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**Article:**

Chapman, R, Mileham, T, Allan, M et al. (1 more author) (2017) A Distinctive Pd-Hg Signature in Detrital Gold Derived from Alkalic Cu-Au Porphyry Systems. *Ore Geology Reviews*, 83. pp. 84-102. ISSN 0169-1368

<https://doi.org/10.1016/j.oregeorev.2016.12.015>

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## Accepted Manuscript

A Distinctive Pd-Hg Signature in Detrital Gold Derived from Alkalic Cu-Au Porphyry Systems

Rob Chapman, Tom Mileham, Murray Allan, Jim Mortensen

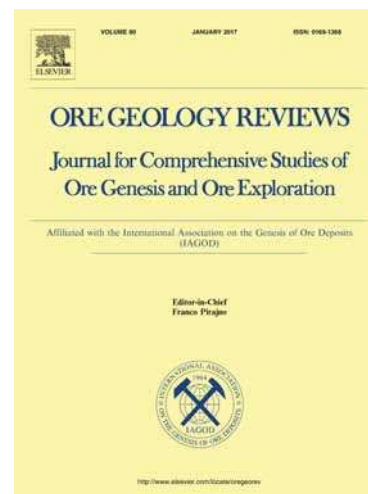
PII: S0169-1368(16)30500-5  
DOI: <http://dx.doi.org/10.1016/j.oregeorev.2016.12.015>  
Reference: OREGEO 2053

To appear in: *Ore Geology Reviews*

Received Date: 19 August 2016  
Revised Date: 6 December 2016  
Accepted Date: 9 December 2016

Please cite this article as: R. Chapman, T. Mileham, M. Allan, J. Mortensen, A Distinctive Pd-Hg Signature in Detrital Gold Derived from Alkalic Cu-Au Porphyry Systems, *Ore Geology Reviews* (2016), doi: <http://dx.doi.org/10.1016/j.oregeorev.2016.12.015>

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1 **A Distinctive Pd-Hg Signature in Detrital Gold Derived from**  
2 **Alkalic Cu-Au Porphyry Systems**

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19 Keywords: gold, palladium, mercury, alkalic porphyries, microchemical signature, indicator  
20 mineral

21

22

**Abstract**

23 This study comprises the first systematic classification of native gold geochemistry within  
24 alkalic porphyry Cu-Au systems and the placer expression of such systems. The  
25 geochemistry and mineral associations of gold from four alkalic porphyry deposits in British  
26 Columbia, Canada (Afton, Mount Milligan, Mount Polley and Copper Mountain) have been  
27 compared to comment on the likely detrital gold expression of similar systems globally.

28 Populations of gold grains collected from *in situ* hypogene mineralization as well as fluvial  
29 deposits downstream of these deposits have been characterized in terms of their alloy  
30 composition (Au, Ag, Cu, Hg, and Pd) and associated mineral inclusions. These data are  
31 combined to generate a 'microchemical signature'.

32 Gold compositions vary according to the alteration zone within a porphyry system. Previous  
33 compositional studies of gold in porphyry systems have focused on the most economically  
34 important ore associated with potassic alteration, wherein native gold hosted either by  
35 bornite or chalcopyrite comprises tiny blebs (typically 5-20  $\mu\text{m}$ ), containing detectable Cu in  
36 the gold alloy to a maximum of around 5% but quite variable (2-30 wt. %) Ag. The presence  
37 of such grains have been confirmed in hypogene ore from the four systems studied, but they  
38 have been shown to be compositionally distinct from detrital gold collected from nearby  
39 fluvial placers which exhibit a strong Pd and Hg signature, both in the alloy and as mineral  
40 inclusions.

41 Several workers have described late stage veins associated with alkalic porphyries which  
42 contain distinctive Pd-Hg bearing minerals in association with other sulphides and  
43 sulphosalts. This unusual mineralogy has been observed in the mineral inclusion suites of  
44 populations of detrital gold grains collected in the environs of the porphyry systems. We  
45 conclude that whilst the micron-scale Cu-rich gold grains formed in potassically altered rocks  
46 are in general too small to be recovered during routine sediment sampling, those formed in  
47 later stage hydrothermal systems are larger, and exhibit a distinctive microchemical signature  
48 which may be differentiated from those of gold formed in other mineralizing systems.  
49 Consequently, compositional studies of detrital gold could underpin a mineral indicator  
50 methodology in the exploration for alkalic porphyry Cu-Au deposits.

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53

54 **1. Introduction**

55 The recognition that alkaline intrusive rocks can host economically significant mineralization  
56 has attracted sustained interest from the exploration community for over twenty years (e.g.,  
57 Jensen and Barton 2000). An overview of the characteristics, tectonic setting, alteration  
58 signatures and distribution of alkalic porphyry Cu-Au (-Ag-PGE) systems was provided by  
59 Bissig and Cooke (2014). Alkalic Cu-Au porphyry systems may be distinguished from their  
60 more common calc-alkalic counterparts by: i. an association with alkaline igneous rocks; ii. a  
61 metal signature of Cu-Au-Ag that typically lacks Mo; and iii. distinctive Na-rich and Ca-rich  
62 alteration assemblages (Lang et al. 1995). In addition, the systems are relatively sulphur-poor,  
63 and lack the large, well developed sericite-pyrite and advanced argillic alteration zones  
64 typical of most calc-alkalic porphyry systems.

65 The absence of large-diameter hydrolytic alteration footprints in alkalic porphyry systems has  
66 encouraged the development of exploration methods which focus on detrital mineral  
67 indicators (e.g., Averill, 2011). These take advantage of dense and weathering-resistant rock-  
68 forming minerals typical of porphyry systems, such as magnetite (Celis et al. 2014, and  
69 Pisiak et al. 2014), apatite (Bouzari et al. 2010, 2016, Mao, 2016), and tourmaline (Chapman,  
70 2014).

71 Whilst gold is an economic mineral in many porphyry systems, there has been limited study  
72 of its potential as a heavy mineral indicator. Plouffe et al. (2013) recorded the presence of  
73 particulate gold in glacial till samples near the Mount Polley Cu-Au porphyry deposit in  
74 central British Columbia (Fig. 1), but also noted that the large placer deposit of the nearby  
75 Bullion Pit was stratigraphically below the glacial deposits, and hence that gold grains from  
76 several sources could be present in recent surficial sediments. Kelly et al. (2011) and  
77 Eppinger et al. (2013) used the abundance and morphology of detrital gold particles to  
78 establish dispersion trains around the calc-alkalic Pebble Cu-Au-Mo porphyry in Alaska.  
79 They noted that other gold sources in the immediate area probably contributed to the Au  
80 grain populations, and as a result, the morphology of gold grains did not provide a diagnostic  
81 indication of origin. Whilst the survivability of gold in the surficial environment is a useful  
82 attribute for an indicator mineral, it also permits recycling of older gold grains into younger  
83 surficial environments, possibly to a greater degree than is the case with other potential  
84 indicator minerals. Consequently, the simple presence of detrital gold in panned concentrates

85 collected during routine stream sediment sampling may not in itself provide unambiguous  
86 provenance information. In addition, interpretation of the origin of detrital gold grains is  
87 further complicated by the potential for multiple sources of gold in metallogenically complex  
88 regions. For these reasons, information on the source style of mineralization of detrital gold  
89 grains gained from the gold itself would be highly beneficial.

90 In an early study, Antweiler and Campbell (1977) noted the systematic increase in the Ag  
91 content of hypogene and placer gold grains with distance from high temperature alteration  
92 zones at Circle City, Arizona, and suggested this relationship could be exploited as a vector  
93 during exploration. Morrison et al. (1990) developed the link between source style of  
94 mineralization and alloy composition by providing Au-Ag alloy compositional templates.  
95 Gammons and Williams-Jones (1995) showed that the composition of binary Au-Ag alloys  
96 was a consequence of the chemical environment of deposition, and consequently the ranges  
97 (if not absolute values) of electrum compositions associated with different styles of  
98 mineralization is to some degree predictable. These fundamental controls on Au-Ag alloy  
99 composition have been used by Chapman et al. (2010a,b) and (Chapman and Mortensen,  
100 2016) to elucidate the evolution of gold formed in orogenic hydrothermal systems in the  
101 Klondike District (Yukon) and the Cariboo Gold District (British Columbia), respectively.

102 Gold grain characterization in these studies has not only assessed the minor alloying metals  
103 (Hg, Cu, Pd), but also suites of associated mineral inclusions, which are typically  
104 petrographically justified as representing the mineral assemblage coeval with gold  
105 precipitation (e.g., Chapman et al. 2000a). Systematic recording of the mineral inclusion  
106 assemblages has proved a very valuable discriminant as ore mineralogy varies between sites  
107 of mineralization. The combination of gold alloy data with mineral inclusion assemblages for  
108 a statistically meaningful population of gold grains generates a potentially diagnostic  
109 'microchemical signature', which may provide geochemical insights into specific ore-  
110 forming conditions.

111 The study of gold grains from porphyry systems presents some challenges over and above  
112 mineralization formed under a narrower set of hydrothermal conditions (e.g., orogenic gold).  
113 Porphyry systems normally involve alteration assemblages spanning a range of temperatures  
114 from near-magmatic to epithermal temperatures, and a wide range of fluid compositions  
115 controlling the solubilities of gold and other metals. Alteration zones may also exhibit  
116 systematic lateral and/or vertical zonation, or exhibit overprinting relationships, especially in  
117 systems that have been telescoped. Gold may thus be associated with a range of hydrothermal

118 features in porphyry settings, including high-temperature potassic alteration, moderate-  
119 temperature quartz-sericite-pyrite alteration, and low-temperature epithermal styles of  
120 mineralization. As a result of the diverse possible hydrothermal conditions of gold  
121 precipitation, any interpretation of the detrital gold signature of porphyry systems requires an  
122 appreciation of the complexities of the hydrothermal system and its spatial attributes,  
123 including those which may have been present above the current erosional level.

124 In this paper we report the first systematic study of the mineralogy of particulate gold derived  
125 from Cu-Au alkalic porphyry systems. The rationale of the present study was based not only  
126 on the need to explore new directions in indicator mineral research, but also on the  
127 recognition of the distinctive geochemical signature of alkalic porphyry systems. Thompson  
128 et al. (2002) suggested that the apparent enrichment of Pd in alkalic systems may be a  
129 consequence of magma evolution and/or enhanced transport capacity in oxidized magmas.  
130 Rubin and Kyle (1997) identified Pd in the Au-Ag alloys of gold grains from potassic  
131 alteration zones of the calc-alkaline Grasberg porphyry in Indonesia, and suggested that  
132 routine screening of local placer grains recovered during exploration could provide useful  
133 information. Previous studies by Nixon and Laflamme (2002), Nixon (2004), Nixon et al.  
134 (2004), and Hanley and MacKenzie (2009) established the presence of Pd and to a lesser  
135 extent Pt in Cu-Au alkalic porphyries in British Columbia. The current study seeks to  
136 establish whether this and/or similar characteristics are generic in placer gold grains derived  
137 from alkalic porphyries in British Columbia. Parallel investigations of *in situ* gold from  
138 hypogene mineralization were designed to identify systematic changes in gold geochemistry  
139 according to the alteration environment, and where possible, to correlate these signatures to  
140 the local placer inventory. Four economically significant alkalic porphyry systems in British  
141 Columbia were chosen for study: Mount Milligan, Mount Polley, Copper Mountain and  
142 Afton (Fig. 1). The overall aim of the work is to establish whether gold geochemistry has  
143 value in porphyry exploration, especially in metallogenically complex regions, where alkalic  
144 porphyry mineralization is the target, but where detrital gold derived from other styles of  
145 mineralization may also be present.

## 146 **2. Behavior of gold and other key elements within the porphyry environment.**

### 147 2.1 Potassic alteration

148 Potassic (biotite or K-feldspar dominant) alteration hosts the most economically important  
149 Cu-Au ore zones within both alkalic and calc-alkalic porphyry systems and consequently,

150 studies of gold grains formed in calc-alkalic porphyry systems have relevance to the present  
151 study.

152 Chalcopyrite and bornite precipitate in response to cooling, and Gammons and Williams-  
153 Jones (1997) suggested that gold may be co-precipitated even though the fluid is under-  
154 saturated with respect to native gold. Gold blebs hosted by bornite and chalcopyrite have  
155 been observed in several Au-bearing Cu porphyries (e.g., Kessler 2002; Arif and Baker 2004;  
156 Samellin 2011), and their formation has been reproduced synthetically by Simon et al.  
157 (2000), who generated small, ca. 10  $\mu\text{m}$  gold grains by exsolution from Au-bearing sulphides.  
158 Kessler et al. (2002) reported that gold grains up to 100  $\mu\text{m}$  in diameter formed from a  
159 metastable Au-bearing sulphide, and was a generic feature of porphyry Cu-Au  
160 mineralization. The evolution of gold is also strongly influenced by fluid phase separation  
161 into brine and vapour, a ubiquitous feature of shallow-crustal porphyry settings. Gold has  
162 been shown by fluid inclusion microanalytical studies to partition strongly into the low  
163 salinity, S-enriched vapour phase, along with As, B, and Sb (Audétat et al. 1998; Heinrich et  
164 al. 1999; Ulrich et al. 1999). Gammons and Williams-Jones (1997) also suggest that where  
165 fluids cool above the fluid immiscibility envelope, phase separation does not occur, and gold  
166 and copper may be transported to lower temperatures as chloride complexes, forming Au-  
167 bearing chalcopyrite on cooling.

168 Studies of gold alloy composition in porphyry systems have been undertaken at various  
169 localities worldwide and these are summarised in Table 1. Analytical protocols varied  
170 between studies and the compositional data presented comprises Au and Ag values ( $\pm$  Cu,  
171 Pd). The large study of Arif and Baker (2004) showed that gold grains exsolved from bornite  
172 were richer in Cu and lower in Ag than their chalcopyrite-hosted counterparts. Additionally, a  
173 population of gold grains hosted in quartz within potassically altered rock exhibited much  
174 lower Cu contents than those associated with sulphides, suggesting that exsolution from  
175 sulphides is not the only viable mechanism of gold mineralization in potassic alteration  
176 zones.

177 Nixon et al. (2004a) studied the distribution of PGE within potassic alteration zones in  
178 different alkalic Cu-Au porphyries in British Columbia. Palladium, and to a lesser extent Pt,  
179 were more highly concentrated in pyrite as opposed to chalcopyrite, but discrete grains of  
180 merenskyite ( $\text{PdTe}_2$ ), temagamite ( $\text{Pd}_3\text{HgTe}_3$ ), mertieite II ( $\text{Pd}_8\text{Sb}_3$ ), kolutskite ( $\text{PdTe}$ ) and  
181 melonite ( $\text{Ni,Pd,PtTe}_2$ ) were also observed. Hanley and MacKenzie (2009) showed that both  
182 Pd and Pt were concentrated in the Co-rich cores of pyrite grains which pre-dated the main



183 Cu ore stage at Afton and Mount Milligan. However, Pasava et al. (2008) recorded higher  
184 levels of Pd in chalcopyrite than in pyrite in a study of PGE distribution at the Kalmakyr  
185 alkalic Cu-Au porphyry in Uzbekistan. Nixon et al. (2004) considered PGE abundance in the  
186 Afton Cu-Au porphyry, southern British Columbia (Fig. 1), but did not undertake any  
187 mineralogical analyses, whereas Garagan (2014) undertook a systematic evaluation of  
188 palladium and gold concentrations in the context of alteration assemblages. Gold and  
189 palladium concentrations varied according to two separate trends. In the potassic zone where  
190 values of 2.6 ppm Au and 2.9 ppm Pd were recorded (in core intersections of 0.2m and 0.3m  
191 respectively), Au and Pd were generally inversely correlated. However, Au and Pd were  
192 positively correlated in a later phase of mineralization focussed parallel to the main fault  
193 zone. The only mention of Hg-bearing minerals within the potassic zone is in the form of  
194 temagamite (Nixon, 2004).

## 195 2.2 Phyllic and Propylitic alteration

196 Cu-Au mineralization is poorly developed in the distal propylitic alteration aureole of alkalic  
197 porphyry systems compared to the high-temperature potassic cores. Phyllic zones are  
198 typically weak or absent in alkalic porphyry systems (Bissig and Cooke, 2014), and are  
199 therefore not considered further here. The summary of previous studies presented in Table 1  
200 shows that there is no generic change in the Ag content of gold alloy associated with the  
201 transition from potassic to lower-temperature alteration zones. However, it seems likely that  
202 higher alloy concentrations of Cu are associated with gold grains generated through  
203 exsolution from sulphides, with the bornite-Au association generating higher Cu gold than  
204 the corresponding Au-chalcopyrite association. Gold-bearing veins outside the potassic zone  
205 could have formed according to one of a number of genetic models and/or at different  
206 temperatures. Whilst the controls on Au/Ag<sub>alloy</sub> may extrapolated from experimental studies  
207 (e.g., Gammons and Williams-Jones, 1995), commonly encountered physicochemical  
208 gradients in pH or temperature may act to either increase or reduce the Ag content of the Au-  
209 Ag alloy. Consequently, linking the Ag content of native gold to prevailing conditions  
210 requires a detailed understanding of the physicochemical environment, informed, for  
211 example, by petrographically constrained fluid inclusion analyses.

212 The waning stage of hydrothermal activity in porphyry systems may permit the  
213 remobilization of early-formed gold through interaction with lower temperature fluids  
214 containing reduced sulphur (Gammons and Williams-Jones, 1997). Copper sulphides formed  
215 with potassic alteration may be leached through interaction with Cl-bearing fluids convecting

216 at the periphery of the system (Dilles and Einaudi 1992). Bornite/chalcopyrite digestion  
217 would also redissolve gold, facilitating subsequent redistribution in the hydrothermal system.  
218 Dissolution of pre-existing Pd tellurides is perhaps less likely, as Mountain and Wood (1998)  
219 suggested that the presence of Te can reduce Pd solubility. The presence of Hg has not been  
220 reported in potassic zone mineralization, except as temagamite ( $\text{Pd}_3\text{HgTe}_3$ ), but the potential  
221 for remobilization of Hg from this mineral is unclear.

222 Overall, there is insufficient thermodynamic data available for Hg and Te bearing systems to  
223 develop a complete generic understanding of variations in gold mineralogy as a function of  
224 physicochemical gradients in the evolving magmatic hydrothermal system.

### 225 2.3 Subepithermal veins

226 Relatively low grade, late-stage base metal-Ag  $\pm$  Au veins associated with propylitically  
227 altered rocks was termed “subepithermal” by Sillitoe (2010). LeFort et al. (2011) described  
228 Au-PGE bearing veins of this type (labelled ‘Va veins’) within the porphyry mineralization  
229 at Mount Milligan in central B.C. (Fig. 1). These authors proposed that metal precipitation  
230 was induced by fluid mixing of a contracted magmatic vapour with relatively Cl-rich, heated  
231 groundwater. The complex mineralogy of the Au-Pd bearing veins was attributed to the  
232 vapour transport of As, Sb, Bi and Te, and contained Pd ( $\pm$ Pt) arsenides, Pd antimonides and  
233 Pd tellurides. Mercury was present to 7 wt. % in early-stage pyrite. Analysis of three native  
234 gold grains present as fracture-filling stringers up to 100  $\mu\text{m}$  in length hosted by pyrite  
235 showed them to be Au-Ag alloys ranging from 11-20 wt. % Ag. Copper was recorded in the  
236 assemblage both as chalcopyrite and tetrahedrite-tennantite. Hanley and Mackenzie (2009)  
237 also noted Hg-rich Pd-Pt-As-Sb and Pd-Te-Hg mineral association in late stage carbonate-  
238 chlorite veins at both Mount Milligan and Afton, although the accessory mineralization was  
239 not described. Veins containing 1.07 ppm Au and 2.63 ppm Pd in a quartz-carbonate  
240 chalcopyrite host were reported at Afton by Garagan (2014). This association was presumed  
241 to have been emplaced later than the propylitically altered host. Garagan (2014) concluded  
242 that the palladium-bearing veins at Afton were equivalent to the subepithermal veins at Mt  
243 Milligan described by LeFort (2011).

244 Brothers et al. (1963) provided a detailed description of gold-bearing copper veins at Friday  
245 Creek, located about 5 km south of the Copper Mountain mine and about 500 m from the  
246 creek’s confluence with the Similkameen River (Fig. 1). Mineralization comprised bornite  
247 and chalcopyrite in quartz carbonate veins within faults. Pegmatite veins were also reported

248 at this locality, but these are distinct from the chalcopyrite and bornite mineralization. Fischl  
249 (2015) reported the results of subsequent exploration which provided a more detailed  
250 mineralogical characterization including temagamite, palladium tellurides and copper  
251 sulphides. Grab samples of veins and drill intersections showed a range of gold and  
252 palladium values from 0.264 to 6.3 g/t and 0.42 to 57.8 g/t, respectively. More recent  
253 confirmatory testing has generated assays of 28.16 ppm Au, and 18.19 ppm Pd (Anglo-  
254 Canadian Mining Corp, 2010). Similar veins were reported at the Ilk occurrence (Fig 1.),  
255 located 800 m to the north (Fischl 1991). The mineralization here is reported to contain both  
256 gold and palladium but no detailed mineralogical studies have been undertaken.

257 The late stage veins at the three localities described above strongly suggest a generic feature  
258 of alkalic porphyry systems in which quartz- carbonate veins host Au, Pd, Hg and Cu. Whilst  
259 the mineralogy may vary slightly between localities, this association could be expected to  
260 manifest in detrital gold grains at the different localities.

#### 261 2.4. Epithermal veins

262 High sulphidation epithermal mineralization is not associated with alkalic Cu-Au porphyry  
263 systems because of the overall low S budget. For the porphyry sites considered in the present  
264 study there is also an absence of low sulphidation systems, although such mineralization is  
265 present at the Endeavor 41 Prospect, Cowal District, new South Wales, Australia (Zukowski  
266 et al. 2014) where it is proposed that there is an association with Cu-Au alkalic porphyry  
267 mineralization at depth. At Mount Milligan, Le Fort et al. (2011) hypothesized that such  
268 systems may have been present above the present erosional level, and this is likely to be the  
269 case at the other localities where the core of the mineralized system is close to surface.  
270 Consequently no examples of low-sulphidation epithermal mineralization were sampled for  
271 the present study, although it is possible that detrital gold samples could include low-  
272 sulphidation epithermal sources.

### 273 3. Methodology

#### 274 3.1 General approach

275 The overall approach of this study is establish relationships between the compositional  
276 signatures and mineral associations of particulate gold in the hypogene environment with the  
277 microchemical signature of populations of gold grains collected from local drainages. This  
278 correlation has been possible for three of the localities studied, but the drainage around  
279 Mount Polley (Fig. 1) is not well developed and no detrital gold grains were recovered for

280 study. Nevertheless, the hypogene sample suite from the Mount Polley mine help constrain *in*  
281 *situ* gold signatures. Ideally, large numbers of gold grains liberated directly from well  
282 constrained and characterised hypogene ore would be available for analysis; however, in  
283 practice, isolation and collection of gold grains from ore specimens has been challenging.  
284 Rock samples include a range of alteration types in Mount Milligan, Mount Polley and  
285 Copper Mountain, where gold assays were relatively high. However, gold grains were  
286 typically well below the size threshold for recovery using traditional gravity concentration  
287 methods, or gold was present as inclusions or in solid-solution in sulphides. Collection of  
288 bulk samples of hypogene ore for crushing and subsequent gold recovery was undertaken in  
289 an attempt to obtain more gold grains for analysis. Preparation of thin sections provides a  
290 more robust approach for revealing tiny gold grains, but the abundance of gold particles is  
291 usually low, resulting in an expensive and inefficient screening process.

### 292 3.2 Sample collection and preparation

293 Ore samples of around 20 kg were collected from different geological settings within the  
294 Mount Milligan, Mount Polley and Copper Mountain deposits (Fig. 2 and Table 2). In  
295 addition, samples from the research collection of Leeds University permitted consideration of  
296 the Afton deposit and the now exhausted Ingerbelle Pit at Copper Mountain (Fig. 1). Polished  
297 sections and blocks were prepared from some of this material and the remainder was crushed  
298 in two stages using a jaw crusher and ceramic disc mill at the University of British Columbia,  
299 Vancouver. The sand-sized product was processed using a Wilfley wet shaking table and the  
300 concentrate retained for hand panning to isolate gold grains. Not all ore samples yielded  
301 particulate gold, and the number of grains recovered from other samples was typically very  
302 small. Polished sections were prepared from ore samples to permit characterization of  
303 alteration assemblages which hosted gold grains. Samples of placer gold were obtained from  
304 placer miners (e.g., Whipsaw Creek, near Copper Mountain; Figure 2d), whereas others were  
305 collected from drainages which, although not mined, are downstream of *in situ* mineralization  
306 (e.g., Cherry Creek, near Afton; Figure 2c). Collection of placer samples was undertaken  
307 using specialised field techniques developed for efficient collection of sample populations in  
308 areas of low gold grain abundance, as described by Leake et al. (1997), which involves either  
309 panning or the use of a small portable sluice to process fluvial gravel. Gold grains were  
310 recovered from sluice concentrates by hand panning.

### 311 3.3 Analytical

312 All gold grains over about 60  $\mu\text{m}$  in longest dimension were mounted according to size as  
313 described by Chapman et al. (2000). The extremely small size of some of the other gold  
314 particles from both hypogene and placer environments necessitated the design of a new  
315 polishing technique. This involved introducing the grains into small pools of resin placed on  
316 a glass slide. The gold grains were exposed during controlled polishing of the slides using the  
317 same approach as routinely employed to ensure the correct thickness of thin sections.

318 Gold grain analyses were carried out in Leeds University using a Jeol 8230 Superprobe,  
319 (EMPA). Limits of detection (LOD) defined at  $3\sigma$  were as follows: Cu: 0.02%, Hg: 0.09%,  
320 Pd: 0.07%, Ag: 0.07%, Au: 0.11%. All analyses are reported in weight percent (wt. %).  
321 Mineral inclusions in polished sections were identified through inspection in BSE imaging  
322 using the EDS facility of an FEI Quanta 650 FEG-ESEM SEM. The stoichiometry of Pd-Te  
323 and Pd-As-Sb mineral inclusions was not determined by EMP and consequently these have  
324 been reported in terms of their constituent elements rather than as specific mineral names.  
325 Native gold-ore mineral associations were established through inspection of polished blocks  
326 by both reflected light microscopy and using the SEM. Quantitative analysis of gold grains  
327 hosted by copper sulphides was undertaken only on grains of over 8  $\mu\text{m}$  (longest dimension  
328 in section) to minimise the possibility of electron beam interaction with the underlying  
329 mineral. Mineral associations of liberated grains could sometimes be deduced through  
330 observation of inclusions (e.g., Fig. 5A). Alloy heterogeneity (with respect to Au and Ag)  
331 was evaluated by visual inspection of grey scale of BSE images for every gold particle. Semi  
332 quantitative alloy compositions in heterogeneous grains were obtained using the EDS facility  
333 of the SEM, and although these are not reported here they informed selection of targets for  
334 quantitative analysis by EMP.

335

336

### 337 3.4 Data presentation

338 This study considers the significance of Ag, Cu, Hg and Pd concentrations in gold alloy.  
339 These data are integrated with mineral inclusion suites revealed in polished section. The  
340 standard approach of evaluating the content of minor alloys within a population of grains  
341 with cumulative percentile plots has been adopted here both for Ag and Hg (e.g., Fig. 4C),  
342 because it allows direct comparisons of populations comprising different numbers of grains.  
343 The significance of other minor alloying elements is evaluated either by considering the

344 proportions of grains which contain the metal in detectable amounts, or through their co-  
345 variance (e.g., Cu-Ag bivariate plots), in which each point represents a different gold grain.  
346 Such plots may also indicate those compositions which correspond to other notable features,  
347 e.g., specific inclusions or elevated concentrations of other alloy components.

348 Silver was recorded in virtually all gold particles studied but other elements were not always  
349 detectable. Table 3 records the percentage of each sample population that contained each  
350 element to above detection limit together with the maximum value recorded.

351 The interpretation of mineral inclusion suites revealed in polished sections of gold grains is a  
352 key element of compositional characterization, although reporting and characterization of this  
353 information may be challenging for various reasons. Firstly, the incidence of inclusions varies  
354 considerably between localities, and is revealed only after completion of analysis following  
355 the sample collection program. Whilst this problem can be mitigated by collection of large  
356 populations of gold grains, time constraints during sampling programs can limit the number  
357 of grains available for study. Secondly, a large number of inclusion species may be  
358 recorded; for example, in the present study, 27 different opaque mineral species were  
359 observed. The combination of low inclusion incidence and a wide number of mineral species  
360 is not suited to statistical analysis of individual mineral species. Thirdly, the presence of some  
361 inclusion species may be diagnostic for a particular mineralizing environment (e.g., Pd-  
362 bearing minerals), whereas other minerals such as pyrite are ubiquitous and undiagnostic.  
363 Mineral suites are characterized for individual populations by establishing the proportion of  
364 grains that exhibit inclusions of a specific mineral, although in some cases grains containing  
365 two or more different inclusion species may be particularly useful in predicting placer-lode  
366 relationships.

#### 367 **4. Characterization of *in situ* mineralization**

368 The localities at which ore samples were collected from the alkalic porphyry systems at  
369 Mount Milligan, Mount Polley, and Copper Mountain are provided in Table 2, and illustrated  
370 in Figure 2. A summary description of the samples, including associated ore mineralogy, is  
371 included in Table 3A. Illustrations of representative hypogene gold grains are provided in  
372 Figure 3.

373 One aim of the study has been to identify any systematic variation in gold grain chemistry  
374 associated with host alteration assemblage. Samples were collected from different gold-  
375 bearing lithologies on site, according to the prevailing alteration type. In most cases,

376 inspection of polished blocks confirmed the gold-alteration association, but in others  
377 overprinting alteration types were recorded (Fig. 3A). The potential for relict gold in  
378 subsequently altered rock is discussed in a later section. Where gold grains were liberated  
379 from bulk ore samples, the alteration style was assumed to be that of the host ore.

#### 380 4.1 Alloy variation as a function of alteration type

381 The majority of hypogene gold grains observed during this study were hosted by bornite or  
382 chalcopyrite occurring in potassically altered rocks (Fig. 3, A-E). Gold particles were  
383 typically 5 to 20  $\mu\text{m}$  in maximum diameter (Figs. 3A, B) although one larger grain (50 $\mu\text{m}$ )  
384 was observed (Fig. 3C). In some cases gold was associated with chalcopyrite  $\pm$  bornite which  
385 post-dated pyrite (Figs. 3D, E). Figure 3F shows a small gold grain infilling a crack in pyrite  
386 in a sample which exhibits a propylitic alteration assemblage from the Ingerbelle Pit at  
387 Copper Mountain.

388 Figure 4A shows that the compositions of the hypogene gold grains formed in the potassic  
389 zone at Copper Mountain and Afton exhibit different alloy compositions in terms of Cu and  
390 Ag. In addition, there is compositional disparity between the two gold grains occurring with  
391 propylitic alteration at the Ingerbelle Pit at Copper Mountain. One gold grain hosted by a  
392 carbonate vein in the potassic zone from Afton contains relatively high Cu and Ag, but it is  
393 also the only grain to contain Pd (0.9 wt. %). All grains contained Hg very close to, or well  
394 above LOD to a maximum of 1 wt. %. Figure 4B shows that the Ag contents of grains from  
395 the potassic zone in the Wight Pit at Mount Polley vary according to association with bornite  
396 or chalcopyrite.

397 The sample suites from Mount Milligan have been considered both in terms of the co-  
398 variance of Cu and Ag, and according to Hg and Pd contents. Figure 4C shows a clustering of  
399 compositions between 15 and 30% Ag, 0.1-0.1% Cu for grains occurring in potassically  
400 altered rock (MtM001). The alloy compositions of gold from two different propylitic  
401 environments differs substantially, with the sample from MtM 003 forming a small coherent  
402 compositional field of low Ag and Cu. Whilst some grains from sample MtM002b are  
403 compositionally very similar, two others show Cu values to around 1%. However, all grains  
404 from the propylitic environment exhibit higher Hg contents than those sampled from potassic  
405 alteration zones (Fig. 4E). Two grains hosted in potassic stage mineralization contained Pd to  
406 marginally above LOD, whereas one of two grains from mineralization in the propylitic zone  
407 contained 0.2% Pd.

## 408 4.2 Mineral Inclusions

409 A few gold grains liberated from *in situ* mineralization contained inclusions of ore minerals,  
410 and two such grains are illustrated in Figures 5A and 5B. The similarity in inclusion  
411 mineralogy in both hypogene and placer gold underlines the assertion that these features are  
412 hypogene in origin and persist into the placer environment (also depicted in Fig. 5).

## 413 4.3 Compositional heterogeneity of gold alloys

414 Alloy heterogeneity could be indicative of partial overprinting by successive generations of  
415 gold-mineralizing fluid. Identification of such features could help resolve uncertainty on the  
416 association of gold grains at localities where alteration overprinting is present. In this study,  
417 all hypogene grains appeared homogenous when viewed in BSE mode by SEM. (e.g., Figs.  
418 5A, B). However, a few placer grains were heterogeneous and these are discussed in a  
419 following section.

420 **5. Characterization of placer gold samples**

## 421 5.1 Morphology

422 Images of the placer grains from the Copper Mountain and Afton localities are provided in  
423 Figure 6. The sample from King Richard Creek (Mount Milligan area) comprises very small  
424 grains and an image was not recorded. Gold grains with different morphological  
425 characteristics are present in each of the populations, although the Whipsaw Creek (Copper  
426 Mountain) sample comprises grains which were predominantly waterworn, which implies a  
427 larger degree of fluvial transport.

## 428 5.2 Alloy compositions

429 The Cu and Ag concentrations in hypogene gold from Afton and Mount Milligan are  
430 compared with the corresponding alloy signature for local detrital gold in Figures 4C and D,  
431 respectively. In most cases, hypogene grains show Cu contents exceeding the compositional  
432 field of placer grains, and particularly those from the potassic zone. Both placer populations  
433 show a similar co-variance of Cu and Ag (Figs. 4C, D), with a broad inverse correlation  
434 between Ag and Cu. A few grains contain Hg to above 1 wt. % (Table 3A), but there is no  
435 covariation with either Ag or Cu. Palladium was recorded in four grains from King Richard  
436 Creek (Fig. 4C), which exhibit a wide range of Ag contents, but three of the four correlate  
437 with high Hg (Fig. 4E). The placer population from Cherry Creek also contains some high Hg



438 grains, which appear to be associated with lower Ag values. Three grains contained Pd >LOD  
439 (to a maximum of 1.1 wt. %), although these grains were not correspondingly high in Hg.

440

441 The compositional variation in populations of placer grains from the Copper Mountain area  
442 are shown in Figure 7. The cumulative plots for Ag in detrital grains from Friday Creek,  
443 Whipsaw Creek and the Similkameen River are very similar (Fig. 7A), and this similarity  
444 extends to the co-variance of Cu and Ag (Fig. 7B). There is a suggestion of a distinct Cu  
445 population at low Ag concentrations (Fig. 7B), and more detailed information has been  
446 incorporated in Figure 7C in an attempt to confirm this through identification of any co-  
447 variation of Cu/Ag with either other minor alloying elements or specific inclusion species.  
448 Grains containing high Hg and Pd are present throughout the populations, and whilst Pd-  
449 bearing inclusions are more common in the Ag-poor gold alloy they are not confined to this  
450 host composition. Bornite-bearing inclusions appear to be hosted by high-Cu alloy regardless  
451 of the Ag content.

452

### 453 5.3 Alloy heterogeneity

454 Figure 8 provides examples of alloy heterogeneity observed during this study. Native Cu was  
455 observed coating a gold grain from Cherry Creek (Fig. 8A). Very complex heterogeneity  
456 such as that observed in a few grains from the Similkameen River (e.g., Fig. 8B) was rare, but  
457 where present, may indicate steep physicochemical gradients during gold growth... In all  
458 cases, later stage gold-poor alloy appears to replace pre-existing gold-rich alloy (Figs. 8B, C).  
459 The decrease in the gold content of the alloy is usually mirrored by increased Ag, but in some  
460 cases it is due to increased Pd and Hg (e.g., Fig. 5F). Overall, there is insufficient evidence to  
461 correlate stages in gold grain paragenesis (indicated by alloy heterogeneity) with successive  
462 alteration stages. Some of the heterogeneous placer grains from the Copper Mountain area  
463 show high Hg and Pd values, which suggests a genetic association with late stage veins such  
464 as those described at Friday Creek (e.g., Figs. 8B, C). In these cases it appears that local  
465 changes in physicochemical conditions within a single stage of gold growth influenced the  
466 textural distribution of alloy compositions, rather than a wider scale temporally controlled  
467 alteration regimes.

### 468 5.4 Mineral inclusions

469 The relative abundance of mineral inclusions observed within placer gold grains is provided  
470 in Table 4, and some general observations are possible. Pyrite and/or pyrrhotite inclusions are  
471 present in all samples, and chalcopyrite is present in all but the sample from King Richard  
472 Creek, in which inclusions were very rare. Bornite occurs in all placer samples from the  
473 Copper Mountain area, but not at any other localities. Minerals containing both Ag and Te  
474 are present in grains from most localities, as are Pd-bearing minerals. Sulpharsenide  
475 inclusions (mainly arsenopyrite but also gersdorffite and cobaltite) are far more common in  
476 gold grains from the Similkameen River than at other localities. A wide range of other  
477 inclusion species is observed and the implications for hypogene mineralization is discussed in  
478 a later section.

479

480

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481 *Table 4. Inclusion species recorded in placer gold grains.*

482 *Key: Mineral abbreviations as per Table 3 plus: Asp = Arsenopyrite (FeAsS), Cc =*  
 483 *Chalcocite (CuS), Cob = Cobaltite (CoAsS), Cn= Cinnabar (HgS), Gb= unconfirmed Pb-Bi*  
 484 *sulphide, Hs = Hessite (Ag<sub>2</sub>Te), Ger = Gersdorffite (NiAsS), Lo = Loellingite (FeAs<sub>2</sub>), Mo =*  
 485 *Molybdenite (MoS), PdTe= unconfirmed Pd telluride, PdSbAs = unidentified Pd arseno-*  
 486 *antimonide, Ptz = Petzite (Ag<sub>3</sub>AuTe<sub>2</sub>), Spy = Sperrylite (PtAs<sub>2</sub>), Stp = Stibiopalladinite*  
 487 *(Pd<sub>5</sub>Sb<sub>2</sub>), Tbi= Tellurobismuthite, (Bi<sub>2</sub>Te<sub>3</sub>), Tem = Temagamite (Pd<sub>3</sub>HgTe<sub>3</sub>), U= Ullmanite*  
 488 *(NiAsS).*

## 489 **6. Discussion**

### 490 6.1 Characterization of gold formed in different hypogene environments

491 Gold blebs less than 50 µm in diameter hosted in potassically altered rock were most likely  
 492 formed by exsolution of gold from either bornite or chalcopyrite *in situ* and are typical of gold  
 493 occurrences reported in many other alkalic and calc-alkalic porphyry Cu-Au systems (e.g.,  
 494 Simon et al. 2000; Arif and Baker 2004; Samellin 2011).

495 The Cu and Ag concentrations in *in situ* hypogene gold grains in the present study spans a  
 496 similar compositional range to those analysed from the Batu Hijau porphyry, Indonesia (Arif  
 497 and Baker, 2004) and the Santo Tomas II porphyry, Philippines (Tarkian and Koopman,  
 498 1995) (Figure 9). In general, gold exsolved from bornite exhibits higher Cu and lower Ag  
 499 than equivalent particles associated with chalcopyrite. Grains not associated with bornite or  
 500 chalcopyrite, or those associated with propylitic alteration, tend to have lower Cu contents, in  
 501 a similar compositional range to placer grains (see Figs. 4C, D).

502

503 This study is limited to a relatively small number of hypogene gold grains, either observed in  
 504 section or liberated from ore samples. In some cases, the majority of data points correspond  
 505 to gold grains in a single polished block, where the very similar gold compositions may  
 506 simply reflect uniform local mineralizing conditions. Although these data may or may not be  
 507 typical of gold compositions in a particular setting, they are generally similar to those  
 508 recorded in other studies, and are consequently of use when considering placer-lode gold  
 509 relationships.

### 510 6.2 Placer-lode relationships

511 The majority of gold grains analysed from potassically altered rock are compositionally  
512 incompatible with gold grains recovered in surficial materials surrounding the deposits  
513 studied. In addition, placer grains are also significantly larger than the gold grains observed in  
514 potassically altered ore samples, both in the present study and in others previous studies (e.g.,  
515 Arif and Baker 2004). This observation suggests that detrital gold grains are likely derived  
516 from gold precipitated during a paragenetically separate stage of mineralization, for example  
517 in late, subepithermal veins developed within the propylitic halo of these deposits. Whilst it  
518 has not been possible to study gold grains from any *in situ* samples of subepithermal veins,  
519 Figure 10 presents a comparative matrix of the mineralogy of auriferous veins and associated  
520 placers at Copper Mountain, Afton and Mount Milligan. The relationship of detrital grains to  
521 potential lode sources is discussed below.

522

#### 523 6.2.1 Afton

524 The sampling site at Cherry Creek is within 3 km of the Afton Pit (Fig. 2A), and within the  
525 headwaters of the catchment. The Wood occurrence, comprising chalcopyrite-molybdenite  
526 mineralization peripheral to the Afton deposit (Barlow 2013) is also situated within the  
527 Cherry Creek drainage and could also potentially have contributed detrital gold grains to the  
528 placer (although native gold was not reported). Kwong (1982) provided a detailed account of  
529 the mineralization in the Afton orebody and noted the presence of native Cu in the well-  
530 developed supergene zone. Native Cu was observed in one grain from Cherry Creek (Fig.  
531 8A) and this very unusual association provides strong evidence for the presence of Afton  
532 grains in the placer population. Various mineral associations observed in hypogene  
533 mineralization at Afton are reflected within inclusion assemblages of detrital gold from  
534 Cherry Creek (Fig. 10). Palladium bearing inclusions of a Pd-As-Sb mineral (possibly  
535 mertieite) and temagamite were observed in detrital grains, but the gold-bornite association  
536 observed in the hypogene samples was not evident in the placer sample. One detrital grain  
537 contained an inclusion of molybdenite, and this could originate from either the Wood  
538 occurrence or localized molybdenite mineralization within the Afton orebody (Kwong 1982).

#### 539 6.2.2 Mount Milligan

540 Comparison of the Cu contents of hypogene and placer grains suggests that the placer  
541 population from King Richard Creek was either only partly derived or unrelated to gold  
542 formed in the potassic environment (Fig. 5A). Figure 5E shows that the Hg contents of grains

543 formed in the propylitic environment are consistently higher in Hg than the majority of  
544 placer grains. LeFort et al. (2011) provided Ag contents of three hypogene gold grains from  
545 Mount Milligan (10, 12 and 20% Ag) whose compositions were determined using SEM-EDS.  
546 These data are not directly comparable with those produced in the present study because of  
547 the different analytical method and because the analytical data were normalised. In addition,  
548 Cu, Pd and Hg were reported as below the LOD, and, although detectable limits were not  
549 specified, it is almost certain that they are considerably higher than those relating to EMPA  
550 data generated in the present study. The Ag range of the hypogene gold grains are compatible  
551 with that recorded in the detrital grains (Fig. 4C ), but better evidence for the presence of type  
552 Va vein gold in the placer sample is provided by the presence of a sulphosalt and a carbonate  
553 inclusion in a gold grain containing 0.29% Pd. The relatively small number of placer grains  
554 collected from King Richard Creek and the low incidence of inclusions have prevented a  
555 more thorough analysis of the importance of gold derived from type Va veins in the placer  
556 population.

### 557 6.2.3 Copper Mountain area

558 The microchemical signatures of the placer gold populations from the Similkameen River,  
559 and Friday and Whipsaw creeks (Figs. 7A, B) suggests commonality in the origins. However,  
560 the sampling localities are geographically widespread (Fig. 2D), which suggests that the  
561 major contributing gold source signature likely has a large footprint. has a corresponding  
562 range.

563  
564 Hypogene mineralization at Copper Mountain is paragenetically complex, and many of the  
565 22 vein types described by Stanley et al. (1995) have only present locally. In the present  
566 study, gold grains were identified in hypogene ore from two localities, whereas the  
567 Similkameen River has eroded large parts of the Copper Mountain mineralized system (Fig.  
568 2D), particularly the western part of the ore deposit near the Ingerbelle Pit. Stanley et al.  
569 (1995) described the major ore and gangue minerals of different vein types within the Copper  
570 Mountain and Ingerbelle Pits. Two of these vein types were subsequently studied by Nixon et  
571 al. (2004a), and although the terminology of Stanley et al. (1995) was not adopted by these  
572 authors, it seems likely that the “chalcopyrite stringer veins” correspond to the sample “Cu  
573 Mt1” veins, whilst “bornite-chalcopyrite-veins” correspond to “Cu Mt 2” sample of Nixon et  
574 al. (2004a). Both sets of veins were classified as “early stage” by Stanley et al. (1995). The  
575 mineralogy of the “Cu Mt1” and “Cu Mt “ samples of Nixon et al. (2004a) are summarized in

576 Figure 10, where they are seen to differ substantially, with Pd-bearing minerals recorded in  
577 the chalcopyrite-pyrite mineralization only, and gold confined to the bornite-chalcopyrite ore.  
578 This association is consistent with the assertion of Nixon et al. (2004a) that pyrite is the  
579 favoured host of PGEs in potassic zone mineralization, whereas gold shows far higher  
580 affinity for bornite (Kessler et al., 2002).

581

582 A comparison of early and late stage mineralization at the various localities is shown in  
583 Figure 10. There is clearly a much stronger correlation between the mineralogical signatures  
584 of late stage veins and placer samples than between placer samples and early stage  
585 mineralization. Several mineral species are common to both early and late stages (e.g.,  
586 bornite, chalcopyrite and sphalerite) and the appearance of such minerals in an inclusion  
587 assemblage is thus undiagnostic for provenance. However, several gold grains contain two or  
588 more inclusions, sometimes hosted by gold alloy of distinctive composition, and in these  
589 cases it is easier to propose genetic links. Examples of individual grains that contain multiple  
590 characteristics compatible with the Friday Creek veins (Fischl 2015) are presented in Table 5.  
591 The vein systems exhibit an unusual mineralogy comprising bornite, chalcopyrite,  
592 temagamite, Pd-tellurides and chalcocite, all of which have been recorded as mineral  
593 inclusions, sometimes in intimate association (e.g., Figs. 5F and 8C). We conclude that this  
594 type of vein is more widespread than is currently recognised and has made a substantial  
595 contribution to the local placer inventories. Alternatively, similar veins may have been  
596 present above the main ore zones but have been lost to erosion. Gold grains derived from  
597 such veins could have formed placers in lag deposits such as those sampled during this study.

598 Table 4 shows that placer gold from the Similkameen River contained arsenopyrite,  
599 gersdorffite and cobaltite inclusions. This appears to be the only difference between this  
600 sample population and those from Friday and Whipsaw creeks. Arsenopyrite is not  
601 mentioned as an accessory mineral either by Stanley et al. (1995) or Nixon et al (2004a), or in  
602 any of the MINFILE reports describing mineralization at Copper Mountain (Meredith-Jones  
603 2016). Figure 7C shows that the alloy compositions of the grains which host sulpharsenides  
604 are all relatively low in Cu, with a Ag range of 12-31%. It seems most likely that this  
605 association is related to an episode of late stage veining in the Copper Mountain-Ingerbelle  
606 zones, which has not been reported.

607 Richardson (1995) described the Whipsaw porphyry system (Fig. 2D) and associated gold-  
608 bearing pyrite-chalcopyrite-molybdenite and chalcopyrite-sphalerite veins extending towards

609 the Friday Creek catchment. Molybdenite inclusions were observed in one grain from both  
610 Friday and Whipsaw creeks, and a sphalerite inclusion was recorded in a Similkameen River  
611 grain. These data are not considered necessarily indicative of a clear placer-lode relationship.  
612 An inclusion of sperrylite in a gold grain from Whipsaw Creek with a high Pd content (Table  
613 5) may be related to a small outcrop of ultramafic rocks about 5 km southeast of the Whipsaw  
614 porphyry (Fig 2D). Alternatively it could represent a subordinate Pt signature, as reported by  
615 Hanley and Mackenzie (2009) at Afton and Mount Milligan, and recognised more widely in  
616 flotation concentrates from alkalic porphyries elsewhere (e.g., Tarkian and Stribny 1999).

617 The commonality between the compositional signatures of detrital gold from the three placer  
618 localities around Copper Mountain strongly suggests that similar sources have contributed to  
619 each placer. It seems likely that a range of different vein sources of gold are possible, and the  
620 mineralogical compatibility of these with inclusion species (Fig. 10) supports this assertion.  
621 The presence of gold grains exhibiting different morphological features (indicative of  
622 different fluvial transport distances; Fig 6) supports the hypothesis of different source  
623 localities. The most distinctive microchemical signature is compatible with the mineralogy of  
624 the veins at Friday Creek, and was observed in each of the placer samples. In some cases the  
625 mineralogy of these grains indicates a paragenesis in which Hg becomes more important in  
626 the later stages.

## 627 **7. Application of placer gold signatures to exploration within British Columbia**

628 Volcanic sequences of the allochthonous Quesnellia arc terrane, which host the alkalic  
629 porphyries described in this study, are commonly in close proximity to metaclastic rocks of  
630 adjacent parautochthonous North American strata, which may themselves host orogenic gold  
631 mineralization. For example Mount Polley is situated about 10 km south of the historic placer  
632 workings of the Bullion Pit and 15 km southeast of various lode and placer occurrences near  
633 Spanish Mountain (McTaggart and Knight 1993). Chapman and Mortensen (2011, 2016)  
634 undertook studies of populations of both lode and placer gold grains from throughout the  
635 Cariboo Gold District and identified a regionally pervasive signature comprising a binary Au-  
636 Ag alloy and a simple inclusion suite normally comprising pyrite and base metal sulphides.  
637 The signatures of lode samples persisted into the local placer populations, and it seems  
638 reasonable to assume that the microchemical signatures of gold grains derived from alkalic  
639 porphyries would also be inherited by their detrital counterparts. This hypothesis provides a  
640 basis upon which to evaluate the provenance of gold grains collected during future stream  
641 sediment or till sampling.

642 The Ag content of gold grains is the most commonly reported of the minor alloying elements,  
643 and may vary widely between grains formed in the same mineralizing system, as illustrated  
644 by Fig. 8B. Consequently, Ag concentration of an individual grain does not constitute a  
645 useful diagnostic parameter, although the distributions of Ag concentration in a population of  
646 grains may prove informative (e.g., Fig. 7A). Copper concentrations in populations of gold  
647 grains derived from porphyry systems in general are higher than those generally encountered  
648 in gold from orogenic mineralization, although the ranges may overlap. For this reason, the  
649 Cu content of detrital grains may not be used as a primary discriminant, but can provide  
650 useful supporting evidence of origin.

651 The Pd microchemical signature is potentially extremely useful as a diagnostic criterion for  
652 alkali porphyry systems. The Pd signature has been recorded consistently in 3 to 10% of  
653 placer grains collected from the environs of alkalic porphyries (Table 3B), whereas Pd-  
654 bearing gold has not been identified using EMP in gold grains from either calc-alkalic  
655 porphyry settings, or in other deposit types such as orogenic gold throughout the northern  
656 Cordillera (Chapman et al. 2010a,b, 2011, 2014, 2016). Elevated Pd is also commonly  
657 associated with elevated Hg contents in the alloy. Although not previously highlighted,  
658 alkalic porphyries appear to be generally Hg-rich, for example in parts of the Afton deposit  
659 (Kwong 1986). LeFort et al. (2011) described pyrite containing up to 7 wt. % Hg in  
660 subepithermal veins at Mount Milligan, and the present study recorded Hg to above detection  
661 limit in hypogene gold grains from all localities studied. Nixon et al. (2002) noted that the  
662 last stages of mineralization in the bornite-temagamite veins at Friday Creek were more Hg-  
663 rich, and this observation is consistent with data from the present study where the Hg content  
664 of late Au-Ag alloys in heterogeneous gold grains is higher than the pre-existing alloy (e.g.,  
665 Fig. 5F). In addition an inclusion of cinnabar was observed in one such late stage Hg-rich  
666 alloy. High levels of Hg have been reported in Au-Ag alloy from some orogenic gold  
667 systems, usually in tandem with high Ag values (e.g., Violet occurrence, Klondike District,  
668 Chapman et al. (2010a); Dragon Creek, Cariboo District, Chapman and Mortensen (2016).  
669 Nevertheless, the relatively simple microchemical signature of gold from most orogenic  
670 systems, comprising binary Au-Ag alloys with Cu around LOD and inclusion suites  
671 dominated by pyrite  $\pm$  base metal sulphides  $\pm$  sulpharsenides, are clearly distinguishable from  
672 the more complex and commonly PGE-bearing microchemical signatures of gold derived  
673 from alkalic porphyries. In addition, compositional studies of gold from calc-alkalic porphyry



674 systems in the Yukon by Chapman et al. (2014, 2016) showed Hg concentrations in the gold  
675 to be far lower than those observed during the present study.

## 676 **8. Consideration of Pd in alkalic porphyries globally**

677

678 The identification of palladium as a powerful indicator for alkalic porphyry mineralization in  
679 BC suggests it may be globally applicable. Palladium has been recorded in several Cu-Au  
680 porphyry systems, not all of which are of alkalic affinity. Most previous studies have focused  
681 on the concentration of palladium in mine flotation concentrates, as these provide both a  
682 convenient and accessible sample source, whose palladium content may have implications for  
683 smelter credits. A few studies have recorded palladium minerals in either flotation  
684 concentrates or core, but these mainly correlate to ore associated with potassic alteration.

685 Table 6 is a collation of data describing the abundance of palladium in flotation concentrates  
686 linked to mineralogical studies and the potential for a palladium signature to be inherited by  
687 gold grains of sufficient size to report to associated placers. The data describing palladium  
688 (and platinum) in flotation concentrates is a subset of that presented by Economou-Eliopoulos  
689 (2005), selected either because of high palladium values or because other studies can provide  
690 information relevant to the present study. Large gaps are recognized in the information  
691 available, particularly in relation to detrital grains. In addition, most studies focus on the ore  
692 grade mineralization, such that paragenetically distinct veins of particular interest to the  
693 present study could be under-reported. Table 5 shows that the palladium contents of the  
694 British Columbian flotation concentrates is of the same order of magnitude to those of  
695 obtained from various other mines in Greece, Bulgaria, the Phillipines, Indonesia, Malaysia,  
696 Papua New Guinea and Uzbekistan. Where observed, palladium minerals in the potassic  
697 mineralization are tellurides with subordinate Pd-Sb minerals, although Hanley and  
698 MacKenzie note that palladium-bearing pyrite is the most important source at Afton and Mt  
699 Milligan. McFall et al. (2016) report both discrete palladium-bearing minerals and palladium-  
700 bearing inclusions within chalcopyrite in quartz-chalcopyrite-bornite veins at Skouries,  
701 Greece.

702 Palladian gold had been reported previously in the context of oxidizing, low temperature  
703 chloride hydrothermal systems where transport is facilitated by highly oxidizing lithologies  
704 and precipitation occurs at redox fronts (Chapman et al. 2009). Gold precipitated in such  
705 environments exhibits very low concentrations of Ag, (<2%), but may contain elevated Cu,

706 and or Pd, and/or Hg. The close spatial association with haematite-rich rocks is a clear  
707 marker for the potential presence of this gold type.

708

709 The palladium content of a flotation concentrate from Grasberg reported by Economou-  
710 Eliopoulos (2005) was 58 ppm; i.e., over two orders of magnitude lower than some of the  
711 other highest values (e.g., Mount Milligan, 6,300 ppm). Nevertheless, Rubin and Kyle (1997)  
712 recorded palladium in Au-Ag alloys in native gold grains recovered from drill core and noted  
713 that the palladium-bearing gold grains at Grasberg were associated with late stage veins.  
714 Thus, whilst the detection of palladium in a flotation concentrate provides clear evidence of  
715 palladium within the system, the magnitude of the palladium concentration does not  
716 necessarily indicate the extent to which palladian Au alloys are present in later stage  
717 mineralization. It seems more likely that variation between the palladium concentrations  
718 recorded in flotation concentrates from the same mine indicates the degree to which later  
719 stage veins have been co-extracted with the target ore.

720

## 721 **9. Development of a new exploration tool**

722

723 The porphyry deposits from BC investigated in the present study are broadly similar in their  
724 palladium abundance and mineralogy to other alkalic porphyries localities worldwide. In  
725 addition, the available evidence suggests that the distinctive Pd-Hg signature of  
726 subepithermal veins is also generic, and an inevitable consequence of the Hg-Pd abundance  
727 in this style of mineralization. It follows that Au which inherits this palladium signature in  
728 alloy or in palladium-bearing mineral inclusions could be present as detrital gold grains  
729 eroded from many other Cu-Au porphyry systems, and that this feature could underpin a new  
730 exploration tool.

731

732 The discussion in sections 7 and 8 highlighted the potential to differentiate gold derived from  
733 different deposit types based on microchemical signature. Development of a standard  
734 methodology finding wider application must take into account various technical and logistical  
735 challenges.

736

### 737 **9.1 Technical considerations**

738

739 Microchemical characterization of populations of gold grains is dependent upon the  
740 availability of a population of gold particles. The requisite size of population may vary  
741 substantially according to the signature itself, as the more factors which contribute to the  
742 signature (e.g., detectable Hg, Cu, Pd) the easier the task of characterization. Alloy signatures  
743 have been shown to be reproducible in populations of around 30 grains, (Chapman et al.  
744 2000b), but placer populations may comprise grains derived from different sources and in  
745 unknown proportions, either because of different source styles represented in the catchment,  
746 or (as in the present study) because different mineralizing environments are associated with  
747 an evolving hydrothermal system. Inclusion signatures are commonly vital components in  
748 characterization, but the incidence of inclusions within sections may vary typically between 2  
749 and 70%. Leake et al. (1997) proposed that a population of 30 grains was sufficient to  
750 establish a signature, based on the incidence of inclusions within gold grains from the British  
751 Caledonides (typically 20%). Subsequent studies in areas such as the Klondike (Chapman et  
752 al. 2010a,b) focussed on gold grains which exhibited a far lower inclusion abundance,  
753 (typically 2-4%), and the numbers of grains collected rose accordingly to facilitate full  
754 characterization of the inclusion suite.

755

756 Development of statistical measures of similarity between populations have been hindered by  
757 the potential for physical mixing of gold from different sources. Instead, interrogation of data  
758 sets is carried out by searching for sub-populations identifiable by specific characteristics (e.g.  
759 elevated palladium, as in this study) or a distinctive mineral inclusion species: e.g. cosalite,  
760 used to define a low-Ag gold type at Wells, BC (Chapman and Mortensen 2016). Populations  
761 of placer gold collected from individual localities are then considered in the context of these  
762 sub-populations whose influence may vary between sample locations. Where inclusion  
763 abundance is low, large numbers of grains are normally screened, but it is not always  
764 necessary to determine the alloy compositions of all grains, and a smaller sample (e.g., 100  
765 grains) is normally adequate. The wide variation in gold signatures from different  
766 environments and consideration of the sampling context have continued to require  
767 interpretation of gold grain populations and their interrelationships. At this point we do not  
768 envisage the development of general automated data analysis methodology.

769

770 In conclusion, placer-lode relationships are inherently complicated, and influences such as  
771 multiple gold sources and geomorphological evolution of the study area may inhibit  
772 establishing clear relationships. Studies of placer gold populations acknowledge these

773 constraints and work within them, using diagnostic features which become evident during  
774 characterization. In this way, even complex relationships may be described with confidence.

775

## 776 9.2 Logistical Considerations

777

778 When approaching a new area, neither the potential complexity of the source population nor  
779 the inclusion abundance is known. This necessitates a field sampling operation capable of  
780 collecting around 100 gold grains even in areas where overall gold grain abundance is low.  
781 Populations of gold grains of this size are only rarely collected during routine heavy mineral  
782 sampling, such that dedicated fieldwork for gold collection is usually required. Specialised  
783 field techniques, adapted from the practices of European amateur prospectors (Leake et al.  
784 1997) has facilitated collection of sample suites where detrital gold particles are rare, but  
785 these demand a relatively skilled field team.

786

## 787 10. Conclusions

788 Native gold forms within different alteration zones and in association with distinct  
789 paragenetic stages of a porphyry system. Hitherto, compositional studies of gold in both  
790 alkalic and calc-alkalic porphyry systems has focused on potassic altered rock, in which gold  
791 is an economically significant by-product of Cu extraction (except in those calc-alkalic  
792 systems with significant phyllic overprints). The hypogene gold observed within potassic  
793 stage mineralization during the present study is present as minute exsolution blebs in bornite  
794 and chalcopyrite, and similar to those reported in equivalent settings elsewhere. The vast  
795 majority of gold particles associated with potassic alteration are too small to concentrate by  
796 fluvial action in erosional settings and consequently, they are also too small to be collected in  
797 the field by conventional heavy sediment sampling techniques. The limited amount of  
798 information available suggests that gold associated with propylitically altered rocks contains  
799 less Cu but more Hg than that present in the potassic zone, and exhibits a larger  
800 compositional overlap with the populations of placer gold. However, it is currently not  
801 possible to evaluate whether gold grains formed in this environment are sufficiently massive  
802 to report to placers.

803 The microchemical signatures of placer populations collected in the immediate vicinity of  
804 alkalic Cu-Au porphyries exhibit generic signatures of high Hg in the alloy, detectable Pd in  
805 up to 10% of the grains, and palladium-bearing mineral inclusions. The Cu content of the

806 alloy is above LOD and the presence of bornite inclusions appears far more likely to be  
807 related to be genetically related to bornite-bearing late stage veins than primary copper  
808 mineralization hosted in the potassic zone, particularly given the more general duplication of  
809 late stage vein mineralogy in the inclusion suites

810 The microchemical signatures of gold grains described above may be applied during  
811 reconnaissance exploration in British Columbia to assess whether detrital gold has been  
812 derived from an orogenic or alkalic porphyry source. In addition, large studies of detrital Au  
813 originating from calc-alkalic porphyries in the Yukon show the gold to contain very little Hg  
814 in the Au alloy, whereas palladium was recorded only once.

815 Previous studies of Cu-Au porphyries worldwide, including the BC examples studied here,  
816 indicate that palladium is common within flotation concentrates. These concentrates are  
817 generally derived from the beneficiation of potassic ore, and exhibit a similar palladium  
818 mineralogy dominated by tellurides. In addition, palladium may be present within  
819 chalcopyrite or pyrite formed in the potassic stage. In many cases the presence and/or  
820 mineralogy of late stage pyritic veins has not been reported, presumably because their metal  
821 values are sub-economic and/or they are distal. However, the overall similarities between Cu-  
822 Au porphyries in terms of palladium endowment and mode of palladium occurrence in the  
823 potassic stage suggest that the late stage palladium and gold-bearing veins recorded at three  
824 localities in BC would be duplicated elsewhere. If correct, this assertion leads to the  
825 possibility that palladium-bearing detrital gold may be a diagnostic indicator mineral that can  
826 be exploited during the early stages of exploration where Cu-Au mineralization is the target.

## 827 **10. Acknowledgements**

828 This project was made possible through several sources of funding. Tom Mileham was a self-  
829 funded M.Sc. student working on alkalic porphyries in British Columbia and received  
830 considerable support from Geoscience BC. Sample collection at Mount Milligan, Mount  
831 Polley and Copper Mountain was possible only with the cooperation of Thompson Creek  
832 Metals, Imperial Metals, and Copper Mountain Mining Corporation, respectively. In  
833 particular we would like to thank Graeme Roper, Gary Roste, Emily Halle, and Jesse Halle  
834 for their time in assisting sampling collection. Tim Baker kindly provided data describing the  
835 compositions of gold grains from Batu Hijau. Fionnuala Devine is thanked for a thorough and  
836 extremely constructive review of a draft manuscript. Two anonymous referees are thanked  
837 for their important contribution during the review process.

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1070 Figure 1: Locations of alkalic Cu-Au porphyry deposits which formed the basis of this study.  
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1072 Figure 2. Sample localities around Mount Milligan (A), Mount Polley (B), Afton (C) and  
 1073 Copper Mountain (D). Maps for Mount Milligan, Mount Polley and Afton adapted from BC  
 1074 Geological Survey (2006). Copper Mountain map adapted from Preto et al. (2004) and  
 1075 Massey et al. (2009).

1076 Figure 3. Examples of hypogene gold grains. Figs A-E: potassic zone, Fig F: propylitic  
 1077 zone. Gold and chalcopyrite in pyrite (sample MtM001), B: Typical occurrence of gold bleb  
 1078 in bornite, (sample MtP005), C: The largest hypogene gold grain observed in this study  
 1079 (MtP005), D: Gold film in chalcopyrite veinlet within pyrite (MtM 002b), E: Gold within  
 1080 chalcopyrite and bornite vein within pyrite (MtM001), F: Gold grain infill in crack in pyrite,  
 1081 within chalcopyrite (Ingerbelle Pit, Copper Mountain).

1082 Figure 4. Alloy composition of hypogene gold grains. A- D Bivariate plots of Cu vs Ag for  
 1083 hypogene gold from Copper Mountain plus Afton, Mount Polley, and Mount Milligan. D:  
 1084 Hypogene gold from Afton compared to the placer population from King Richard Creek. D:  
 1085 Same for Cherry Creek and Afton, E: cumulative Hg plots for the sample suite from Mount  
 1086 Milligan

1087 Figure 5: Figure 5, Examples of mineral inclusions, A: Py in hypogene gold from Mount  
 1088 Milligan; B: Chalcopyrite in hypogene gold from Mount Polley; C: Bornite inclusion in  
 1089 placer grains from the Similkameen River; D: Temagamite inclusions in placer gold from the  
 1090 Similkameen River; E: Unidentified Pd-As-Sb mineral inclusion in a detrital grain from  
 1091 Cherry Creek; F: Placer grain from the Similkameen River showing bornite inclusions in Au-  
 1092 rich alloy (pale grey: Au78%, Ag: 8.9%, Hg: 6.2%, Pd 4.1%) and temagamite inclusions in  
 1093 later alloy (medium grey: Au: 51.9%, Ag: 3.2%, Hg: 23.0%, Pd 15.2%). Figs. A, B, F: BSE  
 1094 images, Figs. C, D, E: SE images.

1095 Figure 6. Examples of placer gold grains and textures. A: Cherry Creek; B: Friday Creek; C:  
 1096 Partially flattened dendritic gold from Friday Creek, D: A range of morphologies in grains  
 1097 from the Similkameen River, E: Flattened Au from Whipsaw Creek. Scale bar has 1mm  
 1098 divisions.

1099 Figure 7. Characterization of hypogene and placer grains from the Copper Mountain area. A:  
 1100 Cumulative Ag plots for the three placer populations; B: Broad inverse relationship and Ag;  
 1101 C: Same, highlighting individual grains hosting specific inclusions or containing elevated Hg  
 1102 or Pd. Copper concentrations in B and C are plotted on a log scale to permit identification of  
 1103 grain compositions which exhibit other features.

1104 Figure 8: BSE images showing examples of alloy heterogeneity in placer gold grains. A:  
 1105 native copper infilling cracks in pre-existing gold (Cherry Creek); B: Highly heterogeneous  
 1106 grain with respect to Ag from the Similkameen R. Brightest BSE response: Au: 92.6%, Ag:  
 1107 6.5%, Cu: 0.53%, Darkest BSE response Au: 70.0%, Ag: 28.4%, Hg: 0.9%; C: Chalcocite  
 1108 and bornite inclusions hosted in alloy of Au: 94.1%, Ag:4.0%, Cu: 0.5%, Hg: 0.3% and Pd:  
 1109 1.9% with Ag- rich tracks comprising a simple Au-Ag alloy of 14% Ag.

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1112 Figure 9. Compositions of hypogene gold from porphyry systems recorded in different  
 1113 studies compared to data obtained in the present study.

1114 Figure 10. Comparative matrix of in situ mineralization and mineral inclusion assemblages  
1115 recorded in adjacent placer samples. Mt M= Mount Milligan. References: 1 = LeFort et al.  
1116 (2011); 2 = Nixon et al. (2004a); 3, 4 = Fischl (1992, 2015); 5 = Hanley and MacKenzie  
1117 (2009); 6 = Garagan, (2014) 7=present study; 8= Jago et al. (2014); 9 = Richardson (1995),  
1118 10 = Barlow (2013); 11 = Kwong (1982); 12 = Nixon et al. (2004b). Shaded area shows Pd-  
1119 bearing minerals.

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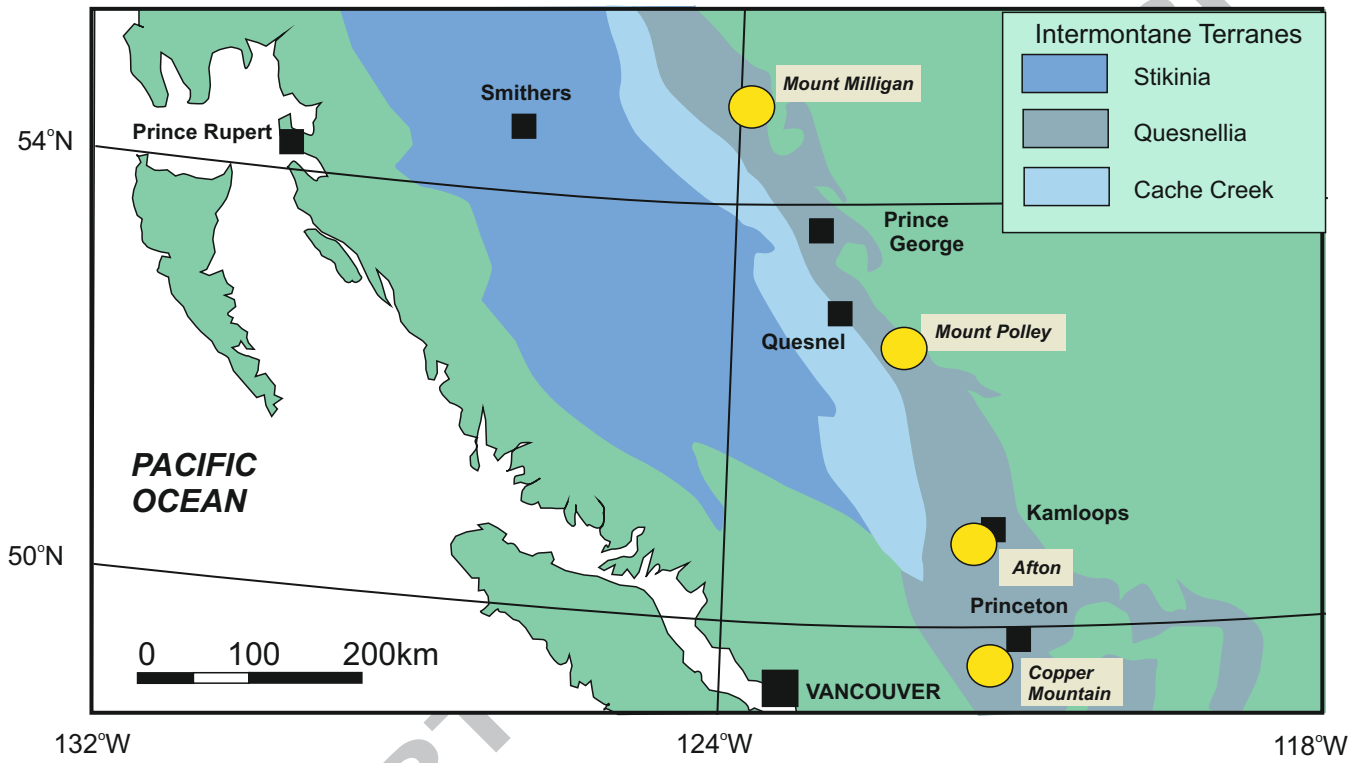
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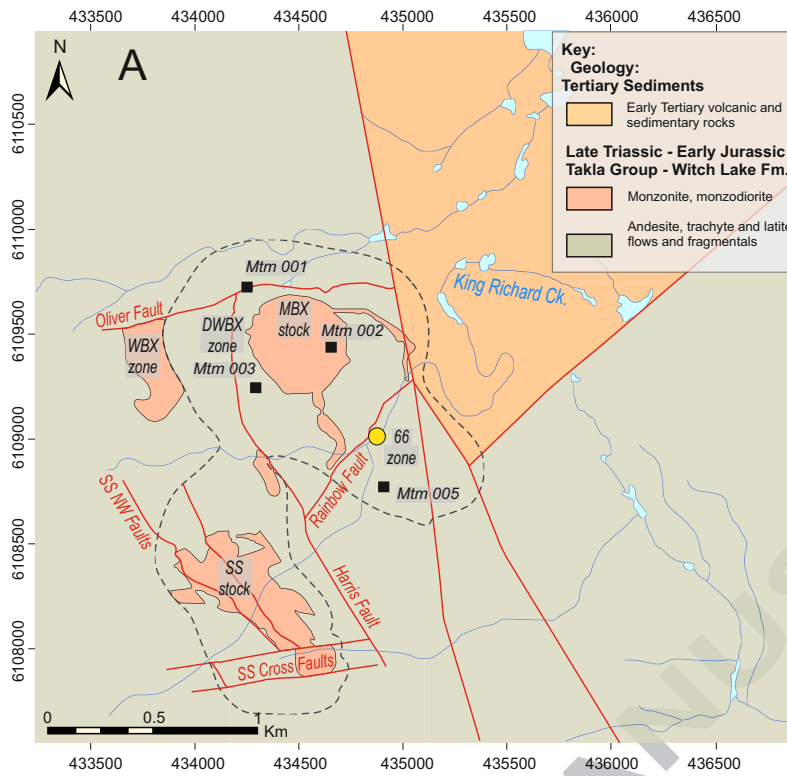
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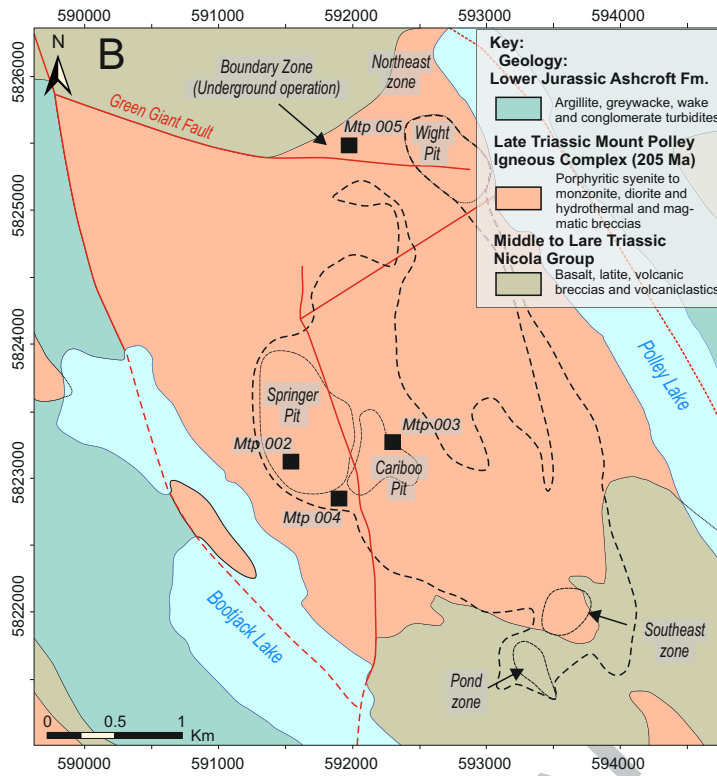
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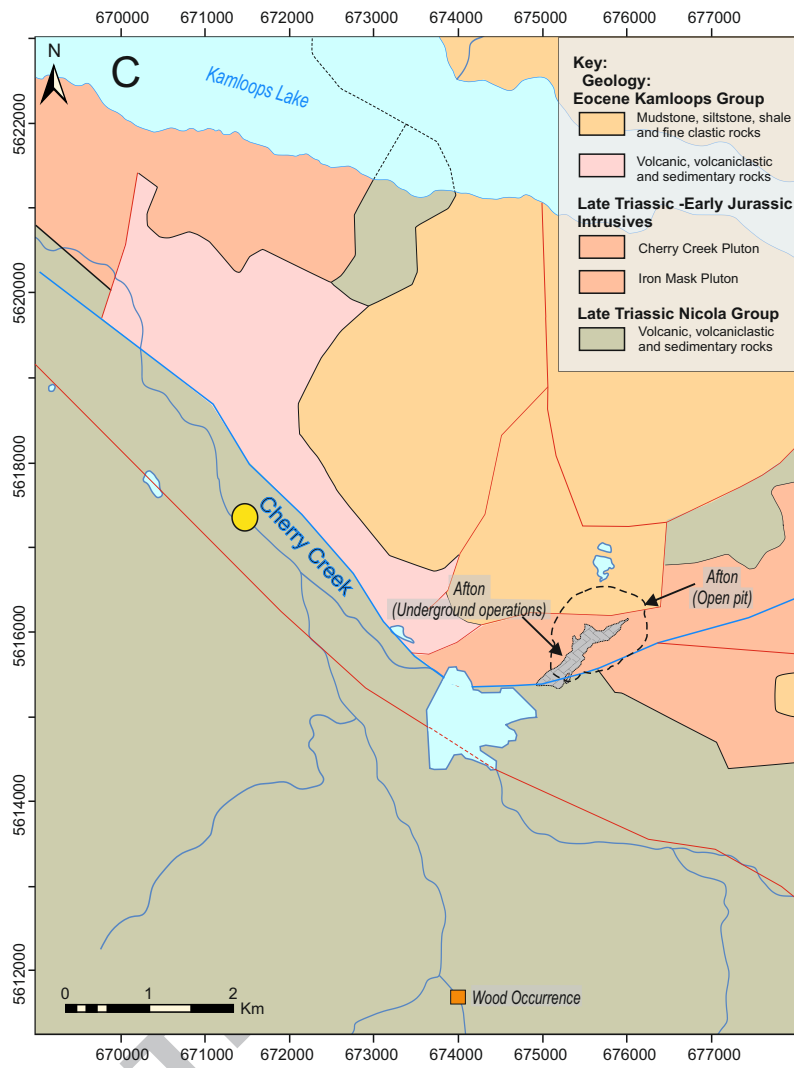


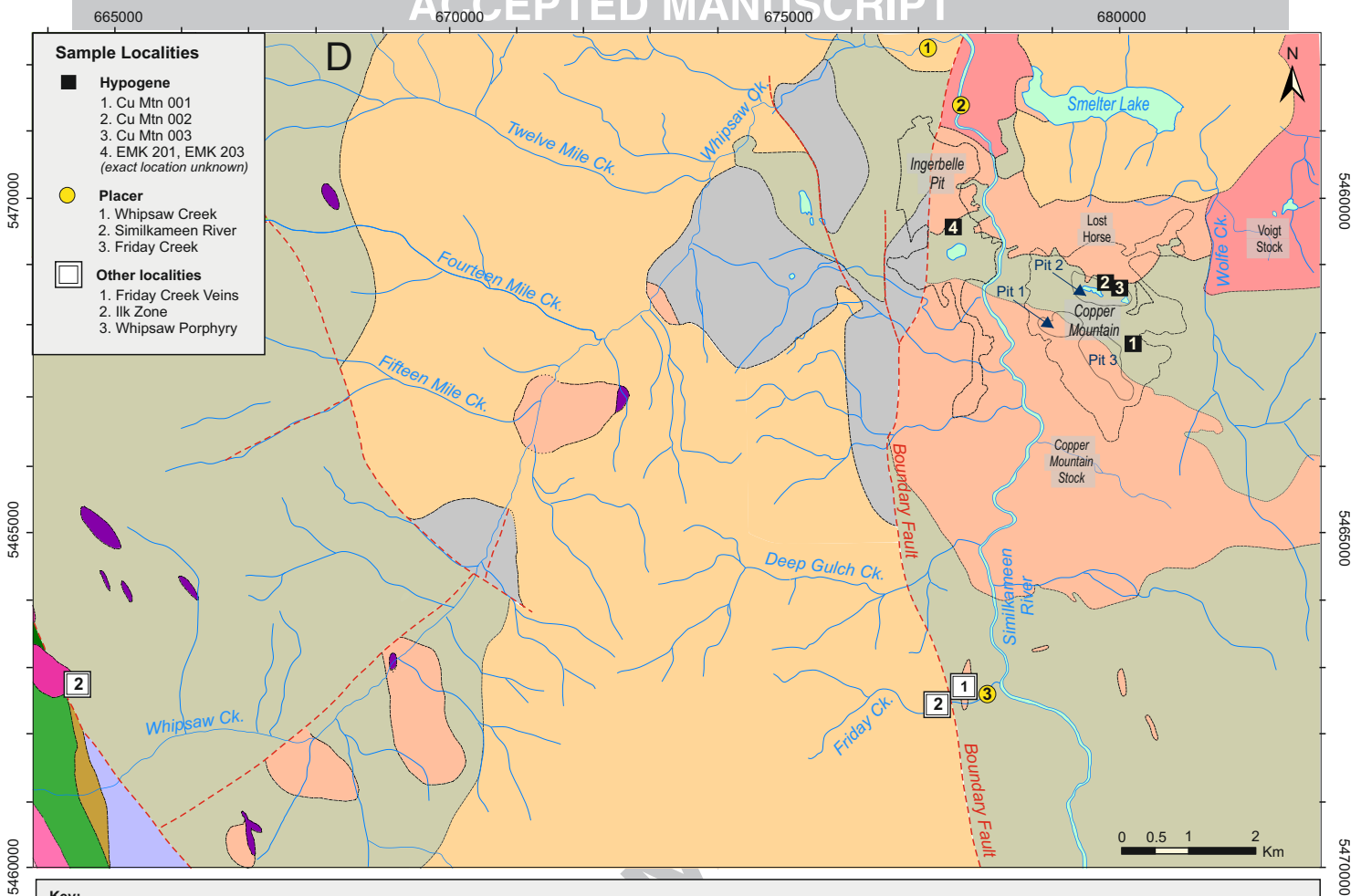






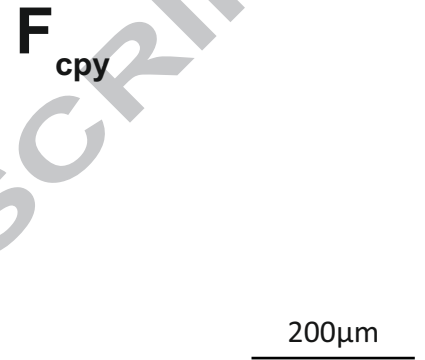
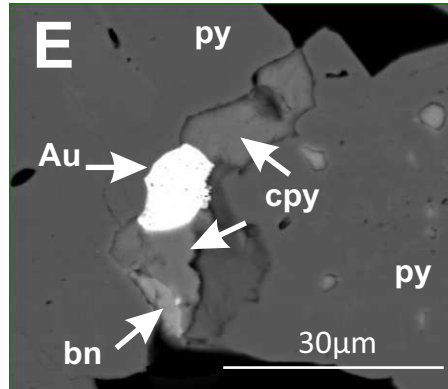
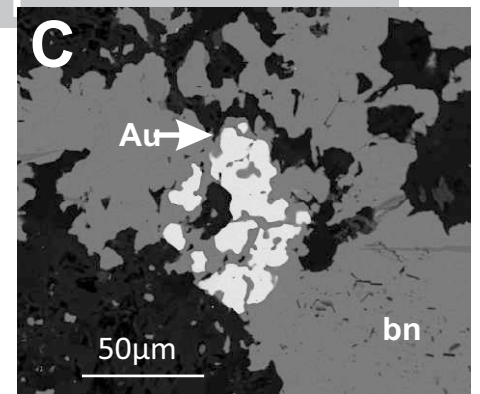
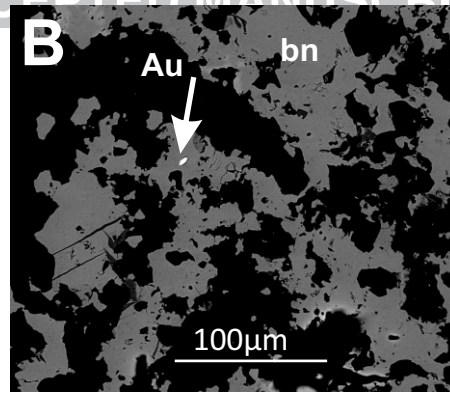
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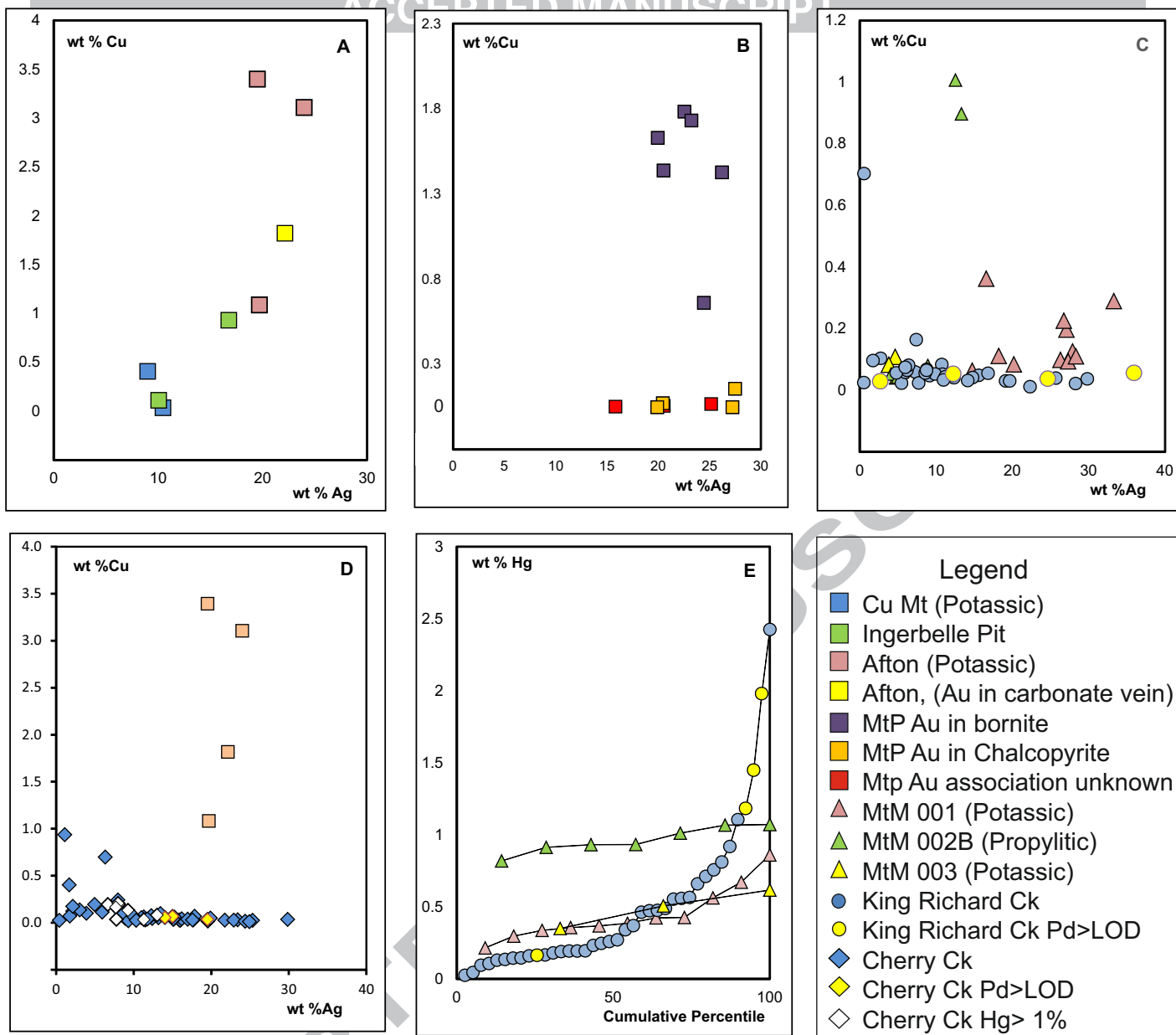


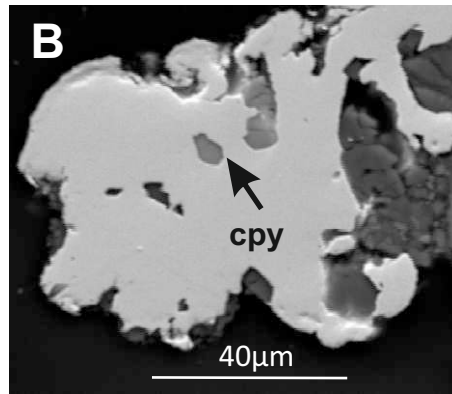
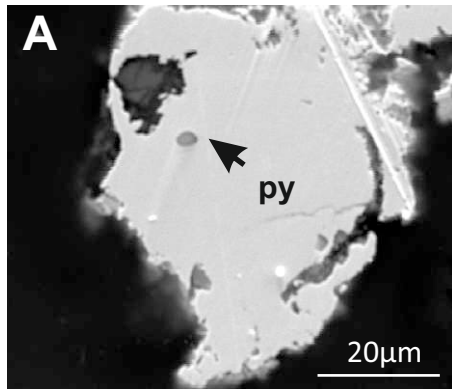


- Sample Localities**
- **Hypogene**
    1. Cu Mtn 001
    2. Cu Mtn 002
    3. Cu Mtn 003
    4. EMK 201, EMK 203 (exact location unknown)
  - **Placer**
    1. Whipsaw Creek
    2. Similkameen River
    3. Friday Creek
  - **Other localities**
    1. Friday Creek Veins
    2. Ilk Zone
    3. Whipsaw Porphyry

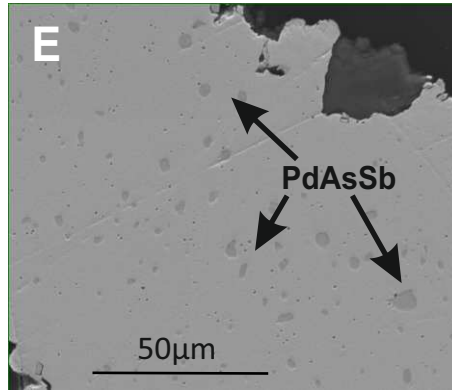
- Key:**
- Geology:**
- Eocene**
    - Whipsaw porphyry: grey to pink quartz-biotite-feldspar porphyry
    - Princeton Group**
      - Undifferentiated mafic to felsic, alkalic volcanic flows; aphyric to porphyritic, massive to volcanoclastic; minor clastic sediments
  - Middle-Late Jurassic**
    - Biotite-feldspar gneiss intruded by massive granodiorite
  - Middle to Upper Triassic**
    - Copper Mountain Intrusions**
      - Microdiorite
      - Pyroxene-hornblende diorite, monzonite (Copper Mountain Stock); pyroxene-biotite diorite (Voigt Stock)
      - Massive to schistose pyroxenite
    - Nicola Group**
      - Undifferentiated volcanics and volcanoclastics
      - Interbedded black argillite, siltstone and sandstone, minor limestone beds
  - Permian or Triassic**
    - Eastgate-Whipsaw Metamorphic Belt**
      - Amphibolite unit
      - Quartzite-biotite-quartz schist unit
      - Mixed metavolcanic-metasedimentary unit







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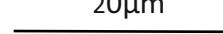
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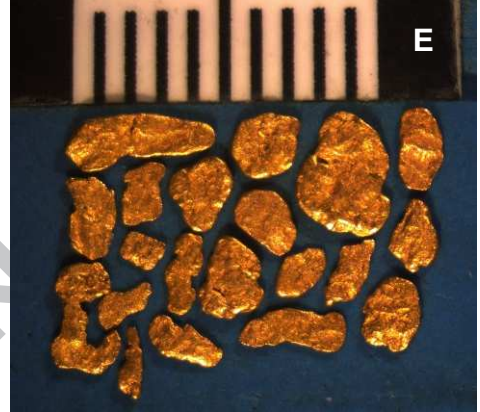
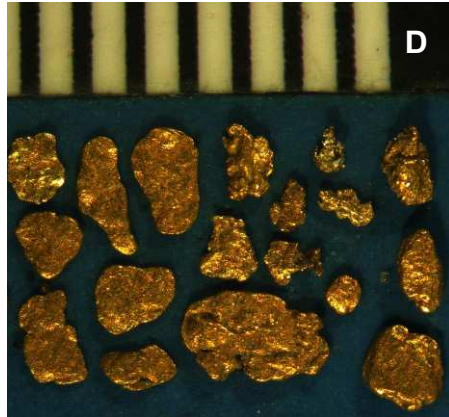
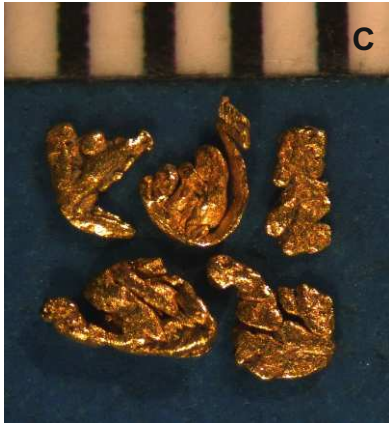
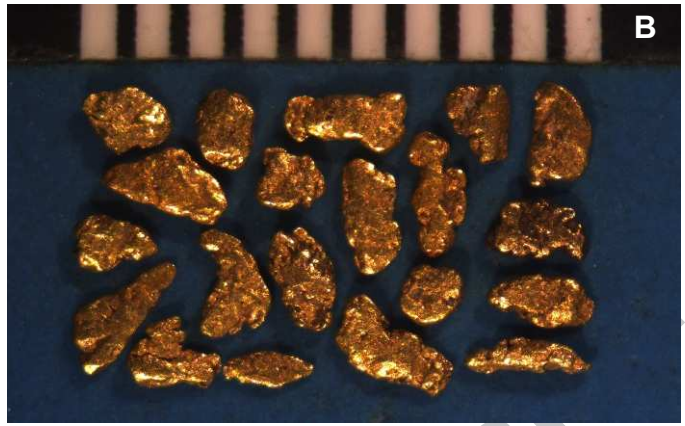
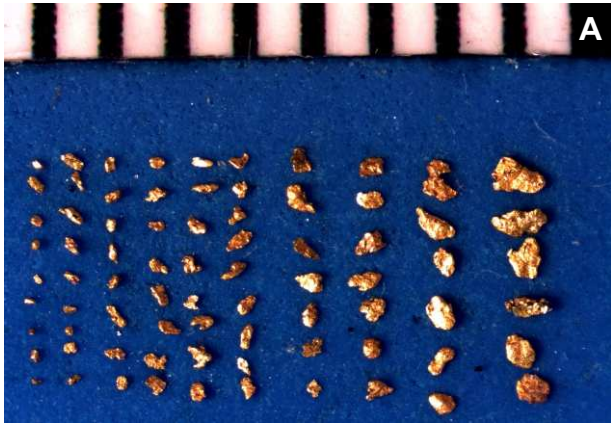


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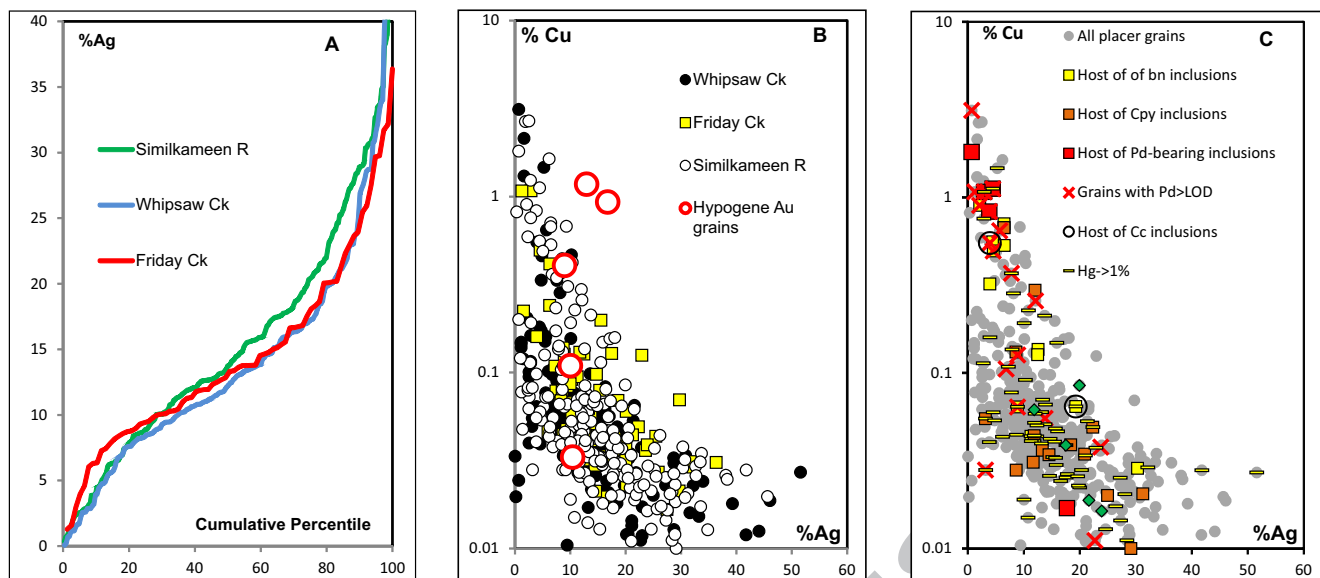
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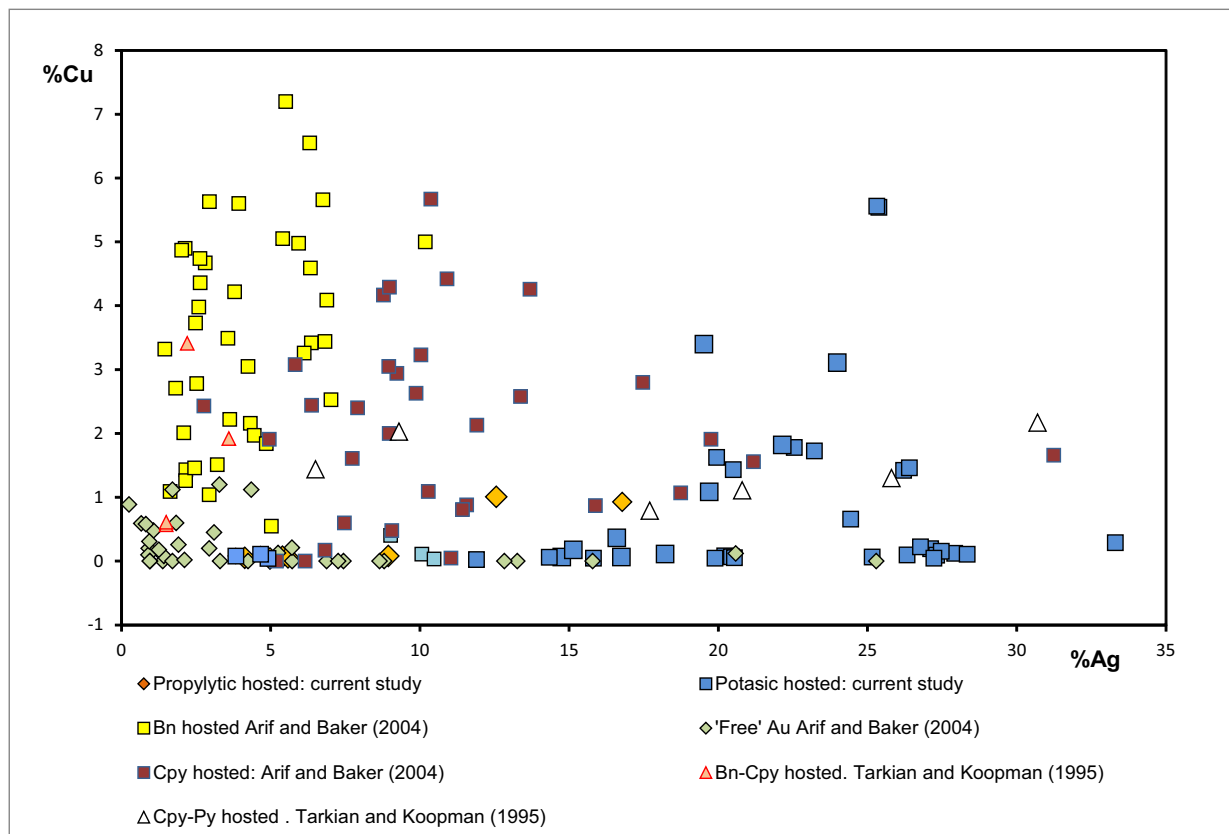


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Mineral Species	Late stage subepithermal veins			Inclusion assemblages of placer populations					Mineralogy of ore stage					
	Mt M Vb veins 1	Friday . Ck veins 2,3,4	Afton and Mt M 5,6	Cherry . Ck 7	King .Richard Ck7	Whipsaw Ck7	Friday Ck7	Simlikameen . R7	Mt.M. Early Veins <sup>8</sup>	Cu Mt 1 <sup>2</sup>	Cu Mt 2 <sup>2</sup>	Whipsaw Porphyry <sup>9</sup>	Wood <sup>10</sup>	Afton Pit 6,11,12
Chalcopyrite	■	■		■		■	■	■	■	■	■	■	■	■
Bornite		■				■	■	■	■		■		■	■
Pyrite	■	■		■	■	■		■	■	■		■		■
Carbonate	■	■			■	■		■						■
Cu sulphosalts	■				■			■			■			■
Chalcocite/covellite		■		■		■	■	■		■				■
Ag-tellurides	■	■		■		■		■		■				■
Galena	■							■	■					
Bi-tellurides	■			■			■	■						
Arsenopyrite	■						■	■						
Sphalerite	■						■	■	■	■	■			
Pyrrhotite				■		■	■	■		■				
Molybdenite				■		■	■	■				■	■	■
Other As-bearing							■	■						
Sperrylite			■			■								■
Merenskyite/ Kolutskite	■	■	■			■	■	■	■					
Temagamite	■	■	■	■				■						■
Mertieite II				■				■	■					■
Stibiopalladinite			■				■	■						

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1168 Table 1. Summary of findings of previous Au compositional studies relating to porphyry  
 1169 systems. CA= calc-alkalic, KCA= potassic rich calc-alkalic. Bn= bornite, Cpy= chalcopyrite,  
 1170 Q= quartz. References: 1=Antweiler and Campbell (1977), 2=Tarkian and Koopman (1995),  
 1171 3= Rubin and Kyle (1997), 4= Palacios et al. (2001), 5= Arif and Baker, (2004), 6= Kelley et  
 1172 al. (2011).

1173 Table 2. Descriptions of samples which form the basis of this study.<sup>1</sup>Jago et al. (2013), <sup>2</sup>  
 1174 Thompson Creek Metals (2014), <sup>3</sup> Pass et al. (2013), <sup>4</sup> Imperial Metals (2013), <sup>5</sup>Nixon  
 1175 (2004a), <sup>6</sup> Ross et al. (1995), <sup>7</sup> Stanley et al. (1995), <sup>8</sup> Copper Mountain Mining Corporation  
 1176 (2011). UTM Zone 10, NAD 83.

1177

1178 Table 3. Characteristics of Au grains from hypogene, eluvial and placer environments.  
 1179 Abbreviations: b = grains observed in polished blocks, f = free Au grains liberated by  
 1180 crushing, and mounted as placer grains. Alteration '1' and '2' indicate overprinting, where 2  
 1181 is the later phase. M= max value, C= % > LOD. Mineral abbreviations: Act= actinolite, Al=  
 1182 albite, Anh= anhydrite, Bio= biotite, Bn= bornite Ca= calcite, Chl= chlorite, Cpy=  
 1183 chalcopyrite, Gn= galena, Ep= epidote, Ksp= orthoclase, Mag= magnetite, Po= pyrrhotite,  
 1184 Py= pyrite, Pum= pumpellyite, Sph= sphalerite, Tet= tetrahedrite, Tem= temagamite.

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1186 Table 4. Table 4. Numbers of grains in which each inclusion species was observed. Key:  
 1187 Mineral abbreviations as per Table 3 plus: Asp = Arsenopyrite (FeAsS), , Cc = Chalcocite  
 1188 (CuS), Cob = Cobaltite (CoAsS), Cn= Cinnabar (HgS), Gb= unconfirmed Pb-Bi sulphide, Hs  
 1189 = Hessite (Ag<sub>2</sub>Te), Ger = Gersdorffite (NiAsS), Lo = Loellingite (FeAs<sub>2</sub>), Mo = Molybdenite  
 1190 (MoS),, PdTe= unconfirmed Pd telluride, PdSbAs = unidentified Pd arseno- antimonide, Ptz  
 1191 = Petzite (Ag<sub>3</sub>AuTe<sub>2</sub>), Spy = Sperrylite (PtAs<sub>2</sub>), Stp = Stibiopalladinite (Pd<sub>5</sub>Sb<sub>2</sub>), Tbi=  
 1192 Tellurobismuthite, (Bi<sub>2</sub>Te<sub>3</sub>), Tem = Temagamite (Pd<sub>3</sub>HgTe<sub>3</sub>), U= Ullmanite (NiAsS).

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1194 Table 5. Signatures of individual placer grains which correlate to the mineralogy of the  
 1195 Friday Creek veins (see Fig. 10). Grain descriptors with 'a' and 'b' suffix denote alloy-  
 1196 inclusion associations within heterogeneous grains. 'nd'= 'not determined'.

1197

1198 Table 6. Comparison of Pd, Pt and Au contents and mineralogy of flotation concentrates,  
 1199 with microchemical signatures of placer gold for various localities worldwide. 1 =  
 1200 Economou-Eliopolous (2005); 2 =McFall et al. (2016) 3= Pašava et al. (2010); 4 = Micko et  
 1201 al. (2014); 5 = LeFort et al. (2011); 6 = Pass et al. (2014); 7 = Nixon et al. (2004a); 8 =  
 1202 Garagan, (2014); 9 = Hanley and Mackenzie, (2009). FC= flotation concentrate, A = alkalic,  
 1203 CA = calc-alkalic, KCA = high-K calc-alkalic, NR= not recorded, Mineral abbreviations as  
 1204 per table 4 plus, Tel= telargpalite (Pd,Ag)<sub>3</sub>Te, So= sopcheite Ag<sub>4</sub>Pd<sub>3</sub>Te<sub>4</sub> Mon= moncheite,  
 1205 (Pt,Pd)(Te,Bi)<sub>2</sub> MeTel= merenskyite, (PdTe<sub>2</sub>) Mer= mertieite, Pd<sub>8</sub>(Sb,As)<sub>3</sub>

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Location	Deposit	Class	Alloy analyses	Major findings
Circle City <sup>1</sup>	Au-Mo	CA	Au, Ag, Cu	Ag increases with decreasing temperature
Santo Tomas II <sup>2</sup>	Cu-Au	CA	Au, Ag, Cu	Ag content of Bn-hosted Au (potassic zone) << than that hosted in Cpy, (potassic and propylitic zones)
Grasberg <sup>3</sup>	Cu-Au	KCA	Au, Ag, Cu, Pd	Pd bearing alloys in late stage veins only. Ag values lower than in other studies
Cerro Casale <sup>4</sup>	Cu-Au	CA	Au, Ag, Cu	Ag in potassic hosted Au higher than in sericitic (phyllitic) veins
Batu Hijau <sup>5</sup>	Cu-Au	CA	Au, Ag, Cu	All potassic phase: Ag in Bn hosted alloy < Ag in Cpy hosted, but Cu broadly equivalent. Cu of Q-hosted Au alloy lower than in sulphides
Pebble <sup>6</sup>	Cu-Au	CA	Au, Ag	Ag content of Au in potassic zone >> than that formed in late stage veins

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Locality	Tonnage	Sample ID	Easting	Northing	Comments
<b>Mount Milligan</b> <sup>1</sup>	1.08 MT Cu, 19.2 T Au. <sup>2</sup>	MtM 001	434363	610938	Margins of the MBX stock
		MtM 002a	434572	610930	Quartz-calcite veins adjacent to the MBX stock
		MtM 002b	434572	610930	Latite volcanics exhibiting propylitic and potassic alteration assemblages
		MtM 003	434698	610946	Pyrite rich associated with propylitic alteration assemblage
		MtM 005	434927	610904	Oxidized samples panned from the '66' Zone
		MtM 006	434927	610904	Non-weathered sample of '66' Zone volcanic rocks
<b>Mount Polley</b> <sup>3</sup>	226 x 10 <sup>3</sup> T Cu, 21.5 T Au, 65.1 T Ag <sup>4</sup>	MtP 002	591942	582282	Northwest face of the Springer pit
		MtP 003	592204	582294	Hydrothermal breccia sample, Cariboo pit
		MtP 004	591942	582282	Sample from the WX Zone
		MtP 005	High Grade ore zone in Boundary Zone Exact location uncertain		Hydrothermal breccia from underground operations. Stockpile in Wight pit
<b>Afton Open Pit</b> <sup>5</sup>	20MT Cu, 14.74 T Au <sup>6</sup>	EMK 230	Location within Afton Pit not recorded		Leeds University specimen 'Afton'
<b>Copper Mountain</b> <sup>7</sup>	0.7 MT Cu, 21.7 T Au, 279 T Ag <sup>8</sup>	Cu Mtn 001	680814	546823	East-trending dilatant magnetite veins running through the floor of the Virginia pit
		Cu Mtn 002	679873	546665	Bornite, chalcopyrite and pyrite disseminations within Nicola Group Volcanics, north wall of Pit 3
		Cu Mtn 003	679873	546665	Late stage calcite veins, with pyrite disseminations, north wall of Pit 3
		EMK 201	Location within Ingerbelle Pit not recorded		Leeds University specimen "Ingerbelle Pit"
		EMK 203	Location within Ingerbelle Pit not recorded		Leeds University specimen "Ingerbelle Pit"

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1217 *Table 3A. Hypogene environments.*

	Gold grains		Alteration assemblage	Alteration		Ore mineral association	Hg		Cu		Pd	
	b	f		1	2		M	C	M	C	M	C
<b>Mt Milligan</b>												
MtM 1	8		Ksp, Bio, Mag, Act	K	CaK	Py, Cpy, Bn, Tet	0.4	100	0.3	100	0	0
MtM 2b	2	5	Ep,Al,Ca,Act	Pr		Py, Cpy, Tet, Gn	1.0	100	1.0	100	0.02	14
MtM 2bK	5		Ksp, Bio, Mag	K		Py, Cpy	0.8	100	0.3	100	0.05	67
MtM3	1	2	Ep-Al-Ca-Act	Pr		Py, Cpy	0.6	100	0.1	100	0	0
<b>Mt Polley</b>												
MtP 3	1	1	Ksp, Bio, Mag, Alb, Chl, Ep	K	Na		1.3	100	0.06	100	0	0
MtP 4	1		Ksp, Bio, Mag, Alb, Chl, Ep	K	Na	Cpy, Sph	0.4	100	1.4	100	0	0
MtP 5	8	6	Ksp, Bio, Mag, Alb	K		Bn, Cpy	0.6	93	1.8	100	0	0
<b>Copper Mountain</b>												
Cu Mt 1	1		Mag			Cpy	0.1	100	1.1	100	0	0
Cu Mt 2	1	1	Dio, Chl-Ep, Ksp, Bio, Mag, Ep, Chl	Na	K	Bn	0.4	100	0.4	100	0	0
EmK 201	1		An, Chl, Ep, Act, Pum	Pr		Py, Cpy	0.2	100	0.9	100	0	0
EmK 203	1		Ksp, Bio, Mag, Ep, Chl	K	Pr	Py	0.4	100	0.1	100	0	0
<b>Afton</b>												
EmK 230	3		Ksp, Mag, Bio	K		Bn, Cpy, Tem	1.0	100	3.3	100	0	0
EmK 230	1		Carbonate vein				0.5	100	1.93	100	0.93	100

1218 *Table 3B. Placer environments.*

Locality	Drainage	Location		No	Hg		Cu		Pd	
		E	N		M	C	M	C	M	C
Mt Milligan	King Richard Ck	434508	6108587	40	0.70	97.5	2.4	95.0	0.3	10.0
Copper Mountain	Similkameen R	678215	546850	248	2.68	73.8	5.20	89.1	4.1	8.5
	Friday Ck	677785	546385	77	1.07	97.4	2.67	100	4.1	5.2
	Whipsaw Ck	677057	547110	204	3.12	88.2	3.77	99.0	2.5	3.4
Afton	Cherry Ck	434580	561587	59	0.9	94.9	3.3	30.5	1.1	5.1

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Locality	Inclusions observed in polished section													
	Py	Po	Gn	Cpy	Bn	Cc	Mo	Tet	As-bearing	Bi-bearing	Ag and Te bearing	Other	Pd-bearing	
<b>Mount Milligan</b>														
King Richard Ck	1							1	Lo					
<b>Afton</b>														
Cherry Ck	1			2		1	1			Tbi	Hs		PdSbAs, Tem	
<b>Copper Mountain</b>														
Similkameen R.	4	1		12	10	1		2	Asp (4), Ger, Cob, Lo, Ul	Gbi	Ptz	Sph, Cn	Iso Stp Tem, PdTe	
Friday Ck		1		1	2	1	1						Stp	
Whipsaw Ck	2	2		5	1		1		Ger		Ptz Ce	Spy		

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Grain	Inclusion assemblage	Au	Ag	Hg	Cu	Pd	Total
<b>Friday Creek</b>							
1	Bornite and chalcocite	94.07	3.97	0.32	0.55	1.94	101.9
<b>Whipsaw Creek</b>							
1	Stibiopalladimite, Chalcocite	93.07	2.96	2.28	1.07	2.60	100.9
2	Sperrylite	95.13	0.72	0.20	3.12	2.46	101.6
<b>Similkameen River</b>							
1	Pd-arseno-antimonide	92.64	3.88	0.09	0.83	2.08	99.52
2	Temagamite	90.61	4.49	2.35	1.12	0.32	98.9
3a	Bornite	78.00	8.90	6.19	0.06	4.12	97.3
3b	Temagamite	51.91	3.21	22.93	0.03	15.21	93.3
4a	Bornite, Chalcocite	92.57	6.53	0.00	0.53	0.00	99.6
4b	Cinnabar	69.81	28.39	0.88	0.02	0.00	99.1
5	Chalcopyrite, Temagamite, Pd-telluride	80.85	17.77	0.64	0.02	nd	99.3
6	Pd-arseno-antimonide , chalcocite	93.26	0.70	0.71	1.81	nd	96.4

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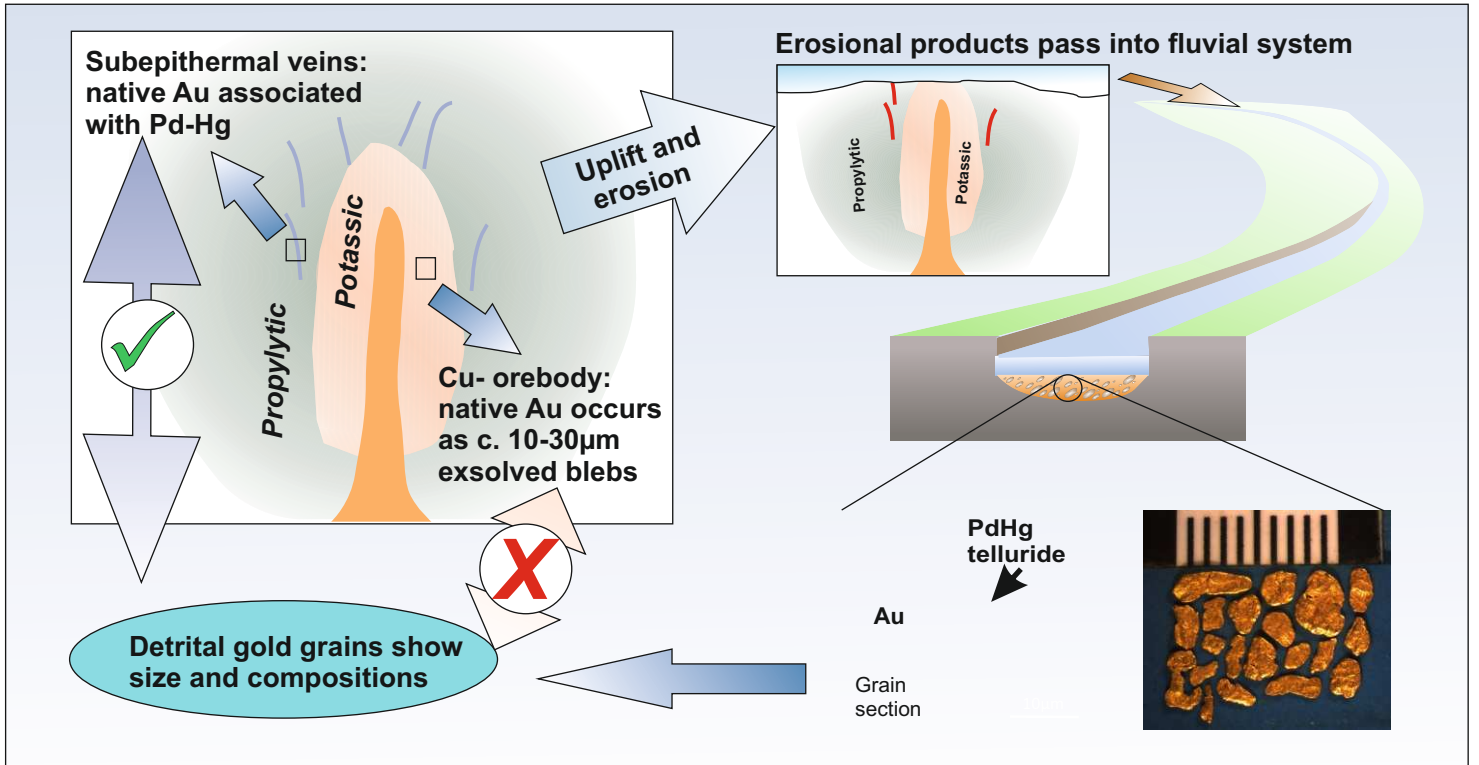
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Deposit	Affinity <sup>1</sup>	Precious metal assays, g/T in FC <sup>1</sup> except *			PGE minerals in hypogene ore	Late stage Au- bearing veins	Placer – lode relationships
		Pd	Pt	Au			
<b>Greece</b>							
Skouries	A	2400	40	22,000	Me <sup>1,2</sup> , So <sup>2</sup> , Te <sup>1,2</sup> , Ko <sup>2</sup>	Elevated Pd in supergene zone: ascribed to supergene processes	NR
<b>Bulgaria</b>							
Elatzite	A	1130	130	16,200	Me <sup>1</sup> , Mon <sup>1</sup>	NR	NR
<b>PNG</b>							
Ok Tedi	KCA	980	24	28,000	NR	NR	NR
<b>Indonesia</b>							
Grasberg	KCA	58	15	18,000	NR	Yes, cited as source of Pd-rich Au	Recommendation to routinely screen placer grains for Pd.
<b>Malaysia</b>							
Mamut	KCA	1400	470	15,200	Me <sup>1</sup>	NR	NR
<b>Phillipenes</b>							
Santo Tomas II		330	67	10	Me <sup>1</sup> , ko <sup>1</sup> , mon <sup>1</sup>	NR	NR
<b>Uzbekistan</b>							
Kalmakyr <sup>3</sup>	A	55* <sup>2</sup>	5.5*	4.1*	In Cpy	Q, sp, ga, tet, py, Au veins in granodiorite. Atypical of primary ore, yielded 292ppm Pd	NR
<b>Canada (BC)</b>							
Galore Ck	A	1300	80	64,000	NR	Yes but maybe be related to change in mineralization regime from Au to Cu <sup>4</sup>	No local placer claims
Mt Milligan	A	6,300	110	18,500	Tem, Me, Mer	Sub epithermal Au- PGE-bearing <sup>5,9</sup>	See Figure 11
Mt Polley	A	320	33	23,600		Yes, PGM not recorded Au present <sup>6</sup>	Poorly developed local drainage
Copper Mountain	A	3250	50	4,200	Me, Mer, Tem	Distal Cu- Au-PGE bearing <sup>7</sup>	See figure 11
Afton	A	130	-	1200	Pd-rich Py <sup>9</sup>	Carbonate veins with cpy Au association <sup>8,9</sup>	See figure 11

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1231 **Highlights**

- 1232 • First compositional study of placer-lode relationships in gold from Cu-Au porphyries
- 1233 • Gold formed by exsolution from Cu minerals are too small to be routinely collected
- 1234 by panning
- 1235 • Gold from associated sub-epithermal veins shows a distinctive Pd-Hg signature
- 1236 • Detrital gold of this type can act as a pathfinder, and is distinct from gold formed in
- 1237 other source styles
- 1238 • Consideration of Cu-Au porphyries worldwide suggest that these features could be
- 1239 generic
- 1240
- 1241

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