum. For example, ~20 tonnes of platinum derived from Alaskan-type source rocks was recovered from placer deposits of Goodnews Bay, Alaska (Tolstykh et al., 2002). Potential relationships with Alaskan-type complexes are inferred for a number of placer occurrences of PGM, documented in Canada (Nixon et al., 1990; Cabri et al., 1996; Barkov et al., 2005, 2008a,b). These species of PGM are dominantly alloys of the platinum-group elements (PGE). On the other hand, Kluane sills forming a 'Kluane-belt' in southwestern Yukon, host Ni-Cu-PGE mineralization including the Wellgreen deposit (Hulbert, 1997; Barkov et al., 2002) and may also supply PGM grains into the adjacent creeks. Possible fragments of other mafic rocks related to continental rifting events were reported in other parts of Yukon (Johnston et al., 2007).

Pt-Fe alloy is the most common type of placer PGM. Its geochemistry and composition of the inclusion suite can shed light on the origin of PGM-host magmas. The present paper documents the first confirmed occurrence of placer grains of Pt-Fe alloy in Burwash Creek and reports a detailed mineralogical and geochemical study of Pt-Fe alloy grains from Burwash, Scroggie and Wolverine creeks in southern-central Yukon. Our objectives are (1) to characterize compositional variations, extents of solid-solutions and minor element abundance present in these placer grains of Pt-Fe alloy, based on the results of electron microprobe analysis (EMP); (2) to characterize the PGMs found as inclusions in Pt-Fe alloy grains; (3) to examine the compositions of silicate melt inclusions in Pt-Fe alloy grains, their mineralogical composition and patterns of trace element concentrations based on the results of laser ablation (LA) ICP-MS; and (4) to identify a potential provenance for these placer grains of PGM.

### SAMPLE LOCATIONS

This study uses five PGM grains from a gold placer deposit in Burwash Creek, one grain from Scroggie Creek and one grain from Wolverine Creek (Fig. 1). Burwash Creek is situated in the Kluane area in southeastern Yukon, where placer gold was discovered in the 1920s. The Burwash stream is a tributary of the Kluane River. No occurrences of PGM were previously reported from Au-bearing placers in this locality. For this study we used grains donated to the Yukon Geological Survey (YGS) from the estate of placer inspector George Gilbert and grains obtained by W. LeBarge from placer miner Steve Johnson in 2008. The Kluane area is located along the eastern margin of Wrangellia (Fig. 1) and to the west of the Denali fault. The Triassic Kluane sill-like subvolcanic mafic-ultramafic intrusive rocks with Ni-Cu-PGE mineralization serve as magma-conduits for the overlying basalts of the Nikolai Group (Hulbert, 1997). In addition, fragments of oceanic-type serpentinized peridotites, possibly representing the basement of Wrangellia, are known along the Denali fault zone (Mezger, 2000). Detrital chromites, with a composition corresponding to an ophiolitic source, have been recorded in Burwash Creek (Fedortchouk and LeBarge, 2008).

Scroggie Creek (Fig. 1) cuts through rocks of the Yukon-Tanana terrane in central Yukon. It is located in the proximity of Pyroxene Mountain, the best-known example of an Alaskan-type complex in Yukon (Hart *et al.*, 2001). Fragments of oceanic Alpine-type peridotites incorporated into the Yukon-Tanana terrane assemblage are also present in the drainage area of Scroggie Creek.



Figure 1. Regional terrane and sample location map.

Wolverine Creek is located in the southern part of Yukon. It cuts through rocks of the Cache Creek terrane (Fig. 1) consisting of Mississippian to lower Jurassic oceanic volcanic rocks with fragments of Alpine-type peridotites. The Alpine-type peridotites contain associated chromite lenses, which may host PGE mineralization. However, ultramafic intrusive rocks with features distinct from the Alpine-type peridotites have been reported from the Cache Creek terrane and may represent Alaskan-type complexes (Hart *et al.*, 2001).

## ANALYTICAL METHODS

Compositions of the host Pt-Fe alloys and some larger PGM phases in micro-inclusions were analysed using the electron microprobe (EMP) in wavelength-dispersion spectrometry mode (WDS) with a JEOL JXA-8900 instrument (McGill University), at 20 kV and 30 nA, using a finely focused beam (2 µm) and on-line correction procedures. Pure metals (Os, Ir, Ru, Rh, Pt, Pd, Fe and Ni) and PtAs<sub>2</sub>, FeS<sub>2</sub>, CuFeS<sub>2</sub> and Bi<sub>2</sub>Te<sub>3</sub> were used as standards. The L $\alpha$  line was applied for Ir, Pt, Rh, Ru, Te and Cu, the M $\alpha$  line for Os, the L $\beta$  line for Pd and As, and the K $\alpha$  line for Fe, Ni and S. All possible peak-overlaps between the X-ray emission lines employed were checked and corrected. Compositions of PGM micro-inclusions and individual phases of PGM and silicate microinclusions were examined using a Hitachi S-4700 FEG Field Emission Scanning Electron Microscope (FE SEM) at the Institute for Research in Materials, Dalhousie University, equipped with an energy-dispersion spectrometer (SEM-EDS) and a set of well-characterized standards. The obtained results of EDS and WDS analysis are in good agreement with each other.

One placer grain of Pt-Fe alloy from Burwash Creek contained four silicate melt inclusions, which are considered to be primary and represent the melt trapped in the PGM during growth. The inclusions contain multiple crystals, or daughter minerals, which is characteristic of melt inclusions that have cooled relatively slowly after trapping (Bodnar and Student, 2006). The grain was mounted in epoxy and polished to expose the inclusions. The composition of the individual mineral phases in each inclusions was examined using EDS analysis on FE-SEM. As the inclusions in an opaque Pt-Fe alloy have to be exposed by polishing prior to the analysis, they could not be homogenized to obtain the composition of the whole inclusion by EMP analysis. As a result, individual phases were analysed using EDS-SEM analysis and an assumed SiO<sub>2</sub> content of 50 wt% – a realistic estimate for mafic magmas. This estimate was used as an internal standard for the LA ICP-MS analysis. For this reason, the absolute values of the element concentrations obtained by LA ICP-MS analysis are only accurate to approximately ±10%, while the relative concentrations and ratios of the elements are determined with high precision. LA ICP-MS analysis were conducted at Virginia Tech using an Agilent 7500ce guadrupole ICP-MS and a Lambda Physik GeoLas 193 nm Excimer laser ablation system with He gas flow. NIST 610 glass, used as an external standard, was analysed twice, before and after the analysis. The laser spot size was adjusted to the largest possible size, to include the maximum amount of the inclusion material but avoiding the host phase. The time-resolved LA ICP-MS data were reduced using AMS analytical software (Mutchler et al., 2008).

## **MINERALOGY OF PGM**

#### **HOST PT-FE ALLOY**

Seven placer grains of Pt-Fe alloy (0.5 to 2 mm in size) from Burwash, Scroggie and Wolverine creeks were examined and analysed (Table 1, Fig. 2). The polished sections of five of these grains had exposed microinclusions (typically 10-20 µm thick) of various phases of PGM and silicate inclusions and are described below (Fig. 3). Compositional variation in all seven grains of Pt-Fe alloy were examined from the centre to the margins, along EMP profiles with 15 to 30 data points each (Fig. 2). In the Wolverine grain, the analyses were collected along two profiles (WN-1 and WN-2; Fig. 2; Table 1). The observed levels of solid solution in all seven grains typically decrease: Pd (0.49-5.84, mean 2.38 wt%) >Rh (1.05-1.94, mean 1.50 wt%) >Ir (<0.2 to 6.91, mean 1.33 wt%) >Cu (0.17-1.19, mean 0.62 wt%) >Os (<0.1 to 0.90, mean 0.40 wt%) and >Ni (<0.06 to 0.12, mean 0.05 wt%). Concentrations of Ru are low in all of these placer grains (Table 1), ranging from the lower limit of detection (<0.03 wt%; WDS) to 0.11, with a mean value of <0.03 wt% Ru. In contrast, the maximum content of Pd is notably high (5.8 wt%), although higher concentrations, up to 11 wt% Pd, were documented in a Pt-(Pd)-Fe alloy from Arch Creek, Yukon (Barkov et al., 2008b). The ratio  $\Sigma PGE/(Fe+Cu+Ni)$  varies from 2.5 to 5.7, implying a compositional gap between Pt<sub>2</sub>Fe, corresponding to stoichiometry of the mineral isoferroplatinum, and a Pt-Fe alloy richer in Pt (Fig. 2a). In Ir-Rh-Pd compositional space, the composition of the seven Pt-Fe alloy grains plot along

	SC-1	BR-1	BR-2	BR-3	BR06-1	BR06-2	WN-1	
wt%			· · · · · · · · · · · · · · · · · · ·					
Fe	4.99	7.33	4.85	7.24	5.00	4.69	9.03	
Rh	0.45	1.31	1.71	1.42	1.12	1.83	1.24	
S	0.02	0.03	0.02	0.02	0.03	0.03	0.05	
Cu	0.33	0.97	0.31	1.00	0.39	0.49	0.91	
Pt	88.90	85.13	85.46	85.72	87.74	91.03	85.46	
Pd	2.80	0.75	5.64	1.03	3.60	0.58	0.37	
Те	0.02	0.01	0.01	0.01	0.01	0.01	0.01	
lr	0.94	3.21	0.43	2.43	0.86	0.06	2.28	
Ru	0.00	0.00	0.09	0.00	0.00	0.01	0.00	
Ni	0.05	0.01	0.10	0.04	0.05	0.02	0.12	
Os	1.00	0.12	0.33	0.09	0.70	0.74	0.21	
Total	99.63	98.97	99.06	99.12	99.65	99.60	99.76	
Atomic proportions								
Fe	15.04	21.48	14.29	20.78	14.87	14.27	24.99	
Rh	0.73	2.13	2.74	2.22	1.81	3.02	1.86	
S	0.12	0.14	0.13	0.12	0.13	0.15	0.23	
Cu	0.86	2.55	0.79	2.53	1.02	1.30	2.20	
Pt	76.75	69.75	72.09	70.44	74.82	79.36	67.73	
Pd	4.44	0.92	8.72	1.55	5.63	0.92	0.53	
Те	0.02	0.01	0.02	0.01	0.02	0.01	0.02	
lr	0.82	2.81	0.37	2.02	0.75	0.05	1.85	
Ru	0.00	0.00	0.14	0.00	0.00	0.02	0.00	
Ni	0.14	0.03	0.28	0.10	0.15	0.06	0.33	
Os	0.89	0.05	0.29	0.08	0.61	0.66	0.17	
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	

**Table 1.** Representative compositions of Pt-Fe alloy placer grains from three placers. All analyses are the average of 15-30 point analysis. SC = Scroggie, BR = Burwash, WN = Wolverine.



**Figure 2.** Compositional variation observed in Pt-Fe alloy placer grains: (a) plot of values of ratio  $\Sigma$ PGE/(Fe+Cu+Ni) in the compositional profiles through the grains (15-30 data points from each grains); (b) Ir-Rh-Pd diagram (atom %).



the Ir-Rh and Rh-Pd joins (Fig. 2b). Also the grains with  $\Sigma PGE/(Fe+Cu+Ni) < 3.5$  have similar Ir-enrichment trends and the grains with  $\Sigma PGE/(Fe+Cu+Ni) > 5$  plot along the Rh-Pd join (Fig. 2b). Composition of the host PGM grains correlate with the composition of micro-inclusions. The Ir-rich grain BR-3 contains Ir-rich inclusions of bowieite and the more Pd-enriched grain BR-2 contains inclusions with Pd-rich phases (miassite and vasilite; Table 2).

## **PGM INCLUSIONS**

Five placer grains of Pt-Fe alloy contain micro-inclusions that were exposed during polishing. Composition of these inclusions was studied using the EDS mode on the SEM, and some larger inclusions were analysed using the WDS

mode on the EMP (Table 2). The description of the identified phases is given below.

PGMs from the micro-inclusions in the placer grains of Pt-Fe alloy from Burwash Creek:

Members of the bowieite  $Rh_2S_3$  – kashinite  $Ir_2S_3$  series. Bowieite is relatively common in the analysed inclusions. Two observed compositional varieties are: Pt-rich (poor in Ir) and Ir-rich (analysis 1, Table 2). Bowieite and kashinite are isostructural and the existence of a solid-solution series between these end members is not unusual (Desborough and Criddle, 1984; Begizov et al., 1985). The incorporation of Pt is much less common. The phase

**Table 2.** Composition of micro-inclusions of platinum group minerals in grains of Pt-Fe alloy from several placers in Yukon.

No.	1	2	3	4	5	6	7	8	9
wt%									
Fe	0.05	0.02	1.29	0.04	0.04	0.61	2.04	0.34	18.24
Rh	29.90	0.00	3.76	2.30	0.98	1.91	2.06	0.95	0.71
S	25.65	11.41	25.76	34.41	37.27	0.01	0.02	0.00	0.05
Cu	0.01	1.77	0.00	0.01	0.03	0.06	0.13	0.00	0.88
Pt	0.60	2.07	0.89	0.65	0.59	14.12	23.63	2.35	72.01
Pd	0.05	84.69	0.14	0.04	0.05	0.05	0.09	0.11	0.30
Те	0.01	0.00	0.00	0.00	0.02	0.02	0.02	0.01	0.02
lr	42.51	0.11	11.06	2.17	0.95	51.69	48.44	14.92	0.01
Ru	0.01	0.00	1.36	37.43	53.43	0.71	0.44	2.14	0.00
Ni	0.01	0.12	0.02	0.00	0.01	0.03	0.04	0.01	0.14
Os	0.03	0.03	51.05	21.35	5.27	29.28	22.17	78.65	0.12
Total	98.97	100.23	96.76	98.46	98.65	98.57	99.14	99.57	93.56
Atomic	proportions								
Fe	0.07	0.03	1.88	0.04	0.04	2.03	5.93	1.12	43.06
Rh	22.04	0.00	2.98	1.42	0.55	3.47	3.67	1.70	0.91
S	60.69	29.81	65.44	67.32	66.88	0.04	0.08	0.00	0.19
Cu	0.01	2.34	0.00	0.01	0.03	0.18	0.34	0.00	1.81
Pt	0.23	0.89	0.37	0.21	0.17	13.48	20.15	2.20	48.65
Pd	0.04	66.69	0.11	0.03	0.03	0.08	0.14	0.20	0.38
Те	0.01	0.00	0.00	0.00	0.01	0.02	0.03	0.01	0.02
Ir	16.78	0.05	4.69	0.71	0.29	50.34	46.88	14.34	0.01
Ru	0.01	0.00	1.10	23.02	30.40	1.32	0.81	3.90	0.00
Ni	0.02	0.17	0.03	0.00	0.01	0.09	0.11	0.02	0.31
Os	0.01	0.01	21.86	7.21	1.60	28.81	21.77	76.38	0.08
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Note: 1 - inclusion of bowieite - kashinite in BR-3 grain 2 - vasilite matrix in micro-inclusion from BR-2

3 - erlichmanite from WN-1 9 - Pt-Fe alloy from WN-1

4,5 - laurite from WN-1 6,7 - iridium from WN-1 8 - osmium from WN-1

'Pt<sub>2</sub>S<sub>3</sub>' was previously reported in experiments in the Pt-S system (Grønvold *et al.*, 1960) and may require special conditions to stabilize the 'Pt<sub>2</sub>S<sub>3</sub>' component.

**Miassite (Rh, Pt, Pd)**<sub>17</sub>**S**<sub>15</sub>. Miassite forms euhedral grains in a few micro-inclusions. Its composition corresponds to  $Rh_{17}S_{15}$  (cubic, Pm3m) with minor Pd and Pt, a phase that exists in the Rh-S and Fe-Rh-S systems (Okamoto, 1992; Makovicky *et al.*, 2002).

**Cooperite PtS.** The EMP data show some deviation of the few PtS micro-inclusions from an ideal stoichiometry of cooperite, giving a composition of  $Pt_{0.9}S_{1.1}$ . This observed minor nonstoichiometry may represent a compositional feature (*cf.*, synthetic analog of cooperite,  $PtS_{1.1}$ , Grønvold et *al.*, 1960).

**Isoferroplatinum (or Fe-rich platinum).** Ideally  $Pt_3Fe$  (cubic, Pm3m) typically contains 25 to 35 atom % Fe. The related Pt-Fe alloy phase is Fe-rich platinum (20-50 atom % Fe) or "native Pt" (Fe<20 atom % and Pt>80 atom %). Compositions of some inclusions in the Pt-Fe alloy placer grains correspond to a  $Pt_3Fe$ -type alloy, which has stoichiometry of isoferroplatinum, or an Fe-rich platinum.

**Vasilite** (Pd, Cu, Pt)<sub>16</sub>S<sub>7</sub>. Pd-(Cu-) rich sulfide forms a matrix in the micro-inclusion in Fig. 3a. Its composition is most consistent with atomic proportions of vasilite,  $Pd_{16}S_7$  (analysis 2, Table 2). It has elevated levels of Cu (1.9 wt% or 0.6 apfu (atoms per formula unit) and Te-content below the detection limit of WDS analysis (<0.06 wt%). A similar Cu-bearing and poor in Te phase, related to vasilite, was described in the Pustaya River placer deposit associated with an Alaskan-type complex, Kamchatka, Russia, by Tolstykh *et al.* (2000).

**Pt-Pd-Ni-Cu alloy (Pd-rich platinum).** Inclusions of a Pt-dominant alloy were found in vasilite matrix in the inclusion in Figure 3a. Their analyses show unusually high Pd, Ni and Cu, and low Fe (minor concentrations of S, ascribed to contamination by a sulfide phase, were omitted in these results). The three analysed inclusions give the following ranges (expressed in wt%): Pd 20.8-27.7, Ni 2.5-3.1, Cu 2.7-3.2 and Fe 0.7-1.0; or in terms of atom %: Pt<sub>47.7-52.8</sub>Pd<sub>29.3-37.9</sub>Ni<sub>6.3-8.0</sub>Cu<sub>6.1-7.5</sub>. Values of ΣPGE/(Fe + Cu + Ni) vary from 4.5 to 5.9. We note that the maximum value in this range (5.9) is close to the maximum of 5.7 observed for Pt-Fe alloy placer grains. This correspondence implies that these alloy phases, the host and inclusions, have attained equilibrium in the distribution of PGE and base metals. **Keithconnite**  $Pd_{20}Te_7$  (or  $Pd_{3-x}Te$ ; 0.14 <x <0.43). Pd-rich telluride forms tiny grains in the matrix of vasilite in the inclusion in Figure 3a. It has the composition: Pd 71.71, Pt 0.63, Te 27.66, for a total of 100.0 wt%, which corresponds to  $(Pd_{3.01}Pt_{0.01})_{\Sigma 3.02}Te_{0.97}$  or to  $(Pd_{20.3}Pt_{0.1})_{\Sigma 20.4}Te_{6.6}$ , calculated on the basis of a total of 4 apfu and 27 apfu, respectively.

**Unnamed**  $Pd_{11}Te_2S_2$  (?). An unusual phase of Pd-rich sulfotelluride (?) occurs as tiny grains in the inclusion shown in Figure 3a. The composition of the analysed phase is (SEM-EDS): Pd 73.65, Pt 1.28, Au 1.37, Te 19.83 and S 3.87, for a total of 100.0 wt%; the formula is  $(Pd_{10.57}Au_{0.11}Pt_{0.10})_{\Sigma10.78}Te_{2.37}S_{1.84}$  (basis:  $\Sigma$ =15 apfu).



**Figure 3.** Examples of micro-inclusions in Pt-Fe alloy placer grains with **(a)** PGM and **(b)** silicates.  $mi = miassite (Rh,Pt,Pd)_{17}S_{15'}$ ,  $vs = vasilite (Pd,Cu,Pt)_{16}S_7$ ,  $kt = keithconnite (Pd_{20}Te_7)$ , pp = Pd-rich platinum.

PGMs from the micro-inclusions in the Pt-Fe alloy placer grain from Wolverine Creek:

**Erlichmanite OsS**<sub>2</sub>. An inclusion of erlichmanite was found in the grain from Wolverine Creek (analysis 3, Table 2). It has high iridium (11.06 wt%) and elevated Rh and Ru (3.76 and 1.36 wt%, respectively).

**Laurite RuS<sub>2</sub>.** Inclusions of laurite were found in the same grain (analysis 4, 5, Table 2). The two analysed inclusions show elevated content of Os (21.4 and 5.3 wt%) and Rh (2.3 and 0.98 wt%).

**Iridium (Ir, Os, Ru, Pt) and Osmium (Os, Ir).** Inclusions of iridium and osmium are found in the Wolverine grain (analysis 6, 7, 8, Table 2). The iridium inclusion has elevated Os (up to 29.3 wt%), Pt (up to 23.6 wt%) and Rh (~2 wt%). The osmium inclusion has 14.9 wt% Ir, 2.35 wt% Pt and 2.14 wt% Ru.

#### SILICATE MINERALS

One placer grain of Pt-Fe alloy from Burwash Creek contains four silicate micro-inclusions (10 – 40  $\mu$ m in diameter) with various silicate phases (Fig. 3b). The silicates form euhedral and subhedral grains with length up to 10 µm. Using EDS-SEM analysis we have identified clinopyroxene, Cl-bearing amphibole and plagioclase in these inclusions. All phases were too small for WDS-EMP analysis. The clinopyroxene phase is a diopside, which varies in composition from high to moderately rich in Mg:  $Ca_{471}Mg_{480}Fe_{49}$  (mg# 90.7; *i.e.*, [Mg:(Mg + Fe<sup>2+</sup>)]); Ca<sub>47.5</sub>Mg<sub>43.9</sub>Fe<sub>8.6</sub> (mg# 83.6); and Ca<sub>45.7</sub>Mg<sub>37.5</sub>Fe<sub>16.8</sub> (mg# 69.0). The calculated formulae,  $Ca_{0.84}$  (Mg<sub>0.85</sub> Al<sub>0.15</sub>Fe<sub>0.09</sub>)<sub>Σ1.09</sub>Si<sub>1.99</sub>O<sub>6</sub>, Ca<sub>0.84</sub>(Mg<sub>0.77</sub>Fe<sub>0.15</sub><sup>[6]</sup>  $AI_{0.15}Mn_{0.01})_{\Sigma 1.08}(Si_{1.99}AI_{0.01})_2O_6$ , and  $(Ca_{0.85}Na_{0.06})$  $\Sigma_{\Sigma_{0,91}}(Mg_{0,69}Fe_{0,31}^{[6]}AI_{0,10})_{\Sigma_{1,10}}(Si_{1,92}AI_{0,08})_2O_6$  suggest the presence of elevated values of <sup>[6]</sup>Al.

Sodic-calcic amphiboles (0.6 and 1.1 Na apfu) are relatively enriched in Cl (0.72 and 1.17 wt%, or 0.17 and 0.36 Cl apfu, respectively). Similar inclusions of sodiccalcic amphibole, but notably richer in Cl, were observed in the placer grains of a Pt-Fe alloy from Florence Creek, Yukon (Barkov *et al.*, 2008b). Plagioclase in our inclusions from a Pt-Fe grain from Burwash Creek, is albite-enriched in anorthite component:  $Ab_{60}An_{35.1}Or_{4.8}$  and  $Ab_{57.5}An_{39.9}Or_{2.6}$ . Interestingly, a nearly pure albite ( $Ab_{97.8}$ ) occurs as an inclusion in Pt-Fe alloy at Florence Creek, Yukon (Barkov *et al.*, 2008b).

#### TRACE ELEMENT COMPOSITIONS OF SILICATE-MELT INCLUSIONS

Trace element compositions of the four inclusions of silicate melt were determined using LA ICP-MS. Two inclusions are located closer to the margin of the grain and two are in the interior part of the Pt-Fe alloy host grain. Mineralogical and chemical composition of all four inclusions is identical (Fig. 4; Table 3). Concentrations of light and heavy rare earth elements (LREE and HREE) normalized to the chondritic abundances (McDonough and Sun, 1995) show a slightly negative slope for REE (Fig. 4a). The slope of the REE pattern is not steep with the ratio of La/Lu ~3 and a well-developed Eu minimum. Depletion in HREE, if present, is very minor indicating a garnet-absent mantle source for the magmas. The multi-element 'spider-diagram' (Fig. 4b) shows significant decoupling between the two important groups of



*Figure 4.* Composition of silicate melt micro-inclusions in a host Pt-Fe alloy placer grain: *(a)* chondrite normalized (McDonough and Sun, 1995) REE and *(b)* N-MORB normalized (Hofmann, 1988; Hart, 1999) LIL and HFS abundances.

incompatible elements. The large ion lithophile elements (LIL), Sr, K, Rb and Ba are enriched and behave differently than the high field strength elements (HFS), Th – Y, which show much lower concentrations (Fig. 4b). Another important feature on this diagram is the large negative trough at Nb and Ti. The Nb trough shown for inclusion 1 is even larger for the other three inclusions, which have Nb concentrations below the detection limit (Table 3).

#### **DISCUSSION**

# POSSIBLE PROVENANCE OF PLACER GRAINS OF PT-FE ALLOY

In all three localities studied, there are three types of possible source-rocks for the detrital grains of Pt-Fe alloy: oceanic Alpine-type peridotites or ophiolites, subductionrelated Alaskan-type complexes and continental mafic-

**Table 3.** Average major- and trace-element composition of four melt inclusions (Incl 1-4) from BR06-2 (LOD - limit of detection).

	Incl 1	LOD	Incl 2	LOD	Incl 3	LOD	Incl 4	LOD	
LA ICP-MS, wt%									
Si	23.37		23.37		23.37		23.37		
Na	2.09		1.04		1.68		0.58		
Mg	3.35		6.00		5.01		1.10		
Al	9.78		4.95		6.57		16.47		
К	3.17		0.16		1.34		0.44		
Ca	4.82		12.41		9.88		18.50		
Ті	0.10		0.26		0.07		0.53		
Mn	0.10		0.19		0.18		0.15		
Fe	1.83		11.65		4.52		22.01		
LA IC	P-MS, ppm								
Rb	57.65	1.04		7.50	23.06	1.08		20.79	
Sr	453.05	0.11	702.44	0.82	616.55	0.11	2574.14	2.49	
Y	5.49	0.16	11.99	1.04	7.30	0.18	14.87	2.79	
Zr	11.54	0.17	32.69	1.37	14.68	0.14	74.70	2.93	
Nb	0.70	0.27		2.01		0.29		5.87	
Ba	268.12	0.07	211.45	0.35	450.23	0.06	141.09	1.39	
La	2.81	0.10	6.06	0.56	1.28	0.11	14.09	1.88	
Ce	5.88	0.04	9.75	0.50	3.76	0.04	21.98	0.91	
Pr	0.74	0.07	1.36	0.53	0.67	0.08	1.58	1.43	
Nd	4.07	0.68		4.90	4.41	0.71	18.75	12.87	
Sm	1.39	0.29	3.03	2.48	1.20	0.35		6.89	
Eu	0.28	0.10	1.16	0.72	0.31	0.11	2.02	1.76	
Gd	1.17	0.35	5.42	2.13	1.44	0.40		6.41	
Tb	0.21	0.09		0.84	0.24	0.11		2.10	
Dy	1.17	0.46		3.69	0.97	0.61		9.53	
Но	0.18	0.05		0.58	0.28	0.06		1.53	
Er	0.51	0.15		1.02	0.79	0.15	1.97	1.57	
Tm		0.08		0.75	0.11	0.10		1.78	
Yb	0.58	0.16	2.26	1.62	0.47	0.13	4.25	2.32	
Lu		0.35		2.53		0.36		6.70	
Hf	0.32	0.23		1.76	0.67	0.28		4.24	
Та		0.08		0.48		0.06		1.54	
Th	0.54	0.05	0.76	0.37	0.22	0.07	1.15	0.96	

ultramafic intrusions of 'Kluane-type' sills. Compositions of the Pt-Fe alloy grains from the three localities studied here, and the previously studied PGM grains from Florence Creek (Barkov *et al.*, 2008b) are similar, and show an enrichment in Cu, Ir, Rh and Pd, and strong depletion in Ru (Tables 1, 2), indicating that they may have been derived from a similar type of source rock. These compositional characteristics do not agree with derivation from an ophiolite-type source but rather point to an Alaskan-type source.

In general, compositions of PGM present as inclusions in Pt-Fe alloy placer grains cannot provide distinctive mineralogical criteria to recognize their provenance. For example, Rh-Ir sulfides can occur in association with a podiform chromitite (Malitch et al., 2001), a layered intrusion (Oberthür et al., 2004), or with an Alaskan-type complex (Stanley et al., 2005). Also, PGM may experience significant re-equilibration upon cooling of the host intrusion and their composition may be notably changed in the presence of fluids. Nevertheless, the observed assemblage of PGM in the analysed inclusions at Burwash rather corresponds to Alaskan-type mineralization. Indeed, the same association of bowieite-kashinite, miassite, vasilite, cooperite and keithconnite was documented in inclusions in grains of isoferroplatinum-type alloy from a placer of the Miass River, in the Urals (Britvin et al., 2001). Alaskan-type complexes are the recognized source of placer platinum in this region. Furthermore, these types of Rh-Ir sulfides were first discovered in association with Alaskan-type complexes: bowieite in Alaska (Desborough and Criddle, 1984), and kashinite and miassite in the Urals (Begizov et al., 1985; Britvin et al., 2001). Phases corresponding to the composition of vasilite were reported in association with Pt-Fe alloy from Alaskan-type complexes of the Kamchatka-Koryak belt (Rudashevsky and Zhdanov 1983; Tolstykh et al., 2000).

The other possible type of source rock is continental mafic-ultramafic intrusions associated with continental rifting. The Kluane mafic-ultramafic sill-like intrusions developed in the drainage area of Burwash Creek correspond to this type of mafic intrusion. The Quill Creek complex hosts a number of occurrences of Ni-Cu-PGE mineralization, including the Wellgreen deposit, which is economically important and adjoins the Burwash property to the west (Cabri *et al.*, 1993; Hulbert 1997). Fragments of other mafic intrusive rocks, likely formed in continental rifting settings, were identified in other areas of the Cordilleran part of Yukon (Johnston *et al.*, 2007). However, the Wellgreen deposit is characterized by a very

small grain size for most of the PGMs, which are principally Pd-(Pt)-Ni-rich antimono and bismuthotellurides. PGE alloy minerals are very rare in this deposit and in related deposits (Cabri *et al.*, 1993; Barkov *et al.*, 2002). Thus, the Kluane-type source appears to be less likely.

The mg# of inclusions of diopside, in the Pt-Fe alloy detrital grains, attains a maximum of 90.7, which is high and consistent with high-magnesian compositions of their lode source-rocks. These inclusions are notably enriched in octahedrally coordinated Al. Content of <sup>[6]</sup>Al in pyroxene increases with increasing pressure (e.g., Aoki and Kushiro, 1968). Thus, these inclusions of diopside presumably crystallized under high-pressure conditions, similar to inclusions of omphacite-rich clinopyroxene hosted by grains of Pt-Fe alloy from Nizhniy Tagil, which is a 'classic' Alaskan-Uralian-type complex in the Urals, Russia (cf., Johan, 2006). In addition, the observed inclusions of Na-(Cl)-rich amphibole and of albite-rich plagioclase, documented at Burwash, are similar to inclusions of a Na-rich amphibole and sodic plagioclase in nuggets of Fe-bearing platinum, likely derived from an Alaskan-type complex in Papua New Guinea (Johan et al., 2000). The occurrence of sodic-calcic amphiboles enriched in Cl and associated with Pt-Fe alloy implies the presence of fluid phase in the system.

# TECTONIC SETTING BASED ON TRACE ELEMENT GEOCHEMISTRY

Concentrations of trace elements in silicate melt are determined by the nature of the mantle source undergoing partial melting to produce mafic magma, and the processes of magma differentiation, crystallization and contamination. Patterns of REE and other groups of incompatible elements (LIL and HFS) vary greatly in different tectonic environments and their ratios are commonly used as indicators of the tectonic environment of magma generation. In this study, the three main candidates for the type of source rock for the Pt-Fe alloy placer grains belong to very different tectonic settings. The ophiolites or Alpine-type peridotites are products of magmatism at mid-ocean ridges; continental maficultramafic complexes and small bodies, such as Kluane sills, are the result of continental rifting; and Alaskan-type complexes represent subduction zone magmatism present in arc environments.

Ophiolites and oceanic peridotites are characterized by a positive or slightly negative slope of REE. Plagioclase fractional crystallization resulting in the development of a

Eu minimum in REE patterns is rare. These magmas are equally depleted in all the incompatible elements and show similar behavior of LIL and HFS. Such behavior of LIL and HFS is very different from the significant decoupling between these two groups of incompatible elements observed in our samples. The large LIL/HFS ratio of silicate inclusions hosted in Pt-Fe alloy from Burwash Creek can be used to rule out ophiolites or Alpine-type peridotites as the source of the placer platinum. This is also supported by the complex patterns of REE in the studied inclusions. The pattern of high LIL/HFS ratio is a distinctive feature of subduction zone magmas due to the much higher mobility of LIL in aqueous fluids involved in magma generation at subduction zones. To some extent, decoupling between LIL and HFS may also be present in magmas generated during continental rifting, such as the Kluane sills, due to the contribution of fluids in the mantle source region undergoing melting. However, the extremely high LIL/HFS ratio, of over two orders of magnitude, is in better agreement with a subductionrelated Alaskan-type complex as the source of the placer platinum. This is also supported by the presence of a negative trough for Nb that is characteristic of arc magmatism, low Ti and the complex patterns of REE typical for magmas derived from the mantle wedge above the subduction zone with the complex depletion and enrichment history. The trace element ratios in the silicate inclusions suggest that the source of the Pt-Fe alloy placer grains in Burwash Creek is not ophiolite-type or oceanic peridotites. These data cannot undeniably distinguish between the Kluane sills and fragments of an Alaskantype complex, but are much more consistent with an Alaskan-type complex to be the source of this Pt-Fe alloy. The similarity between this grain and the other PGMs from Burwash, Scroggie, Wolverine and Florence Creeks suggests that Alaskan-type intrusions are the best candidates to be the source of PGM in all these creeks.

## ACKNOWLEDGMENTS

This study was made possible with financial support from the Yukon Geological Survey, which is gratefully acknowledged. We thank Lang Shi for his technical assistance with electron-microprobe analysis. Patricia Scallion is thanked for the help with SEM work and the Institute for Research in Materials for the access to the FE-SEM, funded by the Canada Foundation for Innovation.

### REFERENCES

- Aoki, K. and Kushiro, I., 1968. Some clinopyroxenes from ultramafic inclusions in Dreiser Weiher, Eifel.Contributions to Mineralogy and Petrology, vol. 18, no. 4, p. 326-337.
- Barkov, A.Y., Fleet, M.E., Nixon, G.T. and Levson, V.M., 2005. Platinum-group minerals from five placer deposits in British Columbia, Canada. The Canadian Mineralogist, vol. 43, no. 5, p. 1687-1710.
- Barkov, A.Y., Laflamme, J.H.G., Cabri, L.J. and Martin, R.F., 2002. Platinum-group minerals from the Wellgreen Ni-Cu-PGE deposit, Yukon, Canada. The Canadian Mineralogist, vol. 40, no. 2, p. 651-669.
- Barkov A.Y., Martin, R.F., Fleet, M.E., Nixon, G.T. and Levson, V.M., 2008a. New data on associations of platinum-group minerals in placer deposits of British Columbia, Canada. Mineralogy and Petrology, vol. 92, p. 9-29.
- Barkov, A.Y., Martin, R.F., LeBarge, W. and Fedortchouk, Y., 2008b. Grains of Pt-Fe alloy and inclusions in a Pt-Fe alloy from Florence Creek, Yukon, Canada: evidence for a mobility of Os in a Na-H<sub>2</sub>O-Cl-rich fluid. The Canadian Mineralogist, vol. 46, no. 2, p. 343–360.
- Begizov, V.D., Zavyalov, E.N. and Rudashevskii, N.S., 1985. Kashinite (Ir, Rh)2S<sub>3</sub> – a new sulfide of iridium and rhodium. Zapiski Vsesouznogo Mineralogicheskogo Obshchestva, vol. 114, p. 617-622 (in Russian).
- Bodnar, R.J. and Student, J.J., 2006. Melt inclusions in plutonic rocks: Petrography and microthermometry. *In:* Melt Inclusions in Plutonic Rocks, J.D. Webster (ed.), Mineralogical Association of Canada, Short Course, vol. 36, p. 1-26.
- Britvin, S.N., Rudashevskii, N.S., Bogdanova, A.N. and Shcherbachev, D.K., 2001. Miassite Rh<sub>17</sub>S<sub>15</sub> - a new mineral from a placer of the Miass River, Urals. Zapiski Vserossijskogo Mineralogicheskogo Obshchestva, vol. 130, p. 41-45 (in Russian).
- Cabri, L.J., Hulbert, L.J., Laflamme, J.H.G., Lastra, R., Sie, S.H., Ryan, C.G. and Campbell, J.L., 1993. Process mineralogy of samples from the Wellgreen Cu-Ni-Pt-Pd deposit, Yukon. Exploration and Mining Geology, vol. 2, no. 2, p. 105-119.

Cabri, L.J., Harris, D.C. and Weiser, T.W., 1996. Mineralogy and distribution of platinum-group mineral (PGM) placer deposits of the world. Exploration and Mining Geology, vol. 5, p. 73-167.

Desborough, G.A. and Criddle, A.J., 1984. Bowieite; a new rhodium-iridium-platinum sulfide in platinum-alloy nuggets, Goodnews Bay, Alaska. The Canadian Mineralogist, vol. 22, no. 4, p. 543-552.

Fedortchouk, Y. and LeBarge, W., 2008. Sources of placer platinum in Yukon: provenance study from detrital minerals. Canadian Journal of Earth Sciences, vol. 45, no. 8, p. 879–896.

Grønvold, F., Haraldsen, H. and Kjekshus, A., 1960. On the sulfides, selenides, and tellurides of platinum. Acta Chemica Scandinavica, vol. 14, no. 9, p. 1879-1893.

Hulbert, L.J., 1997. Geology and metallogeny of the Kluane mafic-ultramafic belt, Yukon Territory, Canada: eastern Wrangellia – a new Ni-Cu-PGE metallogenic terrane. Geological Survey of Canada, Bulletin 506, 265 p.

Hart, S.R., Blusztajn, J., Dick, H.J.B., Meyer, P.S. and Muehlenbachs, K., 1999. The fingerprint of seawater circulation in a 500-meter section of ocean crust gabbros. Geochimica et Cosmochimica Acta, vol. 63, p. 4059-4080.

Hart, C.J.R., Burke, M. and Stronghill, G., 2001. Yukon Platinum Occurrences and Potential. Exploration and Geological Services Division, Indian and Northern Affairs Canada, Yukon Region, Open File 2001-2, 1:1 000 000-scale map and report, 12 p.

Hofmann, A.W., 1988. Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. Earth and Planetary Science Letters, vol. 90, p. 297-314.

Johan Z., 2006. Platinum-group minerals from placers related to the Nizhni Tagil (Middle Urals, Russia) Uralian-Alaskan-type ultramafic complex: oremineralogy and study of silicate inclusions in (Pt, Fe) alloys. Mineralogy and Petrology, vol. 87, p. 1-30.

Johan, Z., Slansky, E. and Kelly, D.A., 2000. Platinum nuggets from the Kompiam area, Enga Province, Papua New Guinea: evidence for an Alaskan-type complex. Mineralogy and Petrology, vol. 68, p. 159-176. Johnston S.T., Canil D. and Heaman, L.H., 2007. Perian exhumation of the Buffalo Pitts orogenic peridotite massif, northern Cordillera, Yukon. Canadian Journal of Earth Sciences, vol. 44, no. 3, p. 275-286.

Makovicky, E., Makovicky, M. and Rose-Hansen, J., 2002. The system Fe-Rh-S at 900° and 500°C. The Canadian Mineralogist, vol. 40, p. 519-526.

Malitch, K.N., Melcher, F. and Mühlhans, H., 2001. Palladium and gold mineralization in podiform chromitite at Kraubath, Austria. Mineralogy and Petrology, vol. 73, no. 4, p. 247-277

McDonough, W.F. and Sun, S.-S., 1995. Composition of the Earth. Chemical Geology, vol. 120, p. 223-253.

Mezger, J.E., 2000. 'Alpine-type' ultramafic rocks of the Kluane metamorphic assemblage, southwest Yukon: Oceanic crust fragments of a late Mesozoic back-arc basin along the northern Coast Belt. *In:* Yukon Exploration and Geology 1999, D.S. Emond and L.H. Weston (eds.), Exploration and Geological Services Division, Yukon Region, Indian and Northern Affairs Canada, p. 127-138.

Mutchler, S.R., Fedele, L. and Bodnar, R.J., 2008. Analysis Management System (AMS) for reduction of laser ablation ICP-MS data. *In:* Laser Ablation ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues, P. Sylvester (ed.). Mineralogical Association of Canada, Short Course volume 40, p. 318-327.

Nixon, G.T., Cabri, L.J. and Laflamme, J.H.G., 1990. Platinum-group-element mineralization in lode and placer deposits associated with the Tulameen Alaskantype complex, British Columbia. The Canadian Mineralogist, vol. 28, no. 3, p. 503-535.

Oberthür, T., Melcher, F., Gast, L., Wöhrl, C. and Lodziak, J., 2004. Detrital platinum-group minerals in rivers draining the eastern Bushveld complex, South Africa. The Canadian Mineralogist, vol. 42, no. 2, p. 563-582.

Okamoto, H., 1992. Rh-S (Rhodium-Sulfur). Journal of Phase Equilibria, vol. 13, no. 1, p. 108-109.

Rudashevsky, N.S. and Zhdanov, V.V., 1983. Accessory platinum mineralization of a mafic-ultramafic intrusion in Kamchatka. Bull. Moscow Soc. Naturalists, Geology Department vol. 58, no. 5, p. 49-59 (in Russian).

- Stanley, C.J., Criddle, A.J., Spratt, J., Roberts, A.C.,
  Szymanski, J.T. and Welch, M.D., 2005. Kingstonite, (Rh, Ir, Pt)3S<sub>4</sub>, a new mineral species from Yubdo, Ethiopia. Mineralogical Magazine, vol. 69, no. 4, p. 447-453.
- Tolstykh, N.D., Foley, J.Y., Sidorov, E.G. and Laajoki, K.V.O., 2002. Composition of the platinum-group minerals in the Salmon River placer deposit, Goodnews Bay, Alaska. The Canadian Mineralogist, vol. 40, no. 2, p. 463-471.
- Tolstykh, N.D., Sidorov, E.G., Laajoki, K.V.O., Krivenko, A.P. and Podlipskiy, M., 2000. The association of platinumgroup minerals in placers of the Pustaya River, Kamchatka, Russia. The Canadian Mineralogist, vol. 38, no. 5, p. 1251-1264.