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Capital letters only for first word, abbreviations  
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# Trace element quantification in gold as a means of distinguishing the genesis of placer gold

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Affiliation sufficient, address unnecessary

No keywords

**Abstract.** Analyses of placer gold has largely been restricted to the major components, Au, Ag, Cu, Hg from electron microprobe analysis (EMPA) due to the relatively high detection limits for other minor elements. LA-ICP-MS has sub-ppm detection limits for most elements in gold, but by comparison with EMPA is both destructive and penetrates the gold to much greater in depth. We have analysed gold elements to assess which are important to form a basis for the discrimination of gold from different localities and different styles of mineralization. High resolution multi-element maps of selected grains, analysed by icpTOF-MS, reveal some elements are controlled by crystal structure, grain boundaries or random events.

Abstract 200 words, justified

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## 1 Introduction

Southern and central British Columbia (BC) are complex terranes which host different styles of gold mineralization but the natural abundance of gold is low. The ability to identify styles of alloy and mineralogical features of placer gold particles may underpin a new exploration methodology based on gold as an indicator mineral. Gold compositions are traditionally measured using the electron microprobe (EMP), which can easily characterise a population of Au grains in terms of their Ag content. Corresponding data for Cu, Hg and Pd are obtained where their concentrations exceed the limit of detection (c 0.02 wt %, 0.3 wt % and 0.04 wt % respectively). Very often, Cu, Hg and Pd values straddle these detection limits yielding a 'partial' data set. Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can provide quantitative analyses of trace elements within gold. We aimed to establish which elements were present in natural gold, their mode of occurrence and whether the relationship between gold formed in different mineralizing systems.

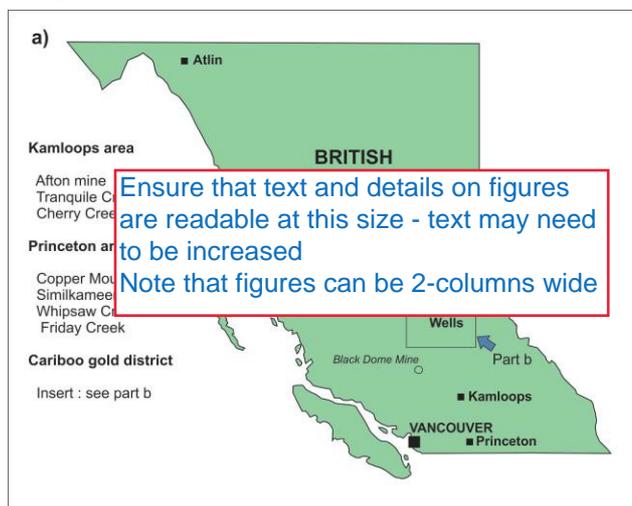
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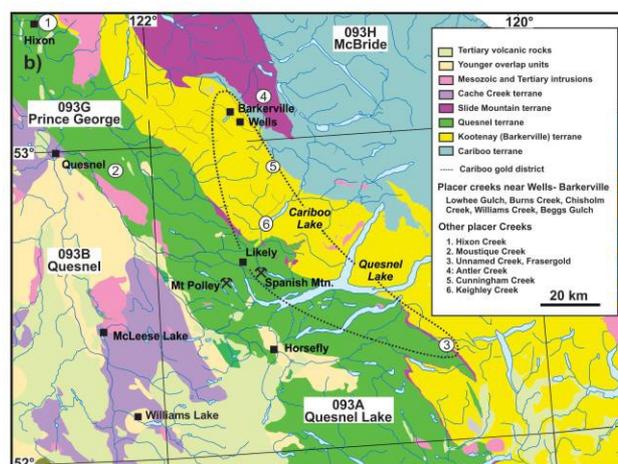
The northern cordillera has been the focus of traditional prospecting for nearly 200 years. Placer-gold occurrences are widespread and have supported a local economy. The Cariboo gold district is exploited, but the relationship between placer gold and its source lode is less clear at other localities, either as a consequence of extensive surficial

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sediments or because complex bedrock geology provides several potential geological settings for source mineralization. Both these factors have constrained exploration in BC. The use of gold compositional studies has elevated the potential value of detrital gold from a simple physical marker to an indicator of the potential style of mineralization. For example, regional studies in the Yukon and the Fortymile district of the Yukon and Alaska have identified the importance of gold derived from orogenic systems in local placer inventories, even



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**Figure 1.** a) Location of the Cariboo gold district (box; see part b) and sample locations near Kamloops (Afton mine, Tranquille River, Princeton area (Copper Mt, Similkamee, Whipsaw C, Friday Creek), Wells, Black Dome Mine, Part b, Kamloops, Princeton). b) Geological map of the Cariboo gold district showing various geological units and placer creeks. Detail of sample locations (1-6) near Wells-Barkerville (Lowhee Gulch, Burns Creek, Chisholm Creek, Williams Creek, Boggs Gulch). Other placer Creeks: 1. Hixon Creek, 2. Moustique Creek, 3. Unnamed Creek, Frasergold, 4. Antler Creek, 5. Cunningham Creek, 6. Keighley Creek. Adapted from Madsen and Chapman (2010).

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when an intrusion-related system was proposed (Wrighton 2013). It has been used in BC to elucidate the mineralogy of detrital gold in placer veins and to infer the relative importance of source veins (Chapman and Mortensen 2016). The alkalic copper-gold porphyries of BC are both potential sources of detrital gold and located within wider auriferous areas. Consequently, the region provides an excellent study area in which to explore the potential of gold compositional studies in the context of exploration in a challenging environment.

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## 2 Methodology

Some 1600 gold grains, mounted in polished blocks, provided populations of grains from the placers derived from different types of source deposits. Individual grains were analysed with a Geolas ablation system that utilises a Compex 193 ArF excimer laser and an Agilent 7500c quadrupole ICP-MS (operated without the reaction cell) with a laser fluence of 6 J/cm<sup>2</sup> and a repetition rate of 5 Hz. At higher energies or repetition rates the gold grains were ablated all the way through too quickly to achieve a sufficiently stable signal and analyses were less reproducible and accurate. As an estimate, it was found that 150 pulses ablated the gold to a depth of around 100 µm. All the gold grains were analysed with spot diameters of 25–100 µm, with 50 µm being the most frequent size used, to ensure ablation continued for the full 150 pulses.

The gold grains were analysed for a large number of elements to see which were detectable and to provide an appraisal of which would be useful in distinguishing between different deposits, metallogenic types, and potentially be indicative of processes operating during precipitation. The elements analysed were <sup>27</sup>Al, <sup>29</sup>Si, <sup>32</sup>S, <sup>47</sup>Ti, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>63</sup>Cu, <sup>66</sup>Zn, <sup>69</sup>Ga, <sup>72</sup>Ge, <sup>75</sup>As, <sup>82</sup>Se, <sup>89</sup>Y, <sup>93</sup>Nb, <sup>95</sup>Mo, <sup>103</sup>Rh, <sup>105</sup>Pd, <sup>107</sup>Ag, <sup>111</sup>Cd, <sup>115</sup>In, <sup>118</sup>Sn, <sup>121</sup>Sb, <sup>125</sup>Te, <sup>139</sup>La, <sup>182</sup>W, <sup>195</sup>Pt, <sup>197</sup>Au, <sup>202</sup>Hg, <sup>208</sup>Pb, <sup>209</sup>Bi, <sup>232</sup>Th, <sup>238</sup>U, all at 10 ms dwell times. Quantification of the full element suite required 4 standards to provide ratios of different elements to the internal standard element Au. NIST 610 silicate glass, AuRM2 London Bullion Standard, NIST 481 gold silver wires and USGS MASS-1 synthetic sulphide standard enabled all the elements to be determined as weight ratios relative to Au and the actual concentrations in ppm to be calculated based on 100% normalization.

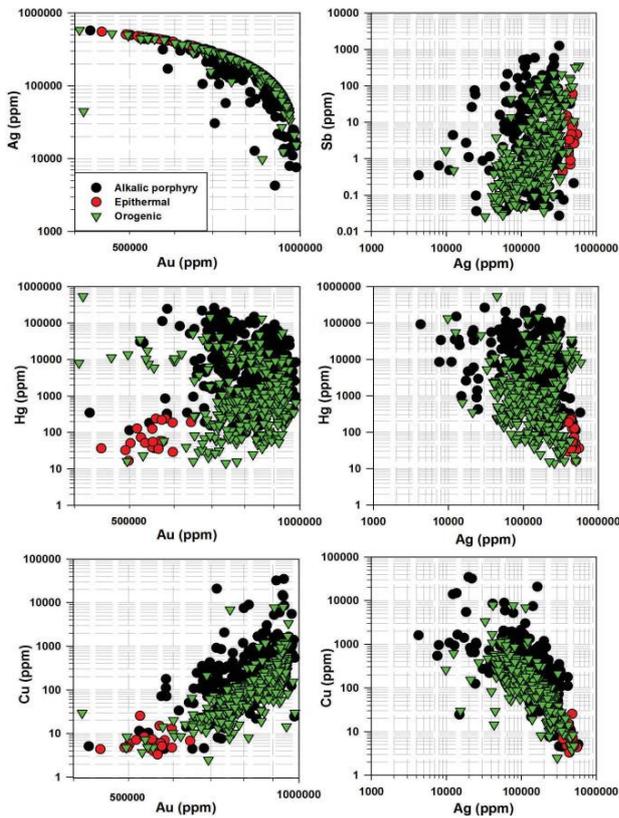
The standard single-spot LA-ICP-MS analysis does not capture any elemental heterogeneity within gold grains. Multi-element mapping with LA-ICP-MS can shed more light on the nature of the grain formation, but the method is very time consuming with standard LA-ICP-MS technology and does not show all the heterogeneities present. Here we have carried out high-speed multi-element mapping of detrital gold by combining the TOFWERK icpTOF (time of flight) mass spectrometer and

Analyte G2 193 nm excimer laser with a recently developed aerosol rapid introduction system (ARIS) from Teledyne CETAC Technologies. All isotopes (in the sample shown approximately 20 elements were determined above the limit of detection) present in a 500 µm gold grain were mapped with 5 µm resolution in less than 15 minutes, therefore 11,000 multi-element spot analyses. The combination of the icpTOF and fast laser ablation systems enables rapid mapping of all elements in gold grains, exposing elemental heterogeneities that are not captured with single-spot analysis. The simultaneous analysis reveals the elemental associations at a single spot which is not possible with a quadrupole-MS system.

## 3 LA ICP-MS quantification

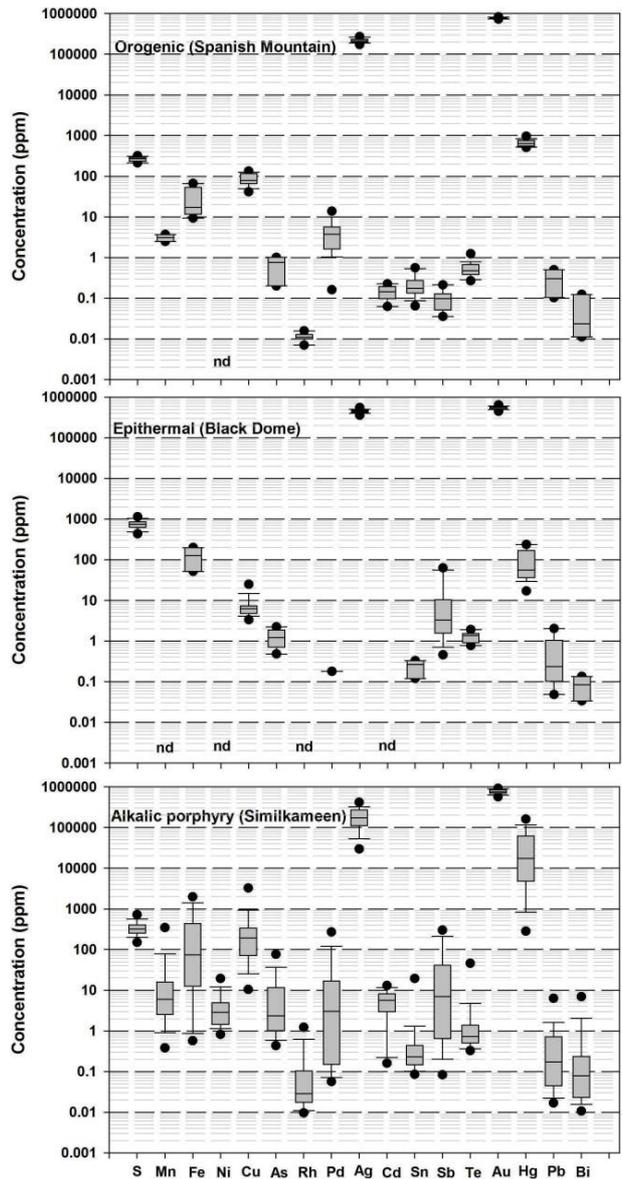
In Figure 2, bivariate plots of the major elements in the gold are shown. Capitalized elements analysed so far, differentiated on the basis of the deposit type from which the gold originated. The alkali porphyry deposits have, in general, the highest concentrations of elements other than the Au and Ag that dominate the gold-grain composition as a binary mixture. The alkali porphyry deposits plot below a binary mixing line due to the high concentrations of Hg, up to 10%, in these grains. There are reasonably strong negative correlations of Hg with Au and Ag, over a large range in Hg concentrations, which is indicative of Hg replacing both Au and Ag in the porphyry gold grains. The dataset available that relates to epithermal deposits is relatively restricted when compared to the other two types. Nevertheless, the initial indication is that, for these types of deposit, there may be distinction based on the higher Ag and the low Cu and Hg concentrations. The number of gold grains from orogenic deposits analysed is relatively large and some clearly defined trends have emerged. The majority of gold grains are binary Au and Ag mixtures, with these elements making up well over 99% of the composition, a result that is well known from previous alloy studies using EMP. In general, other elements are present at lesser concentrations than the alkalic porphyry deposits but greater than the single epithermal deposit studied here. There is a good positive correlation of Ag and Sb, and good negative correlations of Ag with Cu and Hg. These trends have not been previously observed in EMP datasets because of the higher detection limits. It is encouraging, at this level of data interpretation, that different sources of gold grains do seem to have observable differences when looking at the dataset as a whole. The observed correlations from measurement of trace elements at low concentrations show that these are not just random analyses, but may be related to processes during gold deposition.

In Figure 3, three individual deposits (Spanish Creek, Black Dome and Similkameen) have been chosen as examples of gold derived from orogenic, low-sulphidation epithermal and alkalic porphyry systems, respectively. Although some



**Figure 2.** Major elements in all gold grains analysed, differentiated on the basis of the type of deposit from which the placer grains originated.

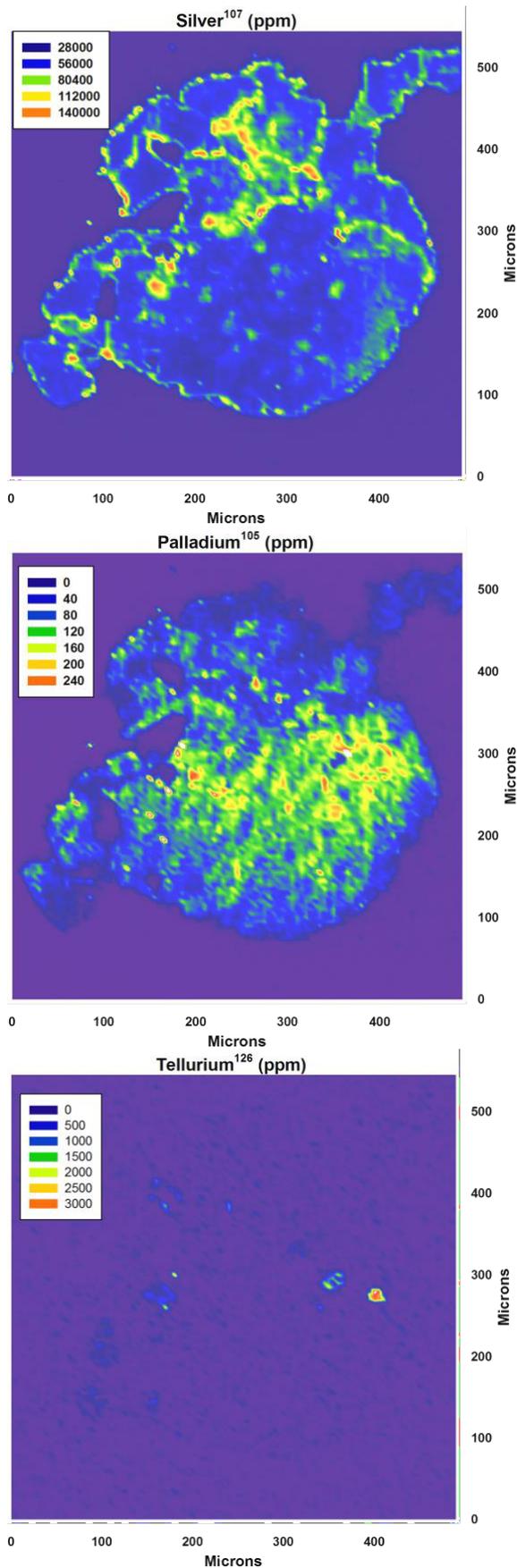
differences in alloy compositions can be identified in the EMP data (and corresponding inclusion assemblages), a number of further differences can be observed in the suite of minor elements whose concentrations have been measured using LA-ICP-MS. Gold from the Similkameen placer (alkalic porphyry related) shows the most complex elemental signatures and with trace elements at the highest concentrations. Gold from the Black Dome deposit contains fewer elements and at lower levels, whereas the signature of gold from Spanish Mountain (orogenic) falls midway between the other two. Three elements are worthy of particular attention: Hg, Cu and Pd. Concentrations of Hg in gold alloy from the alkalic porphyry system are around ten times higher than in the gold from Spanish Mountain, which in turn exhibits Hg concentrations ten times those of the gold from Black Dome. The detection limit for Hg by EMP is around 0.3%, so the use of LA-ICP-MS allows measurement and interpretation of Hg in the alloy at far lower levels. Copper concentrations were generally highest in gold from the alkali porphyry system, although most grains from this sample suite and the Spanish Mountain suite returned quite similar values for Pd; however, some individual grains from the Similkameen River exhibited far higher Pd values. Palladium was absent in the gold from Black Dome, where Cu concentrations were also very low.



**Figure 3.** Analyses of placer grains from different streams in the vicinity of the Copper Mountain porphyry. Elements shown are those that are most prevalent in the grains. In general, the analyses show a good degree of similarity, but Hg, for example, is much higher at Similkameen than the other two placers.

#### 4 Elemental distribution in gold

Several gold grains were analysed using LA-icpTOF-MS which enables all detectable isotopes to be measured from a single laser ablation spot simultaneously. Element distribution maps (Figure 4) show that in some parts of the grains the concentrations are homogeneous while there are areas that are quite heterogeneous. Small inclusions, such as Te, can be associated with other elements that may be present at the same spot as the analysis is simultaneous for all elements. Some elements show migration away from the grain boundaries while others show enrichment, but why this is so is unclear at present.



**Figure 4.** Element concentrations for Ag, Pd and Te illustrating major, trace and inclusion contents in gold at 5  $\mu\text{m}$  resolution.

However, TOF-based MS is clearly the future in element mapping.

## 5 Conclusions

The differences between alloy signatures in gold from different deposit types previously identified by (electron microprobe) EMP analysis are evident in the LA-ICP-MS data, but the quantitative analysis of Cu, Hg and Pd at trace levels permits additional interrogation of these datasets. Most importantly, the use of LA-ICP-MS has identified the potential for other elements (e.g., Sb) to be used as discriminators and the ability to spot trends in element ratios where analyses were close to the detection limit by EMP. It is evident that for analyses to be relevant populations of grains must be analysed to fully appreciate the elemental concentration distribution at each location. Regardless of the preliminary nature of the data, it appears there are reproducible compositional similarities between populations of gold derived from the same source, and that differences exist between signatures of gold from different source types. As yet, there are insufficient data to establish whether such differences are generic or a consequence of specific environments of mineralization.

## Acknowledgements

Geoscience BC are thanked for project grant 2016-06, "Detrital gold as a deposit specific indicator mineral by LA-ICP-MS analysis". Teledyne CETAC Technologies are thanked for the use of their fast laser ablation system which enabled multi-element ablation of gold grains.

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