Detrital gold Grains as Indicators of Alkalic Copper-Gold Porphyry Mineralization

by Robert J Chapman and Thomas J. Mileham
Keywords: alkalic porphyries, placer gold, gold compositions, microchemical characterization

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Cover photo: Placer gold grains, Tranquille Creek, near Kamloops
Executive Summary

The use of gold as a pathfinder for alkalic porphyries has been compromised by the potential for a single heavy mineral concentrate sample to contain gold particles derived from different source styles of mineralization. This report describes compositional studies of gold particles recovered from hypogene mineralization in four alkalic porphyries, and samples of local placer expressions. Gold formed in mineralization associated with the potassic alteration zone is compositionally distinctive, but too small to be collected by standard field techniques. The placer expression of alkalic porphyries comprises grains formed in the later stages of the magmatic hydrothermal system, which exhibit a distinctive copper-mercury enrichment in the alloy coupled with sporadic but ubiquitous palladium signature in both alloy and the suite of mineral inclusions. Consequently, populations of gold grains derived from alkalic porphyries may be distinguished from those originating from orogenic or calc-alkaline related hydrothermal mineralization.
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Abstract

Populations of gold grains collected from hypogene and placer environments at four alkali porphyries in British Columbia have been characterized in terms of their alloy composition (Au, Ag, Cu, Hg, and Pd) and the suite of mineral inclusions revealed in polished section. The synthesis of these data sets has generated a 'microchemical signature' with the ultimate aim of generating a generic compositional template by which other such grains may be recognised during exploration.

Collation of all data sets has facilitated the construction of a compositional template of detrital gold from generic deposit types, which co-exist in the northern Cordillera. Gold grains from alkalic porphyry environments comprise a gold-silver alloy which exhibit higher copper and mercury contents than populations of grains from orogenic mineralization. Comparable data sets describing gold grains from calc-alkaline porphyries in the Yukon suggest that the mercury signature is far stronger in gold from alkalic porphyry systems. Palladium was identified both as a minor alloy component and as palladium-bearing inclusions in gold from alkalic porphyries and these features form a very useful discriminant.

Study of gold grains from in-situ environments has shown that the tiny grains of copper-rich gold alloy formed in the potassic zone are in general too small to be collected by panning methods. Alloy signatures of these tiny grains are generally distinct from proximal placer gold, whose composition is more similar to gold grains hosted in propylitic alteration. Consequently, the use of gold as a PIM is dependent upon an understanding of the compositional nature of gold formed in environments prevalent later in the evolution of the porphyry (or epithermal) systems and their relationship to the target mineralization.
Introduction

The application of indicator methods to exploration for concealed porphyry deposits has become increasingly sophisticated in recent years. Initial studies focused on the suite of rock forming minerals (e.g. magnetite, titanite, garnets and apatite) liberated directly from porphyries in arid regions, and the stable secondary minerals formed from primary sulfides in the associated supergene environment (Averill, 2011). More recently, alkalic copper-gold porphyries in British Columbia have become the focus of sustained study as a consequence of their potential value and likely location, within low lying areas under Quaternary cover. The Porphyry Indicator Minerals (PIMs) project at the Mineral Deposit Research Unit (MDRU) of the University of British Columbia (UBC) has investigated the trace element chemistry of various resistate minerals to elucidate their origins and potential significance in the context of porphyry emplacement and subsequent hydrothermal alteration. Cathodoluminescence studies of apatite undertaken by Bouzari et al. (2010) revealed the hydrothermal alteration history of specific particles. Celis et al. (2014) and Pisiak et al. (2014) examined potential indicator minerals in terms of their origins within the alteration zones of alkalic porphyry systems and correlated trace element chemistry and textures of magnetite and titanite to the prevailing chemistry of the evolving porphyry system. Plouffe et al. (2013) recorded the presence of particulate gold-in-till samples from the environs of Mount Polley, but also noted that the large placer deposit of the Bullion Pit was stratigraphically below the glacial deposits, and hence gold grains from several sources could be present in recent surficial sediments.

The potential to discriminate between native gold originating from different styles of mineralization on the basis of alloy composition was proposed by Morrison et al. (1990) who provided typical compositions of binary gold-silver alloys associated with different styles of gold mineralization. Gammons and Williams-Jones (1995) showed that the composition of binary gold-silver 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 when the model for gold emplacement is understood. The study of gold grains derived from porphyry systems presents some challenges over and above those normally associated with the characterization of grains from single episodes of hydrothermal activity, principally because the term ‘porphyry mineralization’ encompasses a number of temporally and spatially distinct hydrothermal systems, commonly classified by their alteration assemblage. Consequently, the erosional products of porphyry mineralization could be expected to contain gold grains whose various compositions reflect mineralizing conditions at specific points in the evolution of the system. Interpreting the compositions of detrital grains in terms of the source mineralization demands an appreciation of the potential signatures of gold formed in the different stages of porphyry evolution.

Early studies of the compositions of placer gold grains focussed on their silver content, but sometimes involved minor alloying elements such as mercury (e.g. Knight et al., 1999). More sophisticated compositional studies of placer-lode relationships have characterized populations of gold grains through correlation of the alloy composition the suite of mineral inclusions revealed within polished section. Synthesis of alloy and inclusion data to generate a ‘microchemical signature’ permits interrogation of a population to identify multiple sources, (e.g. Chapman et al., 2000, Chapman et al., 2010a and b, Chapman et al., submitted). In the main, these studies have focussed on detrital gold grains derived from orogenic mineralization, and relatively few studies have focussed on the signatures of gold formed in...
magmatic-hydrothermal systems. Cuddy and Kessler (1982) measured silver contents in hypogene gold grains from Bell and Granisle (Central BC) and noted differences in hypogene mineralization, but not gold composition associated with overprinting structurally controlled phyllic alteration. Antweiler and Campbell (1977) suggested a relationship between copper content of gold alloy and temperature of formation based on the correlation of spatial distribution with composition for detrital gold grains collected around the Circle City molybdenum-gold porphyry.

Potter and Styles (2003) differentiated between detrital gold formed in skarns and that presumed to originate in intrusion-related veins on the basis of microchemical signatures of placer gold grains. Wrighton (2013) and Chapman et al. (2014) compared compositional signatures (comprising alloy analyses of Au, Ag, Cu, Hg ±Pd together with mineral inclusion suites) of gold grains from calc-alkaline porphyry systems in the Yukon with those of their placer expressions. Most recently, Chapman et al. (in press) correlated microchemical signatures of eluvial and placer gold from porphyry-epithermal mineralization at Klaza, Yukon with signatures of hypogene gold grains to establish the major contributing sources to the surrounding economic placers.

Notwithstanding these contributions there has been to date no systematic study of the composition of particulate gold formed in 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 in the recognition of the distinctive geochemical signature of alkalic porphyry systems. Thompson et al. (2002) suggested that the apparent enrichment of palladium in alkalic systems may be a consequence of magma evolution and/or enhanced transport capacity in an oxidized magma. The current study sought to establish whether such generic features manifest in a distinctive microchemical signature of the gold, and if so whether these features were identifiable in detrital gold grains. The overall aim of the work is to establish whether gold grain characterization has value to inform exploration reconnaissance in complex geological terranes where alkalic porphyry mineralization is the target, but where different source styles of gold may contribute to the placer inventory.

Calc-alkali and alkali porphyries

Alkalic porphyry systems are distinguished from their calc-alkalic counterparts, (previously described by Lowell and Guilbert (1970)) by

i. An association of alkaline igneous rocks,
ii. A metal signature of Cu-Au-Ag with no distinctive Mo phase, and
iii. Distinctive Na-rich and Ca-rich alteration assemblages, accompanied by magnetite-rich Potassic and propylitic alteration with a near absence of phyllic, argillic and advanced argillic (Lang et al. 1995).

Alkalic porphyry deposits are broadly distributed in Western Canada located within predominantly intra-oceanic arc sequences of British Columbia (Figure 1) and continue along the eastern Rocky Mountain front to Mexico. The general environs of alkalic porphyries remain consistent between deposits and generally all display temporal and compositional similarities with their host plutons (Lang et al., 1995). Although the present study focusses on the alkalic porphyries of British Columbia, a wider aspiration was to contribute to the development of exploration techniques that could be used globally.
**Figure 1.** Locations of alkali porphyries which formed the basis of this study.
Methodology

General approach

The overall approach of this study has been to investigate relationships between the compositional signatures and mineral associations of particulate gold in the hypogene environment with the mineralogy of gold grains collected from local drainage. In an ideal scenario this process would involve identification and analysis of large numbers of gold grains liberated directly from well-constrained and characterised hypogene ore. In practice collection of appropriate samples may be challenging, and often only partially effective, as hypogene gold grains are often very small, and isolation of gold grains of below 50 µm is inefficient using traditional gravity concentration methods. Preparation of the requisite number of thin sections provides a more robust approach, but generation of data describing populations of gold grains is both time consuming and expensive because of the general modest abundance of gold particles. In the present study, samples of hypogene ore from different mineralizing environments were collected from three operating mines in British Columbia (Table 1), and other samples permitted consideration of the Afton deposit. Polished sections were prepared and bulk samples were crushed and ground to provide a sand sized feed to a Wilfley Table, in an attempt to obtain larger populations of gold grains for analysis.

The study of eluvial and placer gold grains collected from the surficial environment provides an additional methodology to characterize in-situ mineralization. In this approach two important criteria must be considered. Firstly, it is necessary to establish that the signature of hypogene grains is unmodified in the surface environment. In practice this is achieved during the characterization process through inspection of sections of gold grains. The subject of gold grain modification in the surficial environment in the context of gold grain characterization is discussed in detail in Chapman et al. (2012) and the reader is referred to that text. Secondly, in the case of samples of placer gold, mobility of detrital material in the surficial environment through either glacial or fluvial action can generate populations of grains originating from multiple sources. Nevertheless, some placer populations may be used to inform the nature of proximal source mineralization if geomorphological considerations permit. For example, in the unglaciated environment of the Klondike, placer samples collected in drainage headwaters frequently comprised gold particles whose rough morphology indicated very limited transport (Chapman et al., 2010a).

Sample collection and preparation

Ore samples of around 20kg were collected from different geological settings within the Mount Milligan, Mount Polley and Copper Mountain complexes (Figure 2–5 and Table 2). Polished sections and blocks were prepared from some of this material and the remainder was crushed in two stages using a jaw crusher and disc mill at UBC, Vancouver. The sand-sized product was processed using a Wilfley shaking table and the concentrate retained for hand panning to isolate gold grains. Not all ore samples yielded particulate gold. In addition, polished sections were prepared from samples of ore from the Afton Mine and the Ingerbelle Pit, Copper Mountain, obtained from the existing research collection at the University of Leeds. Samples of placer gold were obtained from placer miners, (e.g. Whipsaw Creek, near Copper Mountain), some were collected in historical placer mining areas (e.g. Tranquille Creek, in the Afton area) and others were collected from drainages which although not mined are in the proximity of in situ mineralization, (e.g. Cherry Creek, near Afton). Collection of
Table 1. Descriptions of samples which form the basis of this study.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Grade/tonnage</th>
<th>Sample ID</th>
<th>Easting's</th>
<th>Northing</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mount Milligan¹</td>
<td></td>
<td>MtM 001</td>
<td>434363</td>
<td>610938</td>
<td>Margins of the MBX stock</td>
</tr>
<tr>
<td></td>
<td>542.1Mt of 0.20% Cu and 0.355 g/t Au²</td>
<td>MtM 002a</td>
<td>434572</td>
<td>610930</td>
<td>Polymetallic Quartz-Calcite veins adjacent to the MBX stock</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MtM 002b</td>
<td>434572</td>
<td>610930</td>
<td>Latite volcanics exhibiting propylitic and potassic alteration assemblages</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MtM 003</td>
<td>434698</td>
<td>610946</td>
<td>Pyrite rich associated with propylitic alteration assemblage</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MtM 005</td>
<td>434927</td>
<td>610904</td>
<td>Oxidized samples panned from the ‘66’ Zone.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MtM 006</td>
<td>434927</td>
<td>610904</td>
<td>Non-weathered sample of ‘66’ Zone volcanics</td>
</tr>
<tr>
<td>Mount Polley³</td>
<td>226 x 10⁷T Cu, 21.5 T Au, 21.5T Ag⁴</td>
<td>MtP 002</td>
<td>591942</td>
<td>582282</td>
<td>Northwest face of the Springer pit</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MtP 003</td>
<td>592204</td>
<td>582294</td>
<td>Hydrothermal breccia sample, Cariboo pit</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MtP 004</td>
<td>591942</td>
<td>582282</td>
<td>Sample from the WX Zone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MtP 005</td>
<td>Unknown</td>
<td></td>
<td>Hydrothermal breccia from underground operations. Stockpile in Wight pit.</td>
</tr>
<tr>
<td>Afton Open Pit⁵</td>
<td>22 Mt of 0.91% Cu, 0.67g/t Au⁶</td>
<td>EMK 224</td>
<td>Unknown</td>
<td></td>
<td>Leeds University Specimen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EMK 230</td>
<td>Unknown</td>
<td></td>
<td>Leeds University Specimen</td>
</tr>
<tr>
<td>Copper Mountain⁷</td>
<td>1.7 billion pounds of Cu, 700,000 ounces of Au and 9 million ounces of Ag⁸</td>
<td>CuMtn 001</td>
<td>680814</td>
<td>546823</td>
<td>East-trending dilatant magnetite veins running through the floor of the Virginia pit.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CuMtn 002</td>
<td>679873</td>
<td>546665</td>
<td>Bornite, chalcopyrite and pyrite disseminations within Nicola Group Volcanics, N. wall of Pit 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CuMtn 003</td>
<td>679873</td>
<td>546665</td>
<td>Late stage calcite veins, with pyrite disseminations, N. wall of Pit 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EMK 201</td>
<td>Unknown</td>
<td></td>
<td>Leeds University Specimen Ingerbelle Pit</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EMK 203</td>
<td>Unknown</td>
<td></td>
<td>Leeds University Specimen Ingerbelle Pit</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EMK 205</td>
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<td></td>
<td>Leeds University Specimen Ingerbelle Pit</td>
</tr>
<tr>
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<td></td>
<td>EMK 206</td>
<td>Unknown</td>
<td></td>
<td>Leeds University Specimen Ingerbelle Pit</td>
</tr>
</tbody>
</table>

Figure 2. Sample localities around Afton.
Figure 3. Sample localities around Mt Polley.
Figure 4. Sample localities around Mt Milligan
Figure 5. Sample localities around Copper Mountain.
Table 2. Characteristics of gold grains from hypogene, eluvial and placer environments.

2A: Hypogene environments.

<table>
<thead>
<tr>
<th>Location</th>
<th>Au grains</th>
<th>Alteration assemblage</th>
<th>Alteration</th>
<th>Ore mineral association</th>
<th>Hg</th>
<th>Cu</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
<td></td>
<td>M</td>
<td>C</td>
</tr>
<tr>
<td>Mt Milligan</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MtM 1</td>
<td>8 (b)</td>
<td>Ksp, Bio, Mag</td>
<td>K</td>
<td>Py, Cpy, Bn, Tet</td>
<td>0.4</td>
<td>100</td>
<td>0.3</td>
</tr>
<tr>
<td>MtM 2b</td>
<td>2 (f)</td>
<td></td>
<td></td>
<td>Py, Cpy, Tet, Gn</td>
<td>1.0</td>
<td>100</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5 (b)</td>
<td>Ep, Al, Ca, Act</td>
<td>Pr</td>
<td>Py, Cpy</td>
<td></td>
<td></td>
<td>0.02</td>
</tr>
<tr>
<td>MtM 2P</td>
<td>5 (b)</td>
<td>Ksp, Bio, Mag</td>
<td>K</td>
<td>Py, Cpy</td>
<td>0.8</td>
<td>100</td>
<td>0.3</td>
</tr>
<tr>
<td>MtM 3</td>
<td>2 (f)</td>
<td></td>
<td></td>
<td>Py</td>
<td>0.6</td>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td>MtM 3</td>
<td>1 (b)</td>
<td>Ep, Al, Ca-Act</td>
<td>Pr</td>
<td>Py, Cpy</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Mt Polley</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MtP 3</td>
<td>1 (f)</td>
<td>Ksp, Bio, Mag, Alb, Chl, Ep</td>
<td>K</td>
<td>Na</td>
<td></td>
<td>1.3</td>
<td>100</td>
</tr>
<tr>
<td>MtP 4</td>
<td>1 (b)</td>
<td>Ksp, Bio, Mag, Alb, Chl, Ep</td>
<td>K</td>
<td>Na</td>
<td>Cpy, Sph</td>
<td>0.4</td>
<td>100</td>
</tr>
<tr>
<td>MtP 5</td>
<td>6 (f)</td>
<td></td>
<td></td>
<td>Cpy, Bn</td>
<td>0.6</td>
<td>93</td>
<td>5.5</td>
</tr>
<tr>
<td>MtP 5</td>
<td>8</td>
<td>Ksp, Bio, Mag, Alb</td>
<td>K</td>
<td>Cpy, Bn</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Copper Mountain</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuMt 1</td>
<td>1 (b)</td>
<td>Mag</td>
<td>Cpy</td>
<td>0.1</td>
<td>100</td>
<td>1.1</td>
<td>100</td>
</tr>
<tr>
<td>Cu Mt 2</td>
<td>2 (b, f)</td>
<td>Dio, Chl-Ep, Ksp, Bio, Mag, Ep, Chl</td>
<td>Na</td>
<td>K</td>
<td>Bn</td>
<td>0.4</td>
<td>100</td>
</tr>
<tr>
<td>EmK 201</td>
<td>1 (b)</td>
<td>An, Chl, Ep, Act, Pum</td>
<td>Pr</td>
<td>Py, Cpy</td>
<td>0.2</td>
<td>100</td>
<td>0.9</td>
</tr>
<tr>
<td>EmK 203</td>
<td>1 (b)</td>
<td>Ksp, Bio, Mag, Ep, Chl</td>
<td>K</td>
<td>Pr</td>
<td>0.4</td>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td>Afton</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EmK 230</td>
<td>4 (b)</td>
<td>Ksp, Mag, Bio</td>
<td>K</td>
<td>Bn, Cpy, Tem</td>
<td>1.0</td>
<td>100</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Abbreviations: '(b)' = grains observed in polished blocks, '(f)' = free gold 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, Gn = galena, Ep = epidote, Ksp = orthoclase, Mag = magnetite, Po = pyrrhotite, Py = pyrite, Pum = pumpellyite, Sph = sphalerite, Tet = tetrahedrite, Tem = temagamite.
### 2B: Placer environments.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Drainage</th>
<th>Location</th>
<th>No</th>
<th>Hg M</th>
<th>Hg C</th>
<th>Cu M</th>
<th>Cu C</th>
<th>Pd M</th>
<th>Pd C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt Milligan</td>
<td>King Richard Ck</td>
<td>434508</td>
<td>6108587</td>
<td>40</td>
<td>0.70</td>
<td>97.5</td>
<td>2.4</td>
<td>95.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Copper Mountain</td>
<td>Similkameen R</td>
<td>678215</td>
<td>546850</td>
<td>248</td>
<td>2.68</td>
<td>73.8</td>
<td>5.20</td>
<td>89.1</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>Friday Ck</td>
<td>677785</td>
<td>546385</td>
<td>77</td>
<td>1.07</td>
<td>97.4</td>
<td>2.67</td>
<td>100</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>Whipsaw Ck</td>
<td>677057</td>
<td>547110</td>
<td>204</td>
<td>3.12</td>
<td>88.2</td>
<td>3.77</td>
<td>99.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Afton</td>
<td>Cherry Ck</td>
<td>434580</td>
<td>561587</td>
<td>59</td>
<td>0.9</td>
<td>94.9</td>
<td>3.3</td>
<td>30.5</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Tranquille Ck</td>
<td>670719</td>
<td>563891</td>
<td>131</td>
<td>0.91</td>
<td>45.8</td>
<td>4.9</td>
<td>100</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Abbreviations: ‘(b)’ = grains observed in polished blocks, ‘(f)’ = free gold 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, Gn = galena, Ep = epidote, Ksp = orthoclase, Mag = magnetite, Po = pyrrhotite, Py = pyrite, Pum = pumpellyite, Sph = sphalerite, Tet = tetrahedrite, Tem = temagamite.
A 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 sluicing of fluvial gravel. Gold grains were recovered from sluice concentrates by hand panning.

**Analytical**

All gold grains were mounted according to size as described by Chapman et al. (2000) (Figure 6). The extreme small size of some of the gold particles from both hypogene ore and eluvial samples necessitated the design of a new polishing technique specifically for tiny (30-50µm) particles. This involved introducing the grains into small pools of resin placed on a glass slide. The gold grains were revealed 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 using a Jeol 8230 Superprobe. Limits of detection were as follows: Cu: 0.02%, Hg: 0.06%, Pd: 0.02%, Ag: 0.03%. All analyses are reported in mass%. Mineral inclusions in polished sections were identified through inspection in BSE imaging using the EDS facility of an FEI Quanta 650 FEG-ESEM SEM.

**Data presentation and Results**

This study has considered the significance of the minor alloying elements silver, copper, mercury and palladium in gold alloy. Silver was recorded in virtually all gold particles studied but other elements were not always present above LOD. Table 2 records the percentage of each sample that contained each element to above detection limit together with the maximum value recorded. This dual approach is useful to establish both the overall abundance of a minor metal, whilst acknowledging the variation in concentration range.

The silver content of a population of grains is evaluated through the use of cumulative plots in which each grain is expressed as a percentile, (e.g. Figure 7). This approach allows direct comparisons of populations comprising different numbers of grains. The significance of other minor alloying elements has been established either simply by their presence (e.g. palladium) or through their co-variance (e.g. copper-silver relationships). In this study, alloy compositions have been investigated using cumulative plots, which provide a clear indication of the similarity of different populations, and binary Ag vs Cu plots which have proven effective for identifying different compositional fields and which can be augmented by addition of points showing host alloys for specific inclusions or high concentrations of either mercury or palladium.

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. Where possible, this problem can be mitigated by collection of large populations of gold grains, nevertheless in some cases the volume of data available for study is smaller than the ideal. 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 approach to characterize data sets. Thirdly the presence of some
Figure 6. Examples of gold grains (white) in situ in potassic alteration assemblages: A. Mt Polley, B: Afton, C: Copper Mountain, D: Mount Milligan
Figure 7. Compositions of gold grains from the Afton area Study. A: Cumulative Ag plot comparing placer and hypogene gold, B: Co-variance of Cu and Ag for hypogene and lode samples.
inclusion species may be diagnostic for a particular mineralizing environment, (e.g. palladium-bearing minerals) whereas other minerals such as pyrite are commonly encountered in gold from a range of mineralizing environments. Mineral suites are characterized for individual populations by establishing the proportion of the grains that exhibit inclusions of a specific mineral.

Results

Characterization of in situ mineralization

The localities at which ore samples were collected from the alkalic porphyry systems at Mt Milligan, Mt Polley, and Copper Mountain are provided in Table 1, and a summary description of the samples including associated ore mineralogy is included in Table 2A. Illustrations of gold grains in the hypogene environment (potassic zone) are provided in Figure 9, which show a range of gold-sulphide associations.

Alloy variation

The co-variance of silver and copper of the gold particles observed in polished section or recovered from bulk ore samples illustrated in Figure 10. Gold grains from the various potassic zones exhibited a range of silver contents, and the copper contents appeared to vary independently of silver. The highest copper values were recorded in two small gold grains hosted by bornite. Arif and Baker (2004) also recorded the highest copper in gold alloy within bornite. Sample suite Mt P 005 from Mt Polley yielded analyses which suggest two discrete compositional fields for gold formed within the potassic zone, which differ according to their copper content. This may be a consequence of the specific mineral association of the gold grains analysed. The small data sets available for consideration overall suggests that the gold particles hosted by bornite yield the highest copper values with those within chalcopyrite and pyrite yielding lower copper values, typically, less than 0.5%.

The gold grains from zones of propylitic alteration form a tight compositional field (with two exceptions) and contain less silver and copper than their potassic-hosted counterparts. One gold grain containing 1.2% Cu and 13% Ag was recovered from the magnetite-chalcopyrite vein at Copper Mountain.

Mineral Inclusions

A few gold grains liberated from in situ mineralization contained inclusions of ore minerals, and two such grains are illustrated in Figure 8, together with other examples of inclusions observed within placer grains. The similarity in the nature of the inclusions in both hypogene and placer gold underlines the assertion that these features are hypogene in origin and persist into the placer environment.

Characterization of Placer samples

Morphology

Images of the placer grains from the Copper Mountain and Afton localities are provided in Figure 9. The sample from King Richard Creek comprised very small grains and an image was not recorded. Gold grains with different morphological characteristics are present in each
Figure 8. Examples of mineral inclusions, A: Py in hypogene gold from Mt Milligan, B: Chalcopyrite in hypogene gold from Mt Polley, C: Bornite and chalcopyrite inclusions in placer grains from the Similkameen River, D and E temagamite inclusions in placer gold from the Similkameen River and Cherry Creek respectively. F: Placer grain from the Similkameen River showing bornite inclusions in gold-rich alloy and temagamite inclusions in later Pd and Hg-rich alloy. Figs A, B, F: BSE images, Figs C, D, E: SE images.
Figure 9. Examples of placer gold grains and textures. A: Whipsaw Ck, B: Friday Ck, C: Cherry Ck, D: Tranquille Ck. Scale bar has 1mm divisions. Generalized geology of the study area, showing sample locations.
Figure 10. Compositions of gold grains from the Afton area Study. A: Cumulative Ag plot comparing placer and hypogene gold, B: Co-variance of Cu and Ag for hypogene and lode samples.
of the populations, although the Whipsaw Creek sample comprised grains which were predominantly waterworn.

Alloy compositions

Figure 10 compares the alloy compositions of gold grains from Tranquille and Cherry creeks near Afton. The population from Cherry Creek comprises grains between 0 and 27% silver, but the sample from Tranquille Creek shows a wider range of silver contents, with around 16% of the grains containing silver to >27%, to a maximum of 47%. Covariance of silver and copper is similar for both populations (Figure 10B), although two grains from Tranquille Creek exhibit copper contents of over 20% (not shown on Figure 10B).

The silver and copper contents of the placer grains from King Richard Creek adjacent to Mount Milligan are shown on Figure 11. The grains exhibit a range of silver contents between 0 and 55%, and the copper contents are almost always above the detection limit of 0.02%. A few grains contain mercury to above 1% (Table 2A) but there is no co variation with either silver or copper. Palladium was recorded to a maximum of 0.3% but only a small proportion of the population exhibited palladium to >LOD. The compositions of gold grains from propylitic alteration zones corresponds (with one exception) to those of the placer grains, whilst gold form the potassic environment forms a separate compositional field of higher copper and silver. Figure 12 shows a remarkable consistency in the silver ranges of the three placer samples from the vicinity of Copper Mountain. Consideration of the co-variance of copper and silver (Figure 12B) suggests two compositional fields both of which show a general inverse relationship between copper and silver. Figures 9 C and 9D examine co variance of copper and silver with other features such as elevated palladium, mercury and incidence of inclusions. High mercury grains are more abundant in the lower silver group, whereas palladium-rich grains are clustered (though not exclusively) in the higher copper grains. Bornite and chalcopyrite were observed in both populations.

Alloy compositions of placer populations have been represented in two ways: using cumulative plots to compare the silver contents of different populations and using copper-silver binary plots which may indicate different sub populations, especially when specific grains containing elevated mercury, palladium or particular inclusion species are indicated

Heterogeneity of alloy in Gold grains

Several studies have noted heterogeneity in the Gold alloy of both detrital and hypogene gold particles. The phenomenon of the gold-enriched rim, observed in placer grains worldwide (see Figure 10A for an example) was discussed by Groen et al. (1990) and ascribed to surficial processes. Leake et al. (1992) reported heterogeneity both in terms of silver and gold zones and films in different gold grains from various localities in the British Isles, and very similar features were reported by Chapman et al. (2010a) in hypogene gold from orogenic mineralization in the Klondike. In the present study, the overwhelming majority of gold grains comprised homogenous alloys, but where heterogeneity exists it most commonly takes the form of silver-rich alloy postdating relatively gold-rich alloy, (Figure 10A-D). One placer grain from Cherry Creek contained native copper postdating gold alloy, (Figure 10E)

Mineral inclusions

The inclusions observed within polished sections of the placer gold grains are described in Table 3. Figure 8 shows examples of inclusions in both placer and hypogene gold grains
Figure 11. Co variance of Cu and Ag for hypogene and placer samples from Mt. Milligan. In general the gold grains hosted in potassic alteration assemblages show higher Ag and Cu than the grains from a propylitic host. Detrital grains from King Richard Ck are more similar to the propylitic gold signature.
Figure 12. Characterization of hypogene and placer grains from The Copper Mountain area. A and B: Ag contents and Cu-Ag variation of placer and hypogene gold. C data from Fig. 9B indicating Hg and Pd-bearing grains, D: Same, but indicating correlation of inclusion species with alloy host for placers from Similkameen River, Friday and Whipsaw creeks.
Table 3. Inclusion species recorded in placer gold grains.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Inclusions observed in polished section</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Py</td>
</tr>
<tr>
<td>Mount Milligan</td>
<td></td>
</tr>
<tr>
<td>King Richard Ck</td>
<td>1</td>
</tr>
<tr>
<td>Afton</td>
<td></td>
</tr>
<tr>
<td>Cherry Ck</td>
<td>1</td>
</tr>
<tr>
<td>Tranquille Ck</td>
<td>4</td>
</tr>
<tr>
<td>Copper Mountain</td>
<td></td>
</tr>
<tr>
<td>Similkameen R.</td>
<td>4</td>
</tr>
<tr>
<td>Friday Ck</td>
<td>1</td>
</tr>
<tr>
<td>Whipsaw Ck</td>
<td>2</td>
</tr>
</tbody>
</table>

Key: Ac = Acanthite (Ag₂S), Apy = Arsenopyrite, Bn = Bornite, Carb = Carbonate, Ce = Cervellie (Ag₄TeS₂), Cc = Chalcocite, Cpy = Chalcopyrite, Cob = Cobaltite (Co₂S₂), Hes = Hessite (Ag₂Te), Ger = Gersdorffite (NiAs₂), Iso = Isomertieite (Pd₁₁Sb₂As₂), Kfs = K-Feldspar, Kol = Kolutskite, (PdTe), Lo = Lollingite (Fe₃S), Mo = Molybdenite, Nau = Naumannite (Ag₂Se), Ptz = Petzite (Ag₂AuTe₂), Py = Pyrite, Po = Pyrrhotite, Spy = Sperrylite (PtAs₂), Stp = Stibiopalladinite (Pd₃Sb₂), Tbi = tellurobismutite, (Bi₂S₃), Tem = Temagamite (Pd₃HgTe₃), Tet = Tetrahedrite ((Cu,Fe)₁₂Sb₄S₁₃), U = ullmanite (NiAs₂)
Some general observations may be made from the data presented in Table 3. Pyrite, and/or pyrrhotite are present in all samples. Chalcopyrite was commonly observed except in the sample from King Richard Creek, where only a small number of inclusions were observed. Bornite was observed in all the placer samples from the Copper Mountain area, but not at any other localities. Minerals containing both silver and tellurium were present in grains from most localities as were palladium-bearing minerals. Sulfarsenides were far more common in gold grains from the Similkameen River and Tranquille Creek than at other localities.

Figure 8F shows a link between inclusion species and alloy compositions. Bornite was coeval with the initial gold alloy (8.9% Ag, 6.2% Hg and 4.1% Pd) whereas inclusions of a palladium-antimony-arsenic mineral are centred within a later alloy containing 3.2% Ag, 27.8% Hg and 15.2% Pd.

**Characterization of gold formed in different alteration zones**

Kessler et al. (2002) suggested that the amount of gold present in a porphyry system is fixed by the degree of gold precipitation (or co precipitation with copper-iron sulfides) in the earliest high temperature phase of mineralization. Thereafter, gold may be remobilized and spatially redistributed according to the evolution of the system, although in some cases subsequent episodes of hydrothermal activity can augment the gold and silver budget, (e.g. Gregory et al., 2013). Whilst the relative importance of different alteration zones may vary between deposits, the conditions associated with each alteration styles are generic. Consequently, it is likely that gold formed in any particular alteration environment could exhibit a common range of signatures. The number of gold grains available for study was relatively small, but nevertheless some useful observations can be made.

**Potassic Zone**

Gammons and Williams-Jones (1995) noted that gold may be co-precipitated with copper-iron sulfides in the initial stages of porphyry mineralization even though the fluid is under saturated with respect to gold. Simon et al. (2000) established that the concentration of gold within bornite was approximately one order of magnitude greater than that in chalcopyrite and strongly dependent upon both temperature and deviations from the ideal bornite stoichiometry. These authors noted that whereas gold remains in solid solution in chalcopyrite, native gold forms along grain boundaries in bornite. The thin, synthetically produced gold grains reported by Simon et al. (2000) were 10 µm in length, which is a similar size to various gold grains identified in hypogene ore in the present study, (Figure 6). Kessler et al. (2002) report gold grains to 100µm formed in this way are a generic feature of porphyry mineralization, and these have subsequently been reported by Arif and Baker (2004) and Samellin (2011). This model of gold formation by exsolution is consistent with the observations made in the present study, where the gold-bornite association was commonly observed in hypogene ore (Figure 6) and the particle size of the gold was very small. It remains unclear whether gold may be precipitated from saturated solutions in the potassic zone as opposed to forming via the mechanism described above. If gold were to precipitate directly, the controls on alloy composition would be governed by the prevailing speciation, which is generally accepted to be a chloride complex, (e.g. Williams-Jones and Heinrich 2005).
Propylitic and Phyllic Zones

Williams-Jones and Heinrich (2005) assert that gold transport by thio-complexes assumes a greater importance in the later stages of porphyry evolution. It is generally accepted that in this environment silver is transported as the chloride complex, and consequently the generic controls on gold alloy composition are a function of temperature, \( (\text{Au/Ag})_{(\text{aq})} \), \( a\text{Cl}^-_{(\text{aq})} \), \( a\text{H}^+_{(\text{aq})} \) and \( a\text{H}_2\text{S}_{(\text{aq})} \) (Gammons and Williams-Jones, 1995). Irrespective of the conditions of mineralization, gold alloy would form through precipitation from a saturated solution (i.e. through a different mechanism that the gold formed in the copper-iron sulphides in the Potassic stage). It seems probable that a larger proportion of gold particles formed in this way are sufficiently massive to be concentrated in the fluvial environment post-liberation and erosion.

Gammons and Williams-Jones (1995) provide predictions for gold-silver alloy composition hydrothermal systems up to 400°C, and Gammons and Williams-Jones (1997) suggest that gold could be remobilized during overprinting of potassic zone mineralization by propylitic alteration. Consequently, the \( \text{Au/Ag}_{(\text{aq})} \) ratio would remain unchanged below saturation and persist until conditions favoured precipitation. At constant \( (\text{Au/Ag})_{(\text{aq})} \) the alloy formed through precipitation from a solution in which gold is transported as bisulfide is of lower silver content than for the corresponding chloride complex. However, within the propylitic zone the temperature is likely to be considerably cooler than during potassic alteration, and further evolution to phyllic conditions influenced by a pH change would also alter controls on \( \text{Au/Ag}_{(\text{alloy})} \). A fall in temperature acts to raise the silver content of the alloy, whereas the increased pH has the opposite effect (Gammons and Williams-Jones, 1995). Consequently, it is unlikely that specific silver contents of the alloy could find use as diagnostic markers for conditions of mineralization within propylitic and phyllic environments.

Porphyry epithermal transition

The retention of gold in solution during the later stages of porphyry development is a prerequisite for the subsequent formation of epithermal mineralization. Precipitation of gold alloy can occur for a variety of reasons in the epithermal environment, which has been correlated with potential high variation gold alloy composition (Morrison et al., 1990). In this study, it seems likely that the placer samples from Whipsaw Creek and Friday Creek could contain gold particles formed in environments distal to the parent intrusion. Whilst the overall signature of placer gold from Whipsaw and Friday Creeks is very similar to that of that from the Similkameen River, it is also possible that gold from chalcopyrite-pyrite-magnetite ±haematite veins reported by Stanley et al. (1995) to be both relatively gold-rich and peripheral provide a major contribution to the placer inventory. The presence of bornite inclusions in some detrital grains (Table 2B) suggests either a contribution from atypically large gold grains formed in the potassic alteration environment or the later bornite-chalcopyrite veins described by Stanley et al. (1995).

Implications of heterogeneous alloys

The evolution of porphyry systems commonly involves overprinting of previous alteration assemblages. New fluid regimes are unlikely to be in equilibrium with pre-existing gold alloys, and it might be expected that re-equilibration would occur. If this process progressed to completion, a homogeneous alloy would result, but partial re-equilibration would generate heterogeneous gold grains. Both hypogene and placer gold grains were examined to establish...
the nature of any grain heterogeneity. The overwhelming majority of gold grains were homogenous, irrespective of alloy composition. Figure 13 shows examples of heterogeneous grains, which all share the common alloy paragenesis of gold-rich gold followed by silver-rich gold. Figure 13 F shows bornite inclusions hosted in gold alloy containing 8.9% Ag and 6.2% Hg, and temagamite (Pd₃HgTe₃) inclusions in a later gold-poor alloy containing 25% Hg, 15% Pd and 3%Ag. The presence of both palladium and mercury in the early alloy phase suggests alteration of the original composition to generate higher palladium and mercury concentrations, by gold and silver replacement, rather than a late influx of an unrelated palladium and mercury-rich fluid. Figure 12C suggests that palladium may be present in gold grains of different genetic origins, and the identification of palladium-bearing minerals in hypogene ore in the potassic zone at Afton suggest that a reservoir of palladium is emplaced during potassic mineralization which, like gold, can be remobilized and concentrated during porphyry evolution.

Implications of concentrations of minor alloying metals

Whilst the controls on the silver content of gold alloy have been explored in terms of the prevailing mineralization environments (Gammons and Williams-Jones, 1995) there is a general lack of information to aid interpretation of the copper, mercury and palladium contents. Consequently the analysis of their significance is based on interpretation of empirical data rather than theoretical predictions. The range of copper concentrations reported in gold alloys formed in the potassic zone varies considerably, most values are less than 0.5% but concentrations of over 7% were recorded in some grains analysed by Arif and Baker (2004). These relatively high values may be a consequence of gold-silver-copper formation by the mechanism of exsolution from copper-iron sulphides as described above.

A limited amount of data is available which describes hypogene gold grains from propylitic alteration zones, but the data presented in Figure 10 suggests that their copper contents are lower than those associated with gold formed in the potassic zone. The general relationships between the hypogene and placer grains in terms of silver and copper (Figures 4, 7, 8, 9) also suggest a fall in copper content of gold alloy between the tiny gold grains formed in the potassic zone and those which accumulate in placers. At present, the controls on copper concentrations in gold-silver alloys formed in hydrothermal systems are not defined, but it is probable that the Cu/(Ag+Au)_(aq) ratio could be an influence, in the same way that Au/(Ag) influences gold-silver alloy composition, (Gammons and Williams-Jones, 1995). In general, the importance of copper decreases with the evolving porphyry system probably as a consequence of the precipitation of copper as chalcopyrite in propylitic and/or phyllic zones and the limited amount of Cl(aq) available to form copper complexes. A systematic reduction of copper content in the porphyry epithermal transition is reported at Klaza by Hart and Langdon (1997), and inferred by Antweiler and Campbell (1977) in their study of detrital gold particles from Circle City. Arif and Baker (2004) recorded far higher copper contents (commonly to 7%) in tiny bornite and chalcopyrite hosted grains in the potassic zone at Bata Haiju, and negligible copper and far lower silver values in the ‘free gold’ presumed to be remobilized, although detailed paragenetic information was not reported.

The interpretation of the presence and concentration of mercury in gold-silver alloys within all styles of gold mineralization has been previously discussed by Chapman et al. (2010a) but remains problematic. In the epithermal environment, mercury is often linked to the low temperature stage of mineralization, on account of the volatility of mercury metal (e.g. Hedenquist, 2000). The presence and concentration of mercury in gold-silver alloys observed
Figure 13. BSE images showing examples of alloy heterogeneity in placer gold grains: A: Tranquille Ck, (showing a small high gold rim) B: Similkameen R., C: Whipsaw, Ck, D, E Cherry Ck, F: Similkameen R. The darker alloy is Ag-rich in figures A-D. Figure E: native copper infilling cracks in pre-existing Gold. Figure F: two stages of Ag rich gold postdating gold-rich alloy which hosts inclusions of bornite (black).
in the present study appears independent of either other alloying metals or inclusion species. This absence of co-variance has been noted in orogenic mineralizing systems (Chapman et al. 2010a, Mackenzie and Craw, 2005). These authors concluded that whilst the fundamental controls on mercury incorporation into gold-silver alloy remained unclear, the high incidence of mercury-rich grains in some populations formed a useful empirical discriminant. This conclusion accords with the results of the present study, where the common presence of mercury to relatively high concentrations has formed a useful additional discriminant to identify gold grains derived from alkalic porphyry systems.

The identification of palladium as a minor alloy component in gold grains derived from Canadian alkalic porphyries is one of the important generic results of this study and in agreement with the observations of previous workers (e.g. Thompson et al., (2002); Nixon, (2003a,b); and Le Fort et al., (2011)), who also reported a clear PGE signature. A general observation was that distribution of palladium within the hypogene mineralization was heterogeneous, which accords with the reports of Rubin and Kyle (1997) who noted a strong correlation between gold, copper and palladium in the centre of the Grasberg copper-gold porphyry. In the present study palladium-bearing minerals have been observed in hypogene ore in the potassic zone at Afton, (isomerteite) and Copper Mountain (temagamite). Palladium could be remobilized from the first stage of mineralization into the late stage veins as proposed by Thompson et al. (2002) although Le Fort (2011) suggested only a hydrothermal pathway to the late stage veins at Mt Milligan. Fischl (2015) reported bornite-temagamite veins at Friday Creek, and it seems likely that these are also late and distal veins in which palladium is concentrated. It could be expected that the palladium-gold association would present in grains of different mineralogy according to their conditions of precipitation, and the data presented in Figure 9E which shows the presence of palladium-bearing grains and palladium minerals in a wide variety of grain compositions is consistent with this hypothesis.

Implications of specific Inclusions

A wide range of inclusion species was recorded, some of which provide insights into the mineralizing environment. The most important of these are discussed below.

Chalcopyrite was the most abundant inclusion species in the placer populations and was also observed in hypogene gold (Figure 8). Chalcopyrite may be present in potassic, propylitic and phyllic alteration zones and therefore it could be expected that the composition of any coeval gold would vary accordingly. The data presented in Figure 12 shows this to be the case. Bornite was only observed as an inclusion in placer gold from the Copper Mountain area, where late stage bornite-bearing veins have been recorded at several locations. Consequently, the bornite-gold association observed in hypogene ore in the potassic zone at Mt Milligan, Mt Polley and Afton is not replicated in the local placer expression.

Palladium-bearing inclusions are typically hosted by palladium-rich gold, and form an important generic marker of alkalic porphyry mineralization. A range of palladium-minerals has been recorded, both as discrete mineral grains in hypogene ore and as inclusions within gold grains. Palladium forms a wide range of mineral species with other elements such as mercury, antimony and tellurium which are also present within magmatic fluids and their derivatives, which accounts for the variation in palladium-bearing minerals observed in this study. Overall, identification of the presence of palladium in both inclusions and alloy is more important than the mineral speciation.
Pyrite and pyrrhotite are present in most placer populations, and are not particularly useful in themselves as diagnostic indicators of source mineralization type. Galena and sphalerite have been recorded as inclusions species in other studies of gold grain mineralogy, related to orogenic mineralization (e.g. Chapman et al. 2010a and b; Chapman et al. 2011) and epithermal mineralization (Chapman et al. submitted) but only galena was recorded during this study, and at a single locality. The importance of lead and zinc increases with the porphyry epithermal transition, such that inclusions could be expected to become more common in distal mineralizing environments. Similarly tellurium-bearing minerals assume greater importance in the epithermal environment. The efficient transport of volatile tellurium-bearing species results in the formation of hessite within low-sulfidation epithermal deposits, (Cooke and McPhail (1995) and Grundler et al. (2013)). Both these studies focus on minerals in the gold-silver-tellurium system, whereas cervelleite (Ag₄TeS) is more commonly observed as an inclusion species. Nevertheless it seems reasonable to ascribe the occurrence of both hessite and cervelleite inclusions to the same mechanism of tellurium transport, with speciation a function of the prevailing \( f_{Te} \). Consideration of the behaviour of antimony and arsenic in porphyry epithermal systems would also suggest that minerals containing these elements would assume a greater importance in the epithermal environment.

Copper sulfides are in general rarely encountered as inclusions, but in this study they form a major component of the inclusion suite in gold from Tranquille Creek. An association between chalcocite and elevated copper in the gold-silver alloy has been reported previously from very minor mineralization at two localities in Ireland, (Chapman et al. (2000) and Moles et al. (2013)). In both cases consideration of the local geology suggested a magmatic association.

**Integration of alloy and inclusion data**

Data sets obtained during the present study have been combined and summarized in Figure 14 in terms of the alloy compositions of gold grains, and their inclusion assemblage. A dual approach to describing alloy compositions has been adopted for copper and mercury because some gold grain populations contain a large subset of grains with one of these minor metals is consistently present just above LOD, whereas other populations contain grain with a smaller number >LOD but with much higher overall values. Cells have been colour coded to aid comparison with similar data sets relating to the Casino calc-alkalic porphyry, (Chapman et al., 2013) and three examples of regional data sets describing placer gold derived from orogenic sources. In addition, the data set describing placer gold from Tranquille Creek has been kept separate as the source remains unknown, and these data may be considered in terms of the generic signatures presented here (see following section).

Some clear signatures emerge for these data sets. Gold from the alkalic porphyry environment is unique by virtue of high incidence and values of copper and mercury, together with a distinctive low, but consistent palladium signature. Whilst the comparable data set describing gold from calc-alkalic porphries is not as robust, the signature of gold from Casino shows no contribution from mercury. For the current exercise, large data describing gold compositions form the reduced calc-alkalic Nucleus and Revenue porphries (Wrighton, 2013) were not included as it seems likely that in these cases gold may be concentrated by the Bi-collector model (e.g. Tooth et al., 2008) and therefore different controls on gold-silver alloy may apply. Nevertheless, mercury is an insignificant contribution to the microchemical
<table>
<thead>
<tr>
<th>Localities</th>
<th>Alloy composition Cu</th>
<th>Hg</th>
<th>Pd</th>
<th>Useful diagnostic inclusions</th>
<th>Supporting inclusion suite</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>&gt;LOD &gt;0.05% &gt;LOD &gt;0.3% &gt;LOD</td>
<td></td>
<td></td>
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<td>Cpy</td>
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<tr>
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<td></td>
<td></td>
<td>28</td>
<td>36</td>
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<tr>
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<td></td>
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<td>14</td>
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<tr>
<td>Thistle Creek</td>
<td>77 14 31 31 na</td>
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<td></td>
<td>60</td>
<td>7</td>
</tr>
</tbody>
</table>

Figure 14. Summary of microchemical signatures of gold from different styles of mineralization in the N American Cordillera, colour coded to aide comparisons. Orogenic gold: data for Indian River (973 grains) from Chapman et al. (2012), data describing gold from the Thistle Creek catchment (434 grains) from Wrighton (2013), data describing gold from the Cariboo Gold District (CGD) (325 grains) from Chapman and Mortensen (submitted). Calc alkaline porphyry systems: data for Casino (171 grains) from Chapman et al. (2014).
signature in these localities which supports the possibility that mercury contents of the alloys may be a discriminant between gold derived from alkalic and calc-alkalic porphyries.

**Specific placer-lode relationships**

This section focuses on the consideration of the relationships of compositional data sets describing gold from in situ mineralization and nearby placer localities.

**The Afton area**

(The sampling site at Cherry Creek was within 3km of the Afton Pit, and it could be expected that erosional products would be present within the sediment. However, other mineral occurrences exist in the Cherry creek catchment, (e.g. Wood, (Barlow, 2013)).

The range of silver contents of hypogene gold grains from Afton only partially overlaps that exhibited by gold from the nearby Cherry Creek placer, (Figs 7A and 7B) shows that these hypogene grains also form a separate compositional field according to their silver and copper contents. The gold-bornite association observed in the hypogene samples was not replicated in the inclusion suite of the placer sample. Chalcocite may form in both hypogene and supergene environments, and by alteration of pre-existing bornite (Stanley et al., 1995). The presence of chalcocite within a gold grain containing 8.0% Ag is interpreted as a hypogene feature, whereas the native copper observed infilling voids in one grain (Figure 13E) was most likely formed as consequence of supergene processes modifying a hypogene grain. The presence of isomertieite and temagamite inclusions in the placer sample (Table 3, Figure 8 E) generated a relatively strong palladium signature not replicated in the small number of hypogene grains, although a palladium telluride was observed in hypogene ore.

The absence of gold grains containing < 19% Ag in the hypogene samples is a clear difference between the mineralogy of gold grains derived from the in situ and placer environments. This distinction is underlined by the data presented in Figure 10B where the elevated copper contents of the tiny hypogene grains lie outside the compositional field of the placer population. These data show that grains formed in the potassic zone are not recoverable from local drainage, which is undoubtedly a consequence of their small size. It follows that the detrital grains collected in Cherry Creek were formed in other environments at later stages of porphyry evolution.

Tranquille Creek is North West of the Afton deposit (Figure 2) and the drainage is situated within the Eocene Kamloops Group. The Creek is a site of historical placer working (MINFILE 092INE106) which included an attempt at dredging, and around 75kg of gold was produced. Possibilities for the source of this gold remain unclear. Figure 15 shows the extent of placer claims in the Tranquille Creek drainage, which extend approximately 5km E-W from the main drainage to the extremity of claims on Watching Creek. Nixon (2004a) reports that picrites may play a role in focussing mineralization, as at Afton, but it seems unfeasible that a single source on Watching Creek accounts for the placer gold in the western fork of Tranquille creek. Overall, this distribution of placer gold seems inconsistent with either a point source, or glacial dispersion from a point source given the truncation of claims up a tributary of Watching Creek. It seems more likely that a number of (possibly related) sources feed into the Tranquille Creek placer, although no such in situ mineralization has been reported.
Figure 15. Placer Titles on Tranquille Creek in relation to bedrock geology.
Figure 14 has been used to compare the signature of placer gold from Tranquille Creek with the compiled data sets describing gold from alkalic, calc-alkalic and orogenic settings. Overall, the signature of the placer gold from Tranquille Creek is most similar to that of gold derived from alkalic porphyries, however, only a small palladium signature was observed, and the inclusion suite contained stronger signatures of silver-tellurium-bearing minerals, chalcocite, arsenopyrite and galena.

A possible interpretation of these data is that the origins of the Tranquille Creek placer lies in either small epithermal or intrusion related sources which have yielded gold with a ‘magmatic’ signature. Whilst this may show some similarities with gold from Cherry Creek, there are differences, particularly between the in the inclusion suites, whose stronger arsenic and tellurium signature could suggest an epithermal genesis.

**Mt Milligan area**

Comparison of the alloy compositions of gold populations from lode and placer at Mt Milligan shows that whilst overall silver ranges are compatible, the placer grains are generally lower in copper (Figure 8). In particular the signature exhibited by gold grains from the potassic zones are not evident in the placer population. Placer grains from King Richard Creek did not contain sufficient inclusions to support a meaningful comparison with lode mineralogy, although the quartz/carbonate/pyrite/tetrahedrite inclusion mineralogy is compatible with the late stage gold/PGE veins described by Le Fort et al. (2011)

**Copper Mountain area**

Consideration of the alloy and inclusion signatures for the three placer samples from the Copper Mountain area suggest a similar source type or range of sources are present in each catchment. Despite these compositional similarities, the location of the sample sites suggest that the placer gold is derived from different mineralized localities, and some possibilities of specific sources are discussed below.

The hypogene mineralization at Copper Mountain is extremely complex, and many of the twenty-two types of veins described by Stanley et al. (1995) have only a local extent. 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 (Figure 5). Consequently, the hypogene sample suite is of limited use as a template for interpretation of the origins of the placer samples. Nevertheless, descriptions of mineral localities within and peripheral to Copper Mountain may be considered in the context of the compositional signatures of the placer grains.

Richardson (1995) described the Whipsaw porphyry system and gold-bearing base metal veins in the vicinity of the Whipsaw porphyry extending towards the Friday Creek catchment. Massive bornite in pegmatite veins was reported at the Ilk zone in Friday Creek by Fischl (1992), who noted trace gold and palladium. A carbonate-rich zone yielded a palladium value of 64 g/T. Subsequent exploration in the area (Fischl, 2015) confirmed the presence of copper-bearing pegmatite veins enriched in both gold (max 411g/T) and palladium (max 717g/T). The presence of broadly similar mineralization close to the three placer sampling sites is a likely explanation for the similarity between placer populations (Figure 12A). Gold grains from bornite-chalcopyrite veins at Copper Mountains described by Stanley et al. (1995) appear to be similar to those reported at Friday Creek. Temagamite (Pd₃HgTe) is also
reported associated with bornite at Friday Creek and in the present study temagamite inclusions are always associated with high mercury in the alloy (0.65 to 25%, e.g. Figure 8F). It seems probable that the grain depicted in Figure 8F is derived from a bornite-temagamite vein, and the low copper content (0.06%) of the earliest alloy phase places this composition in the lower of the two compositional fields suggested by Figures 12B-D. Two other grains containing temagamite inclusions were recorded, hosted by alloys of different composition. Additionally, Figure 12C shows that most of the mercury-rich grains occur in gold of relatively low copper content, whereas palladium appears independent of copper but is most common in grains where Ag<20%. Figure 8F shows a gold grain with a two stage paragenesis in which bornite inclusions are hosted in a gold-rich alloy, overprinted by an alloy elevated mercury and palladium containing palladium-bearing inclusions. This indicates that the paragenesis of distal vein systems is also complex, and a corresponding variation in the microchemical signatures of gold grains could be expected.

Overall it is difficult to ascribe a simple relationship between the compositional ranges evident in the data presented in Figure 12A and hypogene setting; neither does the small data set describing hypogene gold from Copper Mountain greatly illuminate the origins of the placer inventory (Figure 12B). However, it is the case that microchemical signatures of the three placer samples are comparable, and the location of the sample points would strongly suggest that derivation from late-stage veins of common genetic nature is a more likely explanation than invoking gold formed within porphyries. An important consequence of this hypothesis is that the presence of bornite inclusions within placer gold grains is not necessarily indicative of a genesis within the potassic zone.

**Implications for exploration**

**Identification of source style of mineralization**

Several authors have suggested the use of detrital gold as an exploration tool, (e.g. Antweiler and Campbell, (1981), Bowles, (1982) and Grant et al., (1991)). Rubin and Kyle (1996) strongly recommended that the range of elements routinely determined in detrital gold should include copper and palladium as well as silver, particularly when porphyry mineralization was the target. The methodology adopted in the present study further refines the approach through the measurement of mercury in gold alloy and the systematic characterization of the inclusion suite, made possible by the collection of large numbers of detrital gold grains using specialized field techniques.

The data presented in Figure 14 is based on large sample sets and is the first semi-quantitative attempt to characterize the mineralogical signatures of detrital gold derived from different source styles. A qualitative approach to characterizing gold grains in this way was provided by Chapman et al. (2009), but at this time there was very little data available to describe gold formed in porphyry or epithermal environments. Nevertheless, the general observations made concerning the range of signatures exhibited by gold formed in orogenic mineralization remain and have been represented by the sample set presented in Figure 14. Gold grain characterization studies have tended to focus on areas where the source of placer gold is unclear, and generally these are orogenic gold localities. Consequently, the mineralogical signature ranges of orogenic gold can be described with some confidence. Alloy compositions are often simple binary gold-silver, with copper rarely present to above LOD. Mercury may be present in all grains or only a proportion of the population, and
concentrations vary widely. A wide range of silver contents has been observed, in contrast to the general statement of orogenic gold being of high fineness, (Goldfarb et al., 2005). Gold from individual localities may show a narrow silver range, or ranges, such that overall, silver is not a particularly useful discriminator. In the inclusion suites, pyrite is dominant and an overall signature of (pyrite ± chalcopyrite ± galena ± sphalerite ± tellurides) account for the vast majority of inclusions. Whilst the palladium content of gold grains derived for orogenic settings has not been routinely determined, historically, the complete absence of palladium-bearing inclusions, strongly suggests that palladium does not contribute to the overall microchemical signature.

Gold formed from fluids which have a magmatic heritage tends to exhibit a more complex mineralogy. A larger number of elements may contribute to the microchemical signature, not only in the alloy, but particularly in the mineral inclusion assemblage. The present study is the first to systematically characterize gold from alkalic porphyries and their (probable) epithermal expressions, so some conclusions are made tentatively. However, it is the case that generic progressive and systematic changes in the microchemical signature have been identified associated with the evolution of hydrothermal systems both within evolving porphyry and also associated with the porphyry epithermal transition. In many cases these changes are predictable, based on understanding of element behaviour in those evolving hydrothermal systems. Presently, it is possible to distinguish between populations of gold grains derived from alkalic porphyry/epithermal mineralization and orogenic gold, if sufficient gold grains are available for study. The practical issues of obtaining a suitable sample are addressed in the following section.

Earlier studies of placer gold composition have tended to assume that gold formed in different mineralization styles will be characterizable, using some mineralogical or alloy feature. The more data sets become available it seems that some distinctions originally held true are at best generalizations. Examples of this might be that orogenic gold is high fineness, or that epithermal gold always exhibits a wide compositional range with respect to silver. Linking the process of mineralization to microchemical signature has greatly enhanced our ability to interpret the implications of a particular signature. Orogenic gold may be formed in conditions which are broadly similar, (even if the mechanism of gold precipitation was a sudden change in conditions such as pressure release), and the narrow range of alloy compositions often reflects this. In the case of porphyry and epithermal mineralization, the variability of the immediate conditions of gold precipitation is both well documented and diverse. The challenge for explorers is to be able to interpret a mixed signal which presents in a placer population to predict the nature of the source mineralization.

A further practical consideration is the particle size of the hypogene gold grains. Studies of gold alloy in copper-gold porphyry systems have focussed on the gold-Fe-copper sulfide association in the ore within the potassic zone, because this represents the most economically significant stage of metal mineralization. The lower size limit for recovery of gold grains by hand panning is around 60-70 µm, which coincides with the lower size limit at which gold is concentrated by fluvial action. As a result, small gold particles (such as those liberated from the gold-bornite association) are likely to be substantially under-represented in heavy mineral concentrates collected in the field, unless, as Kelly et al. (2013) pointed out, samples are collected routinely from till rather than a fluvial setting. Arif and Baker (2004) and Gregory et al. (2013) recorded a small proportion of grains > 60 µm but in general it appears that only a small minority of the gold grains originating from the zone of potassic alteration could be recovered from the placer environment. In addition, the Similkameen River was the only
locality at which bornite inclusions were observed. The discussion above has concluded that in this case the gold was derived from bornite-temagamite veins, rather than mineralization formed in the zone of potassic alteration. Consequently, a simple approach of correlating hypogene gold compositions gained from the literature with compositional data describing detrital gold grains is not useful in an exploration context. This observation does not detract from the development of placer-lode relationships once the nature of the mineralization and the sedimentological behaviour of the eroded products are appreciated.

**Gold grain studies as an exploration tool: practical considerations.**

The potential strength of compositional characterization of gold grains lies in providing added value to existing exploration methodology. Detrital gold grains are commonly collected during routine stream sediment sampling programmes, and the characteristics of gold particles derived from copper-gold porphyry deposits described in the preceding sections provide the opportunity to gain extra information from either new or existing sample suites. The methodology described in this contribution involves interpretation of data sets describing populations of placer grains, and the complexity of the porphyry systems which manifests as different gold-bearing vein systems (e.g. Copper Mountain) requires large data sets to facilitate characterization of the contributing sub populations. Such large populations of placer gold grains are rarely present in samples collected from conventional geochemical exploration, as only small volumes of sediment are required for standard geochemical analyses. Whilst the aim of stream sediment sampling is to generate comparable data between sampling localities, gold accumulation in fluvial systems is highly specific. Consequently, a different field methodology is required form the collection of detrital gold populations for study, and this draws heavily on techniques developed by amateur prospectors and gold panners. Nevertheless, results of standard stream sediment sampling programs may provide a very useful guide to the design of field work specifically targeted for detrital gold recovery.

**Conclusions**

Alkali porphyry mineralization most frequently comprise a series of temporally and spatially related hydrothermal systems each of which may influence the abundance and nature of gold alloy through either precipitation or remobilization. In this study, gold derived from alkalic porphyry systems commonly exhibited a generic and distinctive alloy composition in which gold-silver alloys contained elevated copper, mercury and sometimes palladium. The palladium signature was also evident in the inclusion suites, and forms an important diagnostic marker for gold from this style of mineralization.

Consideration of various elements of the microchemical signature (alloy composition, and different inclusions) has permitted design of a compositional matrix into which large, related data sets have been distilled. This matrix utilises individual mineral species as opposed to mineral classes, (often previously employed to characterise placer gold from orogenic sources) because the valuable information may be gained from consideration of specific mineral species, e.g. bornite or palladium-bearing minerals. This approach has generated a template for distinguishing gold derived from alkalic porphyries from that formed in the orogenic environment, where the inclusion suite is dominated by simple sulphides hosted by a gold-silver ±mercury alloy. Initial studies of gold grains from calc-alkalic porphyries in the Yukon suggest that lower mercury values are present than within gold formed in the alkalic porphyry systems.
Interpretation of the signatures of placer gold populations in areas of complex metallogeny must be informed by an appreciation of the variation of environments in which native gold can form. The majority of studies which focus on porphyry mineralization (both alkalic and calc-alkalic) have, not surprisingly focussed on the most economically important phase of mineralization, which is normally the potassic zone. Most, if not all the grains of native gold formed in this environment are too small to be concentrated in the fluvial environment and are massively under-represented in placer samples. Consequently, it is important to be able to recognise signatures of larger gold particles, which form in late stages of the porphyry development, even though these may not comprise attractive exploration targets.

Collection of placer gold populations for study provides some practical challenges but specialized field techniques can aid in sample collection from areas of overall low gold abundance.

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