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

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Abstract

This study comprises the first systematic classification of native gold geochemistry within alkalic porphyry Cu-Au systems and the placer expression of such systems. The geochemistry and mineral associations of gold from four alkalic porphyry deposits in British Columbia, Canada (Afton, Mount Milligan, Mount Polley and Copper Mountain) have been compared to comment on the likely detrital gold expression of similar systems globally. Populations of gold grains collected from in situ hypogene mineralization as well as fluvial deposits downstream of these deposits have been characterized in terms of their alloy composition (Au, Ag, Cu, Hg, and Pd) and associated mineral inclusions. These data are combined to generate a ‘microchemical signature’.

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

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

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

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

Whilst gold is an economic mineral in many porphyry systems, there has been limited study of its potential as a heavy mineral indicator. Plouffe et al. (2013) recorded the presence of particulate gold in glacial till samples near the Mount Polley Cu-Au porphyry deposit in central British Columbia (Fig. 1), but also noted that the large placer deposit of the nearby Bullion Pit was stratigraphically below the glacial deposits, and hence that gold grains from several sources could be present in recent surficial sediments. Kelly et al. (2011) and Eppinger et al. (2013) used the abundance and morphology of detrital gold particles to establish dispersion trains around the calc-alkalic Pebble Cu-Au-Mo porphyry in Alaska. They noted that other gold sources in the immediate area probably contributed to the Au grain populations, and as a result, the morphology of gold grains did not provide a diagnostic indication of origin. Whilst the survivability of gold in the surficial environment is a useful attribute for an indicator mineral, it also permits recycling of older gold grains into younger surficial environments, possibly to a greater degree than is the case with other potential indicator minerals. Consequently, the simple presence of detrital gold in panned concentrates...
collected during routine stream sediment sampling may not in itself provide unambiguous provenance information. In addition, interpretation of the origin of detrital gold grains is further complicated by the potential for multiple sources of gold in metallogenically complex regions. For these reasons, information on the source style of mineralization of detrital gold grains gained from the gold itself would be highly beneficial.

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

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

The study of gold grains from porphyry systems presents some challenges over and above mineralization formed under a narrower set of hydrothermal conditions (e.g., orogenic gold). Porphyry systems normally involve alteration assemblages spanning a range of temperatures from near-magmatic to epithermal temperatures, and a wide range of fluid compositions controlling the solubilities of gold and other metals. Alteration zones may also exhibit systematic lateral and/or vertical zonation, or exhibit overprinting relationships, especially in systems that have been telescoped. Gold may thus be associated with a range of hydrothermal
features in porphyry settings, including high-temperature potassic alteration, moderate-
temperature quartz-sericite-pyrite alteration, and low-temperature epithermal styles of
mineralization. As a result of the diverse possible hydrothermal conditions of gold
precipitation, any interpretation of the detrital gold signature of porphyry systems requires an
appreciation of the complexities of the hydrothermal system and its spatial attributes,
including those which may have been present above the current erosional level.

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

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

2.1 Potassic alteration

Potassic (biotite or K-feldspar dominant) alteration hosts the most economically important
Cu-Au ore zones within both alkalic and calc-alkalic porphyry systems and consequently,
studies of gold grains formed in calc-alkalic porphyry systems have relevance to the present
study.

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

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

Nixon et al. (2004a) studied the distribution of PGE within potassic alteration zones in
different alkalic Cu-Au porphyries in British Columbia. Palladium, and to a lesser extent Pt,
were more highly concentrated in pyrite as opposed to chalcopyrite, but discrete grains of
merenskyite (PdTe₂), temagamite (Pd₃HgTe₃), merteite II (Pd₈Sb₃), kolutskite (PdTe) and
melonite (Ni,Pd,Pt)Te₂) were also observed. Hanley and MacKenzie (2009) showed that both
Pd and Pt were concentrated in the Co-rich cores of pyrite grains which pre-dated the main
Cu ore stage at Afton and Mount Milligan. However, Pasava et al. (2008) recorded higher levels of Pd in chalcopyrite than in pyrite in a study of PGE distribution at the Kalmakyr alkalic Cu-Au porphyry in Uzbekistan. Nixon et al. (2004) considered PGE abundance in the Afton Cu-Au porphyry, southern British Columbia (Fig. 1), but did not undertake any mineralogical analyses, whereas Garagan (2014) undertook a systematic evaluation of palladium and gold concentrations in the context of alteration assemblages. Gold and palladium concentrations varied according to two separate trends. In the potassic zone where values of 2.6 ppm Au and 2.9 ppm Pd were recorded (in core intersections of 0.2m and 0.3m respectively), Au and Pd were generally inversely correlated. However, Au and Pd were positively correlated in a later phase of mineralization focussed parallel to the main fault zone. The only mention of Hg-bearing minerals within the potassic zone is in the form of temagamite (Nixon, 2004).

2.2 Phyllic and Propylitic alteration

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

The waning stage of hydrothermal activity in porphyry systems may permit the remobilization of early-formed gold through interaction with lower temperature fluids containing reduced sulphur (Gammons and Williams-Jones, 1997). Copper sulphides formed with potassic alteration may be leached through interaction with Cl-bearing fluids convecting...
at the periphery of the system (Dilles and Einaudi 1992). Bornite/chalcopyrite digestion
would also redissolve gold, facilitating subsequent redistribution in the hydrothermal system.
Dissolution of pre-existing Pd tellurides is perhaps less likely, as Mountain and Wood (1998)
suggested that the presence of Te can reduce Pd solubility. The presence of Hg has not been
reported in potassic zone mineralization, except as temagamite (Pd₃HgTe₃), but the potential
for remobilization of Hg from this mineral is unclear.

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

### 2.3 Subepithermal veins

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

Brothers et al. (1963) provided a detailed description of gold-bearing copper veins at Friday
Creek, located about 5 km south of the Copper Mountain mine and about 500 m from the
creek’s confluence with the Similkameen River (Fig. 1). Mineralization comprised bornite
and chalcopyrite in quartz carbonate veins within faults. Pegmatite veins were also reported
at this locality, but these are distinct from the chalcopyrite and bornite mineralization. Fischl (2015) reported the results of subsequent exploration which provided a more detailed mineralogical characterization including temagamite, palladium tellurides and copper sulphides. Grab samples of veins and drill intersections showed a range of gold and palladium values from 0.264 to 6.3 g/t and 0.42 to 57.8 g/t, respectively. More recent confirmatory testing has generated assays of 28.16 ppm Au, and 18.19 ppm Pd (Anglo-Canadian Mining Corp, 2010). Similar veins were reported at the Ilk occurrence (Fig 1.), located 800 m to the north (Fischl 1991). The mineralization here is reported to contain both gold and palladium but no detailed mineralogical studies have been undertaken.

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

2.4. Epithermal veins

High sulphidation epithermal mineralization is not associated with alkalic Cu-Au porphyry systems because of the overall low S budget. For the porphyry sites considered in the present study there is also an absence of low sulphidation systems, although such mineralization is present at the Endeavor 41 Prospect, Cowal District, new South Wales, Australia (Zukowski et al. 2014) where it is proposed that there is an association with Cu-Au alkalic porphyry mineralization at depth. At Mount Milligan, Le Fort et al. (2011) hypothesized that such systems may have been present above the present erosional level, and this is likely to be the case at the other localities where the core of the mineralized system is close to surface.

Consequently no examples of low-sulphidation epithermal mineralization were sampled for the present study, although it is possible that detrital gold samples could include low-sulphidation epithermal sources.

3. Methodology

3.1 General approach

The overall approach of this study is establish relationships between the compositional signatures and mineral associations of particulate gold in the hypogene environment with the microchemical signature of populations of gold grains collected from local drainages. This correlation has been possible for three of the localities studied, but the drainage around Mount Polley (Fig. 1) is not well developed and no detrital gold grains were recovered for
study. Nevertheless, the hypogene sample suite from the Mount Polley mine help constrain in situ gold signatures. Ideally, large numbers of gold grains liberated directly from well constrained and characterised hypogene ore would be available for analysis; however, in practice, isolation and collection of gold grains from ore specimens has been challenging. Rock samples include a range of alteration types in Mount Milligan, Mount Polley and Copper Mountain, where gold assays were relatively high. However, gold grains were typically well below the size threshold for recovery using traditional gravity concentration methods, or gold was present as inclusions or in solid-solution in sulphides. Collection of bulk samples of hypogene ore for crushing and subsequent gold recovery was undertaken in an attempt to obtain more gold grains for analysis. Preparation of thin sections provides a more robust approach for revealing tiny gold grains, but the abundance of gold particles is usually low, resulting in an expensive and inefficient screening process.

3.2 Sample collection and preparation

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

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

Gold grain analyses were carried out in Leeds University using a Jeol 8230 Superprobe, (EMPA). Limits of detection (LOD) defined at 3σ were as follows: Cu: 0.02%, Hg: 0.09%, Pd: 0.07%, Ag: 0.07%, Au: 0.11%. All analyses are reported in weight percent (wt. %).

Mineral inclusions in polished sections were identified through inspection in BSE imaging using the EDS facility of an FEI Quanta 650 FEG-ESEM SEM. The stoichiometry of Pd-Te and Pd-As-Sb mineral inclusions was not determined by EMP and consequently these have been reported in terms of their constituent elements rather than as specific mineral names. Native gold-ore mineral associations were established through inspection of polished blocks by both reflected light microscopy and using the SEM. Quantitative analysis of gold grains hosted by copper sulphides was undertaken only on grains of over 8 µm (longest dimension in section) to minimise the possibility of electron beam interaction with the underlying mineral. Mineral associations of liberated grains could sometimes be deduced through observation of inclusions (e.g., Fig. 5A). Alloy heterogeneity (with respect to Au and Ag) was evaluated by visual inspection of grey scale of BSE images for every gold particle. Semi quantitative alloy compositions in heterogeneous grains were obtained using the EDS facility of the SEM, and although these are not reported here they informed selection of targets for quantitative analysis by EMP.

3.4 Data presentation

This study considers the significance of Ag, Cu, Hg and Pd concentrations in gold alloy. These data are integrated with mineral inclusion suites revealed in polished section. The standard approach of evaluating the content of minor alloys within a population of grains with cumulative percentile plots has been adopted here both for Ag and Hg (e.g., Fig. 4C), because it allows direct comparisons of populations comprising different numbers of grains. The significance of other minor alloying elements is evaluated either by considering the
proportions of grains which contain the metal in detectable amounts, or through their co-
variance (e.g., Cu-Ag bivariate plots), in which each point represents a different gold grain.
Such plots may also indicate those compositions which correspond to other notable features,
e.g., specific inclusions or elevated concentrations of other alloy components.

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

The interpretation of mineral inclusion suites revealed in polished sections of gold grains is a
key element of compositional characterization, although reporting and characterization of this
information may be challenging for various reasons. Firstly, the incidence of inclusions varies
considerably between localities, and is revealed only after completion of analysis following
the sample collection program. Whilst this problem can be mitigated by collection of large
populations of gold grains, time constraints during sampling programs can limit the number
of grains available for study. Secondly, a large number of inclusions species may be
recorded; for example, in the present study, 27 different opaque mineral species were
observed. The combination of low inclusion incidence and a wide number of mineral species
is not suited to statistical analysis of individual mineral species. Thirdly, the presence of some
inclusion species may be diagnostic for a particular mineralizing environment (e.g., Pd-
bearing minerals), whereas other minerals such as pyrite are ubiquitous and undiagnostic.

Mineral suites are characterized for individual populations by establishing the proportion of
grains that exhibit inclusions of a specific mineral, although in some cases grains containing
two or more different inclusion species may be particularly useful in predicting placer-lode
relationships.

4. Characterization of in situ mineralization

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

One aim of the study has been to identify any systematic variation in gold grain chemistry
associated with host alteration assemblage. Samples were collected from different gold-
bearing lithologies on site, according to the prevailing alteration type. In most cases,
inspection of polished blocks confirmed the gold-alteration association, but in others overprinting alteration types were recorded (Fig. 3A). The potential for relict gold in subsequently altered rock is discussed in a later section. Where gold grains were liberated from bulk ore samples, the alteration style was assumed to be that of the host ore.

4.1 Alloy variation as a function of alteration type

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

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

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

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

4.3 Compositional heterogeneity of gold alloys

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

5. Characterization of placer gold samples

5.1 Morphology

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

5.2 Alloy compositions

The Cu and Ag concentrations in hypogene gold from Afton and Mount Milligan are compared with the corresponding alloy signature for local detrital gold in Figures 4C and D, respectively. In most cases, hypogene grains show Cu contents exceeding the compositional field of placer grains, and particularly those from the potassic zone. Both placer populations show a similar co-variance of Cu and Ag (Figs. 4C, D), with a broad inverse correlation between Ag and Cu. A few grains contain Hg to above 1 wt. % (Table 3A), but there is no covariation with either Ag or Cu. Palladium was recorded in four grains from King Richard Creek (Fig. 4C), which exhibit a wide range of Ag contents, but three of the four correlate with high Hg (Fig. 4E). The placer population from Cherry Creek also contains some high Hg
grains, which appear to be associated with lower Ag values. Three grains contained Pd >LOD (to a maximum of 1.1 wt. %), although these grains were not correspondingly high in Hg.

The compositional variation in populations of placer grains from the Copper Mountain area are shown in Figure 7. The cumulative plots for Ag in detrital grains from Friday Creek, Whipsaw Creek and the Similkameen River are very similar (Fig. 7A), and this similarity extends to the co-variance of Cu and Ag (Fig. 7B). There is a suggestion of a distinct Cu population at low Ag concentrations (Fig. 7B), and more detailed information has been incorporated in Figure 7C in an attempt to confirm this through identification of any co-variation of Cu/Ag with either other minor alloying elements or specific inclusion species.

Grains containing high Hg and Pd are present throughout the populations, and whilst Pd-bearing inclusions are more common in the Ag-poor gold alloy they are not confined to this host composition. Bornite-bearing inclusions appear to be hosted by high-Cu alloy regardless of the Ag content.

5.3 Alloy heterogeneity

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

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

Key: Mineral abbreviations as per Table 3 plus: Asp = Arsenopyrite (FeAsS), Cc = Chalcocite (CuS), Cob = Cobaltite (CoAsS), Cn = Cinnabar (HgS), Gb = unconfirmed Pb-Bi sulphide, Hs = Hessite (Ag₂Te), Ger = Gersdorffite (NiAsS), Lo = Loellingite (FeAs₂), Mo = Molybdenite (MoS₂), PdT = unconfirmed Pd telluride, PdSbAs = unidentified Pd arsenoantimonide, Ptz = Petzite (Ag₃AuTe₂), Spy = Sperrylite (PtAs₂), Stp = Stibiopalladinite (Pd₅Sb₂), Tbi = Tellurobismuthite, (Bi₂Te₃), Tem = Temagamite (Pd₃HgTe₃), U = Ullmanite (NiAsS).

6. Discussion

6.1 Characterization of gold formed in different hypogene environments

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

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

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

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

6.2.1 Afton

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

6.2.2 Mount Milligan

Comparison of the Cu contents of hypogene and placer grains suggests that the placer population from King Richard Creek was either only partly derived or unrelated to gold formed in the potassic environment (Fig. 5A). Figure 5E shows that the Hg contents of grains
formed in the propylytic environment are consistently higher in Hg than the majority of placer grains. LeFort et al. (2011) provided Ag contents of three hypogene gold grains from Mount Milligan (10, 12 and 20% Ag) whose compositions were determined using SEM-EDS. These data are not directly comparable with those produced in the present study because of the different analytical method and because the analytical data were normalised. In addition, Cu, Pd and Hg were reported as below the LOD, and, although detectable limits were not specified, it is almost certain that they are considerably higher than those relating to EMPA data generated in the present study. The Ag range of the hypogene gold grains are compatible with that recorded in the detrital grains (Fig. 4C), but better evidence for the presence of type Va vein gold in the placer sample is provided by the presence of a sulphosalt and a carbonate inclusion in a gold grain containing 0.29% Pd. The relatively small number of placer grains collected from King Richard Creek and the low incidence of inclusions have prevented a more thorough analysis of the importance of gold derived from type Va veins in the placer population.

6.2.3 Copper Mountain area

The microchemical signatures of the placer gold populations from the Similkameen River, and Friday and Whipsaw creeks (Figs. 7A, B) suggests commonality in the origins. However, the sampling localities are geographically widespread (Fig. 2D), which suggests that the major contributing gold source signature likely has a large footprint. Hypogene mineralization at Copper Mountain is paragenetically complex, and many of the 22 vein types described by Stanley et al. (1995) have only present locally. In the present study, gold grains were identified in hypogene ore from two localities, whereas the Similkameen River has eroded large parts of the Copper Mountain mineralized system (Fig. 2D), particularly the western part of the ore deposit near the Ingerbelle Pit. Stanley et al. (1995) described the major ore and gangue minerals of different vein types within the Copper Mountain and Ingerbelle Pits. Two of these vein types were subsequently studied by Nixon et al. (2004a), and although the terminology of Stanley et al. (1995) was not adopted by these authors, it seems likely that the “chalcopyrite stringer veins” correspond to the sample “Cu Mt1” veins, whilst “bornite-chalcopyrite-veins” correspond to “Cu Mt 2” sample of Nixon et al. (2004a). Both sets of veins were classified as “early stage” by Stanley et al. (1995). The mineralogy of the “Cu Mt1” and “Cu Mt2” samples of Nixon et al. (2004a) are summarized in
Figure 10, where they are seen to differ substantially, with Pd-bearing minerals recorded in the chalcopyrite-pyrite mineralization only, and gold confined to the bornite-chalcopyrite ore. This association is consistent with the assertion of Nixon et al. (2004a) that pyrite is the favoured host of PGEs in potassic zone mineralization, whereas gold shows far higher affinity for bornite (Kessler et al., 2002).

A comparison of early and late stage mineralization at the various localities is shown in Figure 10. There is clearly a much stronger correlation between the mineralogical signatures of late stage veins and placer samples than between placer samples and early stage mineralization. Several mineral species are common to both early and late stages (e.g., bornite, chalcopyrite and sphalerite) and the appearance of such minerals in an inclusion assemblage is thus undiagnostic for provenance. However, several gold grains contain two or more inclusions, sometimes hosted by gold alloy of distinctive composition, and in these cases it is easier to propose genetic links. Examples of individual grains that contain multiple characteristics compatible with the Friday Creek veins (Fischl 2015) are presented in Table 5.

The vein systems exhibit an unusual mineralogy comprising bornite, chalcopyrite, temagamite, Pd-tellurides and chalcocite, all of which have been recorded as mineral inclusions, sometimes in intimate association (e.g., Figs. 5F and 8C). We conclude that this type of vein is more widespread than is currently recognised and has made a substantial contribution to the local placer inventories. Alternatively, similar veins may have been present above the main ore zones but have been lost to erosion. Gold grains derived from such veins could have formed placers in lag deposits such as those sampled during this study.

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

Richardson (1995) described the Whipsaw porphyry system (Fig. 2D) and associated gold-bearing pyrite-chalcopyrite-molybdenite and chalcopyrite-sphalerite veins extending towards
the Friday Creek catchment. Molybdenite inclusions were observed in one grain from both
Friday and Whipsaw creeks, and a sphalerite inclusion was recorded in a Similkameen River
grain. These data are not considered necessarily indicative of a clear placer-lode relationship.
An inclusion of sperrylite in a gold grain from Whipsaw Creek with a high Pd content (Table
5) may be related to a small outcrop of ultramafic rocks about 5 km southeast of the Whipsaw
porphyry (Fig 2D). Alternatively it could represent a subordinate Pt signature, as reported by
Hanley and Mackenzie (2009) at Afton and Mount Milligan, and recognised more widely in
flotation concentrates from alkalic porphyries elsewhere (e.g., Tarkian and Stribny 1999).
The commonality between the compositional signatures of detrital gold from the three placer
localities around Copper Mountain strongly suggests that similar sources have contributed to
each placer. It seems likely that a range of different vein sources of gold are possible, and the
mineralogical compatibility of these with inclusion species (Fig. 10) supports this assertion.
The presence of gold grains exhibiting different morphological features (indicative of
different fluvial transport distances; Fig 6) supports the hypothesis of different source
localities. The most distinctive microchemical signature is compatible with the mineralogy of
the veins at Friday Creek, and was observed in each of the placer samples. In some cases the
mineralogy of these grains indicates a paragenesis in which Hg becomes more important in
the later stages.

7. Application of placer gold signatures to exploration within British Columbia
Volcanic sequences of the allochthonous Quesnellia arc terrane, which host the alkalic
porphyries described in this study, are commonly in close proximity to metaclastic rocks of
adjacent parautochthonous North American strata, which may themselves host orogenic gold
mineralization. For example Mount Polley is situated about 10 km south of the historic placer
workings of the Bullion Pit and 15 km southeast of various lode and placer occurrences near
undertook studies of populations of both lode and placer gold grains from throughout the
Cariboo Gold District and identified a regionally pervasive signature comprising a binary Au-
Ag alloy and a simple inclusion suite normally comprising pyrite and base metal sulphides.
The signatures of lode samples persisted into the local placer populations, and it seems
reasonable to assume that the microchemical signatures of gold grains derived from alkalic
porphyries would also be inherited by their detrital counterparts. This hypothesis provides a
basis upon which to evaluate the provenance of gold grains collected during future stream
sediment or till sampling.
The Ag content of gold grains is the most commonly reported of the minor alloying elements, and may vary widely between grains formed in the same mineralizing system, as illustrated by Fig. 8B. Consequently, Ag concentration of an individual grain does not constitute a useful diagnostic parameter, although the distributions of Ag concentration in a population of grains may prove informative (e.g., Fig. 7A). Copper concentrations in populations of gold grains derived from porphyry systems in general are higher than those generally encountered in gold from orogenic mineralization, although the ranges may overlap. For this reason, the Cu content of detrital grains may not be used as a primary discriminant, but can provide useful supporting evidence of origin.

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

8. Consideration of Pd in alkalic porphyries globally

The identification of palladium as a powerful indicator for alkalic porphyry mineralization in
BC suggests it may be globally applicable. Palladium has been recorded in several Cu-Au
porphyry systems, not all of which are of alkalic affinity. Most previous studies have focused
on the concentration of palladium in mine flotation concentrates, as these provide both a
cconvenient and accessible sample source, whose palladium content may have implications for
smelter credits. A few studies have recorded palladium minerals in either flotation
concentrates or core, but these mainly correlate to ore associated with potassic alteration.
Table 6 is a collation of data describing the abundance of palladium in flotation concentrates
linked to mineralogical studies and the potential for a palladium signature to be inherited by
gold grains of sufficient size to report to associated placers. The data describing palladium
(and platinum) in flotation concentrates is a subset of that presented by Economou-Eliopoulos
(2005), selected either because of high palladium values or because other studies can provide
information relevant to the present study. Large gaps are recognized in the information
available, particularly in relation to detrital grains. In addition, most studies focus on the ore
grade mineralization, such that paragenetically distinct veins of particular interest to the
present study could be under-reported. Table 5 shows that the palladium contents of the
British Columbian flotation concentrates is of the same order of magnitude to those of
obtained from various other mines in Greece, Bulgaria, the Phillipines, Indonesia, Malaysia,
Papua New Guinea and Uzbekistan. Where observed, palladium minerals in the potassic
mineralization are tellurides with subordinate Pd-Sb minerals, although Hanley and
MacKenzie note that palladium-bearing pyrite is the most important source at Afton and Mt
Milligan. McFall et al. (2016) report both discrete palladium-bearing minerals and palladium-
bearing inclusions within chalcopyrite in quartz-chalcopyrite-bornite veins at Skouries,
Greece.

Palladian gold had been reported previously in the context of oxidizing, low temperature
chloride hydrothermal systems where transport is facilitated by highly oxidizing lithologies
and precipitation occurs at redox fronts (Chapman et al. 2009). Gold precipitated in such
environments exhibits very low concentrations of Ag, (<2%), but may contain elevated Cu,
and or Pd, and/or Hg. The close spatial association with haematite-rich rocks is a clear marker for the potential presence of this gold type.

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

9. Development of a new exploration tool

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

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

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

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

In conclusion, placer-lode relationships are inherently complicated, and influences such as multiple gold sources and geomorphological evolution of the study area may inhibit establishing clear relationships. Studies of placer gold populations acknowledge these
constraints and work within them, using diagnostic features which become evident during characterization. In this way, even complex relationships may be described with confidence.

9.2 Logistical Considerations

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

10. Conclusions

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

The microchemical signatures of placer populations collected in the immediate vicinity of alkalic Cu-Au porphyries exhibit generic signatures of high Hg in the alloy, detectable Pd in up to 10% of the grains, and palladium-bearing mineral inclusions. The Cu content of the
alloy is above LOD and the presence of bornite inclusions appears far more likely to be related to be genetically related to bornite-bearing late stage veins than primary copper mineralization hosted in the potassic zone, particularly given the more general duplication of late stage vein mineralogy in the inclusion suites.

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

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

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11. References


Figure 1: Locations of alkalic Cu-Au porphyry deposits which formed the basis of this study.

Figure 2. Sample localities around Mount Milligan (A), Mount Polley (B), Afton (C) and Copper Mountain (D). Maps for Mount Milligan, Mount Polley and Afton adapted from BC Geological Survey (2006). Copper Mountain map adapted from Preto et al. (2004) and Massey et al. (2009).

Figure 3. Examples of hypogene gold grains. Figs A-E: potassic zone, Fig F: propylitic zone. Gold and chalcopyrite in pyrite (sample MtM001), B: Typical occurrence of gold bleb in bornite, (sample MtP005), C: The largest hypogene gold grain observed in this study (MtP005), D: Gold film in chalcopyrite veinlet within pyrite (MtM002b), E: Gold within chalcopyrite and bornite vein within pyrite (MtM001), F: Gold grain infill in crack in pyrite, within chalcopyrite (Ingerbelle Pit, Copper Mountain).

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

Figure 5: Figure 5, Examples of mineral inclusions, A: Py in hypogene gold from Mount Milligan; B: Chalcopyrite in hypogene gold from Mount Polley; C: Bornite inclusion in placer grains from the Similkameen River; D: Temagamite inclusions in placer gold from the Similkameen River; E: Unidentified Pd-Ag-As-Sb mineral inclusion in a detrital grain from Cherry Creek; F: Placer grain from the Similkameen River showing bornite inclusions in Au-rich alloy (pale grey: Au:78%, Ag: 8.9%, Hg: 6.2%, Pd 4.1%) and temagamite inclusions in later alloy (medium grey: Au: 51.9%, Ag: 3.2%, Hg: 23.0%, Pd 15.2%). Figs. A, B, F: BSE images, Figs. C, D, E: SE images.

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

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

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

Figure 9. Compositions of hypogene gold from porphyry systems recorded in different studies compared to data obtained in the present study.
Key to Figure 1A-1D:
Symbology:
- Mineable Extent
- Open Pit Outline
- Fault (Observed)
- Geological Boundary (Observed)
- Geological Boundary (Inferred)
- Placer Sample Locality
- Hypogene Sample Locality
- Drainage
- Minfile Occurrence

Geology:
- Tertiary Sediments
  - Early Tertiary volcanic and sedimentary rocks
  - Late Triassic - Early Jurassic Takla Group - Witch Lake Fm.
  - Monzonite, monzodiorite
  - Andesite, trachyte and latite flows and fragmentals

Key:
- Geology:
  - Tertiary Sediments
  - Early Tertiary volcanic and sedimentary rocks
  - Late Triassic - Early Jurassic Takla Group - Witch Lake Fm.
  - Monzonite, monzodiorite
  - Andesite, trachyte and latite flows and fragmentals
Key:
Geology:
Lower Jurassic Ashcroft Fm.
Argillite, greywacke, wacke and conglomerate turbidites
Late Triassic Mount Polley Igneous Complex (205 Ma)
Porphyritic syenite to monzonite, diorite and hydrothermal and magmatic breccias
Middle to Late Triassic Nicola Group
Basalt, latite, volcanic breccias and tuffaceous and tuffaceous
Key:
Geology:
Eocene Kamloops Group
- Mudstone, siltstone, shale and fine clastic rocks
- Volcanic, volcaniclastic and sedimentary rocks
Late Triassic - Early Jurassic Intrusives
- Cherry Creek Pluton
- Iron Mask Pluton
Late Triassic Nicola Group
- Volcanic, volcaniclastic and sedimentary rocks

Kamloops Lake
Afton (Underground operations)
Afton (Open pit)
Wood Occurrence
Biotite-feldspar gneiss intruded by massive granodiorite

Interbedded black argillite, siltstone and sandstone; minor limestone beds

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

Eocene

Princeton Group
Undifferentiated mafic to felsic, alkalic volcanic flows; aphyric to porphyritic, massive to volcanioclastic; minor clastic sediments

Middle-Late Jurassic

Biotite-feldspar gneiss intruded by massive granodiorite

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 volcanioclastic; minor clastic sediments

Middle-Late Jurassic
Biotite-feldspar gneiss intruded by massive granodiorite

Middle to Upper Triassic
Copper Mountain Intrusions

Permian or Triassic
Eastgate-Whipsaw Metamorphic Belt

Mix of metavolcanic and metavolcaniclastic rocks

Amphibolite unit
Quartz-feldspar quartz schist unit
Mixed metamorphic-metasedimentary unit

Microdiorite
Pyroxene-hornblende diorite, monzonite (Copper Mountain Stock); pyroxene-biotite diorite (Voigt Stock)
Massive to schistose pyroxenite
Undifferentiated metavolcanics and metavolcaniclastics
Interbedded black argillite, siltstone and sandstone; minor tuffstone beds
Legend
- Cu Mt (Potassic)
- Ingerbelle Pit
- Afton (Potassic)
- Afton, (Au in carbonate vein)
- MtP Au in bornite
- MtP Au in Chalcopyrite
- Mtp Au association unknown
- MtM 001 (Potassic)
- MtM 002B (Propylitic)
- MtM 003 (Potassic)
- King Richard Ck
- King Richard Ck Pd>LOD
- Cherry Ck
- Cherry Ck Pd>LOD
- Cherry Ck Hg> 1%
Propylitic hosted: current study
Potassic hosted: current study
Bn hosted Arif and Baker (2004)
'Free' Au Arif and Baker (2004)


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

Table 4. Numbers of grains in which each inclusion species was observed. Key: Mineral abbreviations as per Table 3 plus: Asp = Arsenopyrite (FeAsS), Cc = Chalocite (CuS), Cob = Cobaltite (CoAsS), Cn = Cinnabar (HgS), Gb = unconfirmed Pb-Bi sulphide, Hs = Hessite (Ag2Te), Ger = Gersdorffite (NiAsS), Lo = Loellingite (FeAs2), Mo = Molybdenite (MoS), PdTe = unconfirmed Pd telluride, PdSbAs = unidentified Pd arseno-antimonide, Ptz = Petzite (Ag3AuTe2), Spy = Sperrylite (PtAs2), St = Stibiopaladinitic (Pd5Sb2). 

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

Table 6. Comparison of Pd, Pt and Au contents and mineralogy of flotation concentrates, with microchemical signatures of placer gold for various localities worldwide. 1 = Economou-Eliopolous (2005); 2 = McFall et al. (2016); 3 = Pašava et al. (2010); 4 = Micko et al. (2014); 5 = LeFort et al. (2011); 6 = Pass et al. (2014); 7 = Nixon et al. (2004a); 8 = Garagan, (2014); 9 = Hanley and Mackenzie, (2009). FC= flotation concentrate, A = alkalic, CA = calc-alkalic, KCA = high-K calc-alkalic, NR= not recorded, Mineral abbreviations as per table 4 plus, Tel= telargpalite (Pd,Ag)3Te, So= sopeiche Ag,Pd3Te4, Mon= moncheite, (Pt,Pd)(Te, Bi)2 MeTel= merenskyite, (PdTe2) Mer= mertieite, Pd3(Sb,As)3.
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<thead>
<tr>
<th>Location</th>
<th>Deposit</th>
<th>Class</th>
<th>Alloy analyses</th>
<th>Major findings</th>
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<tr>
<td>Circle City¹</td>
<td>Au-Mo</td>
<td>CA</td>
<td>Au, Ag, Cu</td>
<td>Ag increases with decreasing temperature</td>
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<tr>
<td>Santo Tomas II²</td>
<td>Cu-Au</td>
<td>CA</td>
<td>Au, Ag, Cu</td>
<td>Ag content of Bn-hosted Au (potassic zone) &lt;&lt; than that hosted in Cpy, (potassic and propylitic zones)</td>
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<td>Grasberg³</td>
<td>Cu-Au</td>
<td>KCA</td>
<td>Au, Ag, Cu, Pd</td>
<td>Pd bearing alloys in late stage veins only. Ag values lower than in other studies</td>
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<td>Cerro Casale⁴</td>
<td>Cu-Au</td>
<td>CA</td>
<td>Au, Ag, Cu</td>
<td>Ag in potassic hosted Au higher than in sericitic (phylllic) veins</td>
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<tr>
<td>Batu Hijau³</td>
<td>Cu-Au</td>
<td>CA</td>
<td>Au, Ag, Cu</td>
<td>All potassic phase: Ag in Bn hosted alloy &lt; Ag in Cpy hosted, but Cu broadly equivalent. Cu of Q-hosted Au alloy lower than in sulphides</td>
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<tr>
<td>Pebble⁶</td>
<td>Cu-Au</td>
<td>CA</td>
<td>Au, Ag</td>
<td>Ag content of Au in potassic zone &gt;&gt; than that formed in late stage veins</td>
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<td>Tonnage</td>
<td>Sample ID</td>
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<td>Northing</td>
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### Table 3A. Hypogene environments.

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### Table 3B. Placer environments.

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42
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<td>Ok Tedi</td>
<td>KCA</td>
<td>980</td>
<td>24</td>
<td>28,000</td>
<td>NR</td>
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<tr>
<td><strong>Indonesia</strong></td>
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<tr>
<td>Grasberg</td>
<td>KCA</td>
<td>58</td>
<td>15</td>
<td>18,000</td>
<td>Yes, cited as source of Pd-rich Au</td>
<td>NR</td>
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<td><strong>Malaysia</strong></td>
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<tr>
<td>Mamut</td>
<td>KCA</td>
<td>1400</td>
<td>470</td>
<td>15,200</td>
<td>Me¹</td>
<td></td>
<td></td>
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<td><strong>Philippines</strong></td>
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</tr>
<tr>
<td>Santo Tomas II</td>
<td></td>
<td>330</td>
<td>67</td>
<td>10</td>
<td>Me¹, ko¹, mon¹</td>
<td>NR</td>
<td></td>
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<tr>
<td><strong>Uzbekistan</strong></td>
<td></td>
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</tr>
<tr>
<td>Kalmakyr¹</td>
<td>A</td>
<td>55²*</td>
<td>5.5*</td>
<td>4.1*</td>
<td>In Cpy</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td><strong>Canada (BC)</strong></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Galore Ck</td>
<td>A</td>
<td>1300</td>
<td>80</td>
<td>64,000</td>
<td>Yes but maybe be related to change in mineralization regime from Au to Cu⁴</td>
<td>No local placer claims</td>
<td></td>
</tr>
<tr>
<td>Mt Milligan</td>
<td>A</td>
<td>6,300</td>
<td>110</td>
<td>18,500</td>
<td>Tem, Me, Mer</td>
<td>Sub-epithermal Au-PGE-bearing⁵</td>
<td>See Figure 11</td>
</tr>
<tr>
<td>Mt Polley</td>
<td>A</td>
<td>320</td>
<td>33</td>
<td>23,600</td>
<td>Yes, PGM not recorded Au present⁶</td>
<td>Poorly developed local drainage</td>
<td></td>
</tr>
<tr>
<td>Copper Mountain</td>
<td>A</td>
<td>3250</td>
<td>50</td>
<td>4,200</td>
<td>Me, Mer, Tem</td>
<td>Distal Cu- Au-PGE bearing²</td>
<td>See figure 11</td>
</tr>
<tr>
<td>Afton</td>
<td>A</td>
<td>130</td>
<td>-</td>
<td>1200</td>
<td>Pd-rich Py³</td>
<td>Carbonate veins with cpy Au association⁸</td>
<td>See figure 11</td>
</tr>
</tbody>
</table>
Subepithermal veins: native Au associated with Pd-Hg

Propylitic

Potassic

Cu-orebody: native Au occurs as c. 10-30µm exsolved blebs

Erosional products pass into fluvial system

Uplift and erosion

Detrital gold grains show size and compositions

PdHg telluride
Highlights

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