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# **Trace Element Composition of Placer Gold Across the Okanagan Fault, Kelowna, British Columbia, Canada**

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Article abstract

For 100 years, placer gold has been important to the settlement, economic development, and, recently, recreational geology of the Kelowna, British Columbia, area. It is best-known to occur in modern-day, Mission Creek and Lambly Creek sedimentary rocks, as well as a paleoplacer occurrence in Miocene sediments of the historical Winfield mine. The Mission Creek and Winfield localities are east of the west-dipping, low-angle, normal Okanagan Fault, which has been active since the Eocene. Lambly Creek is west of the fault. Late Paleozoic to Eocene igneous and metasedimentary rocks occur in the Lambly Creek catchment but Eocene gneiss units, unroofed by the fault, occur on the Okanagan Valley's east side. This study tests the hypothesis that native placer gold compositions vary across the Okanagan Fault reflecting different sources and histories for the gold. A modest number of Au and Ag analyses (23 analyses) in usefully representative placer gold samples were determined on a scanning electron microscope with an energy dispersive spectrometer (SEM-EDS). Spots analyzed for Au and Ag were also analyzed for 19 trace elements using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Mercury was semi-quantitatively determined in 'unknown' gold grains by first estimating its concentration (~3.69 ppm) in the AuRM2 external standard. Proportions of Au:Ag:Cu in grain cores indicate all the gold came from mesothermal/hypogene or possibly Au porphyry bedrock deposits though primary signatures may have been obscured by metamorphism or weathering. Winfield and Mission Creek grains tend to have higher siderophile Fe, Ni, Pd and Pt and chalcophile elements As, Se, Te, Hg, Pb and Bi but lower Cu and Sb concentrations than Lambly Creek gold. Mercury is distinctly higher in Winfield and Mission Creek gold than in Lambly Creek gold from the west side of the valley; the element appears particularly useful for 'fingerprinting' gold. Lambly Creek gold compositions indicate derivation from two orogenic/hypogene sources from greenstone and plutonic/hydrothermal rocks present in the catchment area. Modern day Mission Creek and Miocene paleoplacer Winfield grains have a similar hypogene trace element signature but there are no known local bedrock gold sources. The Mission Creek and Winfield gold grain cores are surrounded by < 10 µm, Au-rich, Ag- and trace element-poor, rims. Lambly Creek grains lack such rims. The Au-rich rims on modern day Mission Creek and Miocene Winfield gold may reflect prolonged near-surface exposure with surficial electrochemical dissolution of hypogene trace elements or the biological precipitation of gold. Low Ag and red colouration on the surface of grains support the biological precipitation hypothesis. The shared trace element signature, together with the Au-rich rims indicate that modern day placer gold in Mission Creek was multiply reworked from Miocene paleoplacers similar to the Winfield occurrence as a result of uplift and erosion of rocks on the east side of Okanagan Fault.

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# **ARTICLE**



# Trace Element Composition of Placer Gold Across the Okanagan Fault, Kelowna, British Columbia, Canada

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## **SUMMARY**

For 100 years, placer gold has been important to the settlement, economic development, and, recently, recreational geology of the Kelowna, British Columbia, area. It is best-known to occur in modern-day, Mission Creek and Lambly Creek sedimentary rocks, as well as a paleoplacer occurrence in Miocene sediments of the historical Winfield mine. The Mission Creek and Winfield localities are east of the west-dipping, low-angle, normal Okanagan Fault, which has been active since the Eocene. Lambly Creek is west of the fault. Late Paleozoic to Eocene igneous and metasedimentary rocks occur in the Lambly Creek catchment but Eocene gneiss units, unroofed by the fault, occur on the Okanagan Valley's east side. This study tests the hypothesis that native placer gold compositions vary across the Okanagan Fault reflecting different sources and histories for the gold. A modest number of Au and Ag analyses (23 analyses) in usefully representative placer gold samples were determined on a scanning electron microscope with an energy dispersive spectrometer (SEM-EDS). Spots analyzed for Au and Ag were also analyzed for 19 trace elements using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Mercury was semi-quantitatively determined in 'unknown' gold grains by first estimating its concentration (~3.69 ppm) in the AuRM2 external standard. Proportions of Au:Ag:Cu in grain cores indicate all the gold came from mesothermal/hypogene or possibly Au porphyry bedrock deposits though primary signatures may have been obscured by metamorphism or weathering. Winfield and Mission Creek grains tend to have higher siderophile Fe, Ni, Pd and Pt and chalcophile elements As, Se, Te, Hg, Pb and Bi but lower Cu and Sb concentrations than Lambly Creek gold. Mercury is distinctly higher in Winfield and Mission Creek gold than in Lambly Creek gold from the west side of the valley; the element appears particularly useful for 'fingerprinting' gold. Lambly Creek gold compositions indicate derivation from two orogenic/hypogene sources from greenstone and plutonic/ hydrothermal rocks present in the catchment area. Modern day Mission Creek and Miocene paleoplacer Winfield grains have a similar hypogene trace element signature but there are no known local bedrock gold sources. The Mission Creek and Winfield gold grain cores are surrounded by  $\leq 10 \,\mu$ m, Au-rich, Ag- and trace element-poor, rims. Lambly Creek grains lack such rims. The Au-rich rims on modern day Mission Creek and Miocene Winfield gold may reflect prolonged near-surface exposure with surficial electrochemical dissolution of hypogene trace elements or the biological precipitation of gold. Low Ag and red colouration on the surface of grains support the biological precipitation hypothesis. The shared trace element signature, together with the Au-rich rims indicate that modern day placer gold in Mission Creek was multiply reworked from Miocene paleoplacers similar to the Winfield occurrence as a result of uplift and erosion of rocks on the east side of Okanagan Fault.

# RÉSUMÉ

Pendant 100 ans, l'or placérien a joué un rôle important dans le peuplement, le développement économique et, plus récemment, la géologie récréative de la région de Kelowna, en Colombie-Britannique. Il est surtout connu pour se trouver dans les roches sédimentaires modernes de Mission Creek et Lambly Creek, ainsi qu'en tant que gisement paléoplacérien

dans les sédiments miocènes de l'ancienne mine de Winfield. Les localités Mission Creek et Winfield sont à l'est de la faille d'Okanagan, une faille normale à faible pendage vers l'ouest et active depuis l'Éocène. Lambly Creek se trouve à l'ouest de la faille. Des roches ignées et métasédimentaires du Paléozoïque supérieur à l'Éocène sont présentes dans le bassin versant de Lambly Creek, mais des unités de gneiss de l'Éocène, exposées par la faille, se trouvent du côté est de la vallée d'Okanagan. Cette étude teste l'hypothèse selon laquelle les compositions de l'or natif placérien varient le long de la faille d'Okanagan, reflétant différentes sources et histoires pour l'or. Un nombre restreint d'analyses d'Au et d'Ag (23 analyses) dans des échantillons représentatifs d'or placérien ont été effectuées au microscope électronique à balayage avec un spectromètre à dispersion d'énergie (MEB-EDS). Les zones analysées pour l'Au et l'Ag ont également été analysées pour 19 éléments traces à l'aide d'un spectromètre de masse à plasma induit par couplage inductif par ablation au laser (LA-ICP-MS). Le mercure a été déterminé de manière semi-quantitative dans des grains d'or « inconnus » en estimant d'abord sa concentration  $(\sim 3,69 \text{ ppm})$ dans l'étalon externe AuRM2. Les proportions d'Au, d'Ag et de Cu dans les noyaux des grains indiquent que tout l'or provient de gîtes mésothermaux/hypogènes ou éventuellement de gisements rocheux porphyriques aurifères, bien que les signatures primaires aient pu être masquées par du métamorphisme ou de l'altération. Les grains de Winfield et Mission Creek ont tendance à avoir des concentrations plus élevées en éléments sidérophiles Fe, Ni, Pd et Pt et en éléments chalcophiles As, Se, Te, Hg, Pb et Bi, mais des concentrations plus faibles en Cu et Sb que l'or de Lambly Creek. Le mercure est nettement plus élevé dans l'or de Winfield et Mission Creek que dans l'or de Lambly Creek du côté ouest de la vallée; l'élément semble particulièrement utile pour le traçage de l'or. Les compositions aurifères de Lambly Creek indiquent une origine de deux sources orogéniques/hypogènes provenant des roches vertes et des roches plutoniques/hydrothermales présentes dans le bassin versant. Les grains modernes de Mission Creek et des grains paléoplacériens du Miocène de Winfield ont une signature d'éléments traces hypogènes similaire, mais il n'existe aucune source d'or connue dans la roche-mère locale. Les noyaux des grains d'or de Mission Creek et de Winfield sont entourés de bordures de moins de 10 µm de large, riches en Au et pauvres en Ag et en éléments traces. Les grains de Lambly Creek ne présentent pas de telles bordures. Les bordures riches en Au sur l'or moderne de Mission Creek et l'or miocène de Winfield peuvent refléter une exposition prolongée près de la surface avec une dissolution électrochimique superficielle des éléments traces hypogènes ou la précipitation biologique de l'or. La faible teneur en Ag et la coloration rouge à la surface des grains soutiennent l'hypothèse d'une précipitation biologique. La signature commune en éléments traces, ainsi que les bordures riches en Au, indiquent que l'or placérien moderne de Mission Creek a été remanié à plusieurs reprises à partir de paléoplacers du Miocène similaires à ceux de Winfield, résultant du soulèvement et de l'érosion des roches du côté est de la faille d'Okanagan.

*Traduit par la Traductrice*

#### INTRODUCTION

The golden glitter of panned placer gold has captured imaginations for millennia but, curiously, the origins, means of natural concentration and composition of this gold remain poorly understood despite gold's economic importance. At only  $\sim$  4 parts per billion in Earth's crust, gold is rarely visible as the native element in rocks, but it is retrievable in small quantities by panning in many stream and beach sediments (Boyle 1979). Numerous major lode and placer gold deposits have been discovered by following minor placer gold occurrences upstream to their source (McClenaghan and Cabri 2011) and the composition of placer gold can help identify bedrock sources (Garnett and Bassett 2005; McInnes et al. 2008; Banks et al. 2018). However, some placer gold occurrences and economic deposits have elusive sources (McInnes et al. 2008) or are associated with low grade to uneconomic bedrock gold mineralization (Boyle 1979). Gold particles in placers range from dustsized to nuggets that far exceed the size of grains in the bedrock source (Garnett and Bassett 2005). The paradox of gold in clastic sediments being coarser than in the bedrock source has been ascribed to physical amalgamation, chemical precipitation, biochemical precipitation, and precipitation from organic complexes in tropical swamps, soils, and lateritic regoliths (Hough et al. 2009; Reith et al. 2010; 2013; Large et al. 2013). Importantly, this supergene gold appears relatively pure (Groen et al. 1990; McCready et al. 2003).

The lure of placer gold encouraged early European settlement in Kelowna (Roed 2004) and it is not difficult to find 'colour' (i.e. yellow native gold) in streams on both sides of the Okanagan Valley. The geology across the valley is very different (Fig. 1). On the east side, there are amphibolite-facies, midcrustal gneiss units (metamorphic grade indicates 15+ km depth), last metamorphosed during the Eocene. Thus, they have been unearthed by perhaps 15 km of vertical uplift and tens of kilometres of sub-horizontal normal movement on the continental scale (hundreds of kilometres long) low-angle Okanagan Fault (Tempelman-Kluit and Parkinson 1986). Just 10 km to the west, and across the valley, are Pennsylvanian to Triassic rocks added to North America in the Mesozoic, Mesozoic plutonic rocks, and Cenozoic (Eocene) volcanic rocks that erupted when the east-side gneiss units were being metamorphosed (Tempelman-Kluit and Parkinson 1986; Tempelman-Kluit 1989; Greenough and Roed 2014).

This study tests the hypothesis that the chemical compositions of placer gold grains from either side of the Okanagan valley reflect different bedrock geology and sources of placer gold that are the result of prolonged fault movement and uplift of rocks on the east side of the valley. To achieve this, we report 22 chemical analyses of the trace element content of 12 representative gold grains suitably large enough for analysis and/or multiple analysis by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). These data are supplemented by morphology and mineral inclusion descriptions of the chemically analyzed grains. Fryer et al. (1995) predicted that LA-ICP-MS has immense potential for analyzing native gold. Pioneering studies such as Watling et al. (1994, 1995), McCandless et al. (1997), Outridge et al. (1998), Watling



Figure 1. Bedrock geology map of the central Okanagan area (modified from Massey et al. 2005). Yellow stars indicate sampled field sites which occur within 7 m of 49°55'58.1" N, 119°31'11.5" W (latitude and longitude; Lambly Creek), 49°50'57.4" N, 119°22'31.2" W (Mission Creek), and 10 m of 50°03'14.8" N, 119°21'27.4" W (Winfield Mine). Small black stars are MinFile gold mineralization occurrences in the project area that may represent sources of placer gold. Inset shows physiographic belts of the Canadian Cordillera and location of the study area. Gold location references follow: 1) Lambly Creek area: AT (Dun/Esperon), Scott and Osatenko 1980; Lamb, Pautler 1988; Jubilation, Morrison 1989; Zumar, Murray 1991; Bear, Lenard 1996; Bond, Lenard 1987a; Shear, Lenard 1987b; Spod, Gourlay 1989; Blue Hawk, Mark 1988; Lambly, is the Lambly Creek placer gold sampling site. 2) Winfield area: west of Wood Lake, Tick and Nova, White 1968; Osatenko 1980; east of Wood Lake, Ribbleworth, Aitkens/Stables and Stuart, Mathews 1987; Winfield (Mine), Murray 1991. 3) Mission Creek area: BC Ministry of Energy and Mines 1996; Roed 2004.

(1999), Penney (2001), Rasmussen et al. (2006) and Brostoff et al. (2008) showed that gold from different sources tends to have distinct trace element signatures but inter-study concentration comparisons were difficult due to accuracy issues. There has been progress quantifying the trace element composition of native gold (e.g. McInnes et al. 2008; Tetland et al. 2017; Hastie et al. 2020, 2023; Melo-Gómez et al. 2022; Liu and Beaudoin 2021; Liu et al. 2021) and in the use of minor elements and the composition of inclusions in gold for fingerprinting and identifying gold bedrock sources (Chapman et al. 2022, 2023a,b). Our LA-ICP-MS trace element analyses utilize a calibration reference material (AuRM2) where microanalytical heterogeneity is small relative to natural variation in native gold between individual gold deposits (Tetland et al. 2017). The quantitative analyses can be compared with future gold trace element data. We also estimate Hg concentrations in AuRM2, use them to calculate Hg (semi-quantitatively) in our Okanagan samples, and argue that Hg is probably important for fingerprinting gold. Finally, we make the case that gold from either side of the Okanagan Valley appears different in composition and possibly morphology. This apparently reflects different bedrock sources, the history of uplift on

Okanagan Fault and the extent of prolonged gold recycling in fluvial systems.

#### GEOLOGICAL SETTING

The study area is located along the boundary between the Intermontane and Omineca belts of the Canadian Cordillera (Monger and Price 1979) (Fig. 1 and inset). To the east, the Omineca belt contains Proterozoic and Paleozoic rocks that were intensively metamorphosed during the Mesozoic and Cenozoic. To the west are Paleozoic to early Mesozoic arcrelated rocks of the Intermontane belt containing the accreted Slide Mountain and Quesnel exotic terranes (Nesbitt and Muehlenbachs 1995). The Omineca belt formed due to subparallel subduction of the Intermontane belt oceanic plates, subsequent closure of the Slide Mountain ocean, and accretion of an allochthonous volcanic island arc (e.g. Monger and Price 1979). Numerous post-accretion, mid-Jurassic, and Eocene age felsic plutons intrude the two belts (Armstrong 1988; Gabrielse and Yorath 1991).

Structurally, the project area underwent compression and easterly directed thrusting, obduction of oceanic crust, plutonism, and associated metamorphism during the Early to Mid Jurassic. Strike-slip faulting and a second major metamorphic and plutonic event occurred during the mid-Cretaceous to Paleogene (Nesbitt and Muehlenbachs 1995). An east–west extensional tectonic regime followed during the Paleocene– Eocene and produced the ductile to brittle, low-angle, westdipping, extensional, Okanagan Fault (Tempelman-Kluit and Parkinson 1986; Tempelman-Kluit 1989). This extension unearthed large areas of amphibolite-facies orthogneiss and paragneiss on the east side of the Okanagan Valley (Madsen et al. 2006). An episode of recent uplift  $\leq 1000$  m apparently started at  $\sim$  2 Ma (Boyle 1982).

The east side of Okanagan Lake is dominated by the Proterozoic to Phanerozoic, predominantly amphibolite facies metamorphic units of the Omineca belt (Fig. 1). On the west side, dominantly in the Lambly Creek (Bear Creek) catchment (centre-left of the map), Paleozoic volcanic arc-related rocks of the Intermontane belt are present including fine grained siliciclastic rocks, volcaniclastic rocks, and a small greenstone belt (Bond Au-Ag quartz vein showing). Extensive post-accretion plutons (including the Okanagan Batholith) intruded the area during the Mid Jurassic. They are mostly exposed in the northwest of the map area. Eocene alkali feldspar granite intrusions are also exposed along with consanguineous volcanic and sedimentary assemblages forming extensive cover rocks on both sides of Okanagan Lake. Remnants of the extensive Miocene to Pliocene Chilcotin Group basalt also act as cover rocks. The youngest rocks in the project area are the Pleistocene Lambly Creek basalt (Roed et al. 2014). These young volcanic rocks show that the region is by no means geodynamically stable. The Okanagan Fault may be offset by the late, northeast–southwest-trending oblique (normal/right-lateral strike-slip/transcurrent) Mission Creek Fault that underlies our Mission Creek sampling site (Greenough and Roed 1995). Alternatively, the lateral offset of Okanagan Lake at Kelowna may simply reflect the physiographic expression of a small change in dip on the low angle Okanagan Fault (Okulitch 2013; Roed 2014a).

The study area probably experienced multiple glacial–interglacial events over the past 1.8 Ma but the oldest Pleistocene sediments (glacial till and eolian dune deposits) in all Western Canada occur beneath ~ 1 Ma Lambly Creek basalt (Roed et al. 2014) at West Kelowna. Surficial deposits blanketing the Kelowna study area include widespread thin  $(< 1 \text{ m})$  glacial till, varved glacial lake sediments (up to 40 m thick) that rim the valley bottom, and numerous glacial outwash sand and gravel deposits topped with eolian sand (Fulton and Smith 1978). Placer gold is not associated with these glacial/late glacial deposits.

# SAMPLING LOCATIONS

The three placer/paleoplacer gold occurrences sampled appear as yellow stars in Figure 1, with latitude and longitude given in the caption. The Mission Creek sediments and Winfield Mine occurrences to the east are on Omineca belt rocks whereas the Lambly Creek placer is located on Intermontane belt units. Both Mission Creek and the Winfield Mine were economically exploited whereas Lambly Creek was not.

#### Winfield Mine

The Winfield paleoplacer camp consists of the 1930s Winfield mine east of Wood Lake, which we sampled, and similar occurrences to the northeast including the Stuart, Aitkens/Stables and Ribbleworth paleoplacer deposits (Mathews 1987, Murray 1991; Fig. 1). All are hosted in Miocene unconsolidated river gravel or conglomerate overlying basement rocks predominantly made up of orthogneiss and overlain by Miocene to Pliocene Chilcotin Group basalt (Mathews 1987).

The paleoplacer host rocks represent sediment deposited in extensive, structurally controlled, Miocene paleo-river valleys (Boyle 1982). The sinuous channels, up to a kilometre wide, are intermittently preserved from the Winfield Mine in the north down to Hydraulic Lake (southeast of Mission Creek and just off Fig. 1). Paleoflow indicators show drainage from the northwest to southeast. Sediment preservation was enhanced by the capping Chilcotin Group basalt which prevented erosion during Pleistocene glaciations. Paleoclimate studies indicate the region experienced temperate conditions with moderate, uniformly distributed precipitation during sediment deposition (Boyle 1982).

These Miocene sedimentary units serve as host rocks to significant basal-type uranium mineralization (Boyle 1982) including the Tyee deposit near Hydraulic Lake just southeast of Figure 1. They were explored by Union Oil Company for uranium from 1976 to 1979 and U mineralization is interpreted to be post-depositional, specifically post-Chilcotin Group basalt, and resulted from leaching of U from intrusive basement rocks by meteoric water which infiltrated the Miocene sediments through structures that controlled the paleochannels. These oxidized U-bearing fluids encountered reduced organic matter in the sediments depositing mainly urano-phosphate complexes (Boyle 1982).

The Winfield Mine paleoplacer deposit was discovered in 1936 and two exploration drifts of 52 and 107 m were dug. Small-scale mining continued until 1945 yielding a total reported 2.33 kg of gold (Mathews 1987; BC Ministry of Energy and Mines 1993).

## Mission Creek

The Mission Creek placer was the most productive gold deposit in the central Okanagan (Roed 2004). It is hosted in active fluvial sediments and recent bench deposits of Mission Creek. The highest gold abundances occur 12 km east of the mouth of Mission Creek and just downstream from a conglomerate postulated to be the source of the placer gold (Roed 2004, 2014b) due to juxtaposition. There are no reports of gold from the poorly exposed conglomerate. The conglomerate is underlain by sandstone, siltstone and dacite of the Eocene Penticton Group and overlain by Pleistocene till deposits. In the upper reaches of Mission Creek, it is conformably overlain by a dark volcanic unit resembling the Pleistocene Lambly Creek basalt. South of the Mission Creek Fault (Fig. 1), the conglomerate is juxtaposed against Shuswap, Proterozoic to Paleozoic high-grade metamorphic rocks. The conglomerate is apparently an interglacial alluvial deposit (Roed 1995, 2014b), though the only age constraints are that it is

Eocene to pre-Holocene in age. Clasts in the conglomerate are closely packed and mostly well rounded and include granitic, dioritic and argillaceous lithologies. It is mostly lithified with some friability and extensive limonitic alteration yielding a rusty appearance. A cross-section from water well data indicates the conglomerate represents the recharge area of a major aquifer, the Rutland Aquifer, which underlies the east side of Kelowna.

Placer mining in the central Okanagan started with the discovery of gold at Mission Creek in 1861 (Roed 2004). Records of placer gold mining at Mission Creek began in 1876 and mining continued until the 1930s (Roed 2004; BC Ministry of Energy and Mines 1996). Mining methods included both open pit and, apparently, underground operations. During the peak of mining activity (1876–1895) the recorded production, which likely represents a minimum value due to underreporting, is listed at 20.56 kg of gold (BC Ministry of Energy and Mines 1996). Eight overburden drill-holes tested Mission Creek in 1975 and results were considered very promising, yet inconsistent, and no further work was conducted (BC Ministry of Energy and Mines 1996). Today, the area is within the Scenic Canyon Regional Park.

#### Lambly Creek

Lambly Creek contains placer gold in its modern sediments, but it has not been economically significant. Rocks in the catchment include Paleozoic volcaniclastic and fine-grained siliciclastic rocks with minor volcanic arc-related greenstone (Fig. 1). The area is intruded by granodiorites of Late Triassic, Early Jurassic and Mid Jurassic ages. Overlying these are Eocene Penticton Group volcanic rocks and the Pleistocene Lambly Creek basalt. Various types of bedrock mineralization, and potential Lambly Creek gold sources, occur in the drainage basin (Fig. 1). The Bond Au–Ag quartz vein showing is hosted in greenstone with pyrite weathering to limonite. It is epithermal (Lenard 1987a) and vein 'grab' samples assayed up to 12  $g/t$  gold and 7  $g/t$  silver. The Shear occurrence consists of polymetallic stockwork veins containing Ag-Pb-Zn ± Au (Lenard 1987b). Assays up to 18.5 g/t Au are recorded and associated minerals include galena, pyrite and quartz. The Zumar showing is another, sheared, polymetallic stockworktype vein, but it also contains Cu and shows hematite and sericite alteration (Murray 1991). The Lamb occurrence (Pautler 1988) is possibly a skarn-related Ag-Cu  $\pm$  Au showing; bulk assays indicate  $\leq 2.4$  g/t Ag and 0.19% Cu. Northeast of Lambly Creek is the Spod low sulphidation gold mineralization (Gourlay 1989) showing multiple stages of andesite-hosted quartz veins and zones of propylitic alteration. One drill core intercepted 3 m of 0.785 g/t Au. In the north to northwest of the study area is Cu-Mo alkaline-porphyry-related mineralization including the AT (Dun/Esperon) occurrence (Scott and Osatenko 1980). It is possible that gold in Lambly Creek was derived from gravel deposits beneath a flow regarded as Lambly Creek basalt in the upper reaches of the creek (Roed, personal communication 2015). However, these rocks have not been dated and there are no river gravels in the sediment section underlying the Lambly Creek basalt at West Kelowna (Roed et al. 2014).

## METHODS

#### Sampling, Mounting and Petrographic Analysis

Placer gold was hand panned from Mission Creek, Lambly Creek, and the Winfield Mine and the largest grains from each locality ( $n = 7$ , 10 and 7, respectively) examined in detail and geochemically analyzed. Gold from Mission and Lambly creeks came from recent fluvial sediments within 50 cm of the sediment surface; some directly overlying bedrock. Grains from the Winfield mine were panned at the entrance to a 30 m drift into loosely consolidated gravel overlying metamorphosed basement rocks. Sediments were panned down to a heavy mineral concentrate and care taken to ensure recovery of even small  $(< 50 \,\mu m)$  gold particles. Gold grains were removed from the gold pan concentrate using adhesive tape and the pan thoroughly cleaned by repeated rinsing with water, wiping between rinses, and inspecting the pan to ensure no sediment remained.

Gold grain samples were catalogued, photographed, and roundness, particle size, grain morphology, surface texture and colour recorded. They were oriented with their long axis horizontal, set in resin on glass discs, and polished with diamond paste at the Western University. Multiple large grains were put on some discs, but small grains required individual mounting to avoid loss during polishing. The polished grains were examined under reflected light with a Nikon Eclipse 50 iPOL petrographic microscope and the following parameters described: 1) mineral inclusions were subjectively classified as hypogene (internal) or detrital sediment picked up during transport (rounded and near the outside edge); 2) variations in the colour of gold (light yellow to yellow orange) within and between grains; 3) modal abundances of inclusions-by-type and goldby-colour quantified; 4) grain shape, morphology and crosssectional area estimated; and 5) features such as folded edges, rough surfaces and embayments noted.

# SEM-EDS Analysis

Sample discs were carbon-coated to 20 nm thickness at CF Mineral Research, Kelowna. The SEM-EDS analyses were performed at the Fipke Laboratory for Trace Element Research (FiLTER), UBC Okanagan, Kelowna, using a Tescan Mira3 XMU Scanning Electron Microscope (SEM) equipped with an Oxford Aztec™ X-max energy dispersive spectrometer (EDS) containing an 80 mm2 silicon drift detector. Data processing utilized Oxford Aztec<sup>®</sup> software. Instrument operating parameters (Table 1) were optimized daily using a metallic copper strip, with Ag and Au precision and accuracy estimated from replicate analyses of the reference material MAC 80Au – 20Ag with a composition 80 wt.% Au and 20 wt.% Ag. It approximates the average Au and Ag concentrations in our Okanagan placer gold samples.

The SEM-EDS provided Au and Ag concentrations in native gold samples as well as mineral-identifying element con-



1 Laser spot size reduced to 64.1 µm for small Winfield and Lambly Creek gold grains.

centration data for inclusions within the gold grains. The detection limit for most elements was  $\sim 0.1$  wt.%. For Ag and Au in native gold, a minimum of two spot analyses were made per gold grain with at least one core and one rim measurement. Line scans were performed where there was a supergene grain rim, or grain heterogeneity was suspected. Select gold grains were mapped to show elemental zonation of grains. The EDS analyses supplied Ag concentrations used as an internal standard for the LA-ICP-MS trace element analyses.

#### LA-ICP-MS Analysis

Trace element analysis used a Photon Machines Analyte 193 EXCIMER laser coupled with a Thermo Fisher Element XR ICP-MS at FiLTER operated in triple detector mode. Gold and Ag were measured by SEM/EDX. Instrument operating parameters appear in Table 1. Isotopes used to determine the concentrations of 19 trace element concentrations and to use Ag as an internal standard, were measured in low resolution mode and appear in Table 2. Samples and standards went through a one-hour ultrasonic bath in de-ionized water to remove surface contamination. Spot analyses were performed due to the small size of many grains and to avoid inclusions (Table 1). Background was measured for one minute before turning the laser on for a minute. The laser-on time yielded ablation pits with a depth to diameter ratio  $\leq 0.5$  to avoid elemental fractionation effects (Potts et al. 1995; Mank and Mason 1999). Each sample analysis was followed by a minute of washout time and washout was periodically monitored to ensure elements, particularly Hg from samples, did not raise background in subsequent analyses.

GLITTER software (van Achterbergh et al. 2004) was used for data reduction. The laser-on signals for elements were inspected and trace element concentrations calculated from non-anomalous portions of the signal. Silver concentrations from the SEM-EDS analyses on spots of the same size and location as the LA-ICP-MS analyses acted as the internal standard. The London Bullion Market Association (LBMA) AuRM2 gold reference material bearing 22 trace elements (Murray 2009) was used as an external standard. Although AuRM2 appears slightly heterogeneous at a micron-scale (Milidragovich et al. 2016), we used a large laser spot (108.5 µm) and analyzed the standard twice at both the start and end of sample 'runs' to mitigate any effect of microanalytical heterogeneity on calibration. Tetland et al. (2017) showed, using reference material data collected at the same time as our Kelowna area samples were analyzed, that under these analytical conditions AuRM2 is suitably homogeneous for use in LA-ICP-MS 'fingerprinting' given the large natural variations in the composition of native gold. Accuracy estimates used replicate estimates of trace element concentrations in AuRM2 with the Royal Canadian Mint FAU 7 (gold with 14 trace elements added) as an external standard (see results for details).

Four elements, P, V, Hg, and U, not intentionally added during the manufacture of the AuRM2 reference material, were detected by LA-ICP-MS. The contents of P, V, and U in samples are not reported because their concentrations and homogeneity in AuRM2 are unknown. In the case of Hg, Tetland (2015) reported replicate SEM/EDS analyses of two non-Okanagan native gold grains (AUS9 from the Prophet placer gold deposit, Australia and BC1 from an unknown placer occurrence in northern BC) with between 3.1 and 3.5 wt.% Hg. This allowed a semi-quantitative determination of Hg in AuRM2 which was used to estimate concentrations in our Kelowna-area unknowns. We iteratively inserted Hg concentrations into the AuRM2 external reference material file and repeatedly ran GLITTER until the predicted LA-ICP-MS concentrations in the high Hg, non-Okanagan samples matched the concentrations from the SEM/EDS analysis. The match indicates AuRM2 has 3.69 ppm Hg. The estimated Hg concentrations in Okanagan samples are based on this semi-quantitative assessment of the average Hg concentration in AuRM2. An assessment of Hg heterogeneity in the reference material following ISO guidelines described in Jochum et al. (2011) and Tetland et al. (2017) indicates 30% heterogeneity. This is slight-

**Table 1.** Instrument operating parameters.



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 $\frac{7 \text{ Blank cells}}{8 \text{ Average detection limit in ppm from all samples; detection limit is 3 standard deviations above background.}}$ 8 Average detection limit in ppm from all sample analyses; detection limit is 3 standard deviations above background.

7 Blank cells = element not present in FAU7.

ly to somewhat higher than for the 'added' elements in AuRM2 which are generally  $\leq 20\%$  (Tetland et al. 2017). Variability in the reference material will add to analytical uncertainty and be reflected in precision estimates. However, our estimates (results section) indicate that Hg precision is  $\pm$  34%. Precision of 100% reflects variation by a factor of  $\pm$  2, but concentrations vary by a factor of 1900 within the Okanagan data set; far outside what can be ascribed to precision issues. Duplicate analyses of the AuRM2 external reference material at both the start and end of 'runs' helped to average out the impact of any reference material heterogeneity.

The concentrations of 19 trace elements in 23 LA-ICP-MS analyses of Okanagan placer native gold, together with major elements Au and Ag by SEM-EDS, appear in Table 2. Some of the 22 elements (Si, Ca, Cr) added to the AuRM2 reference material were not detected in most of our Okanagan gold analyses and are not reported in Table 2. Silver is a trace element in AuRM2 but a major element in the Okanagan gold analyses. Determination of the semi-quantitative concentrations of Hg in our Okanagan samples (Table 2) was discussed above.

Grains selected for LA-ICP-MS analysis had to be large enough to accommodate a minimum 64.1 µm laser spot diameter and at the same time avoid inclusions. Where present, gold-rich (identified in SEM/EDX scans), yellow-orange 'supergene' rims were avoided because all were significantly thinner than the width of the laser beam and any analyses would be composite.

#### Exploratory Statistical Methods

The exploratory statistical technique known as multi-dimensional scaling (MDS) was used to uncover patterns in sample associations and groupings based on all trace element data for each sample. Greenough et al. (2007) discussed the application of MDS to geochemical data sets. Multi-dimensional scaling has the ability to summarize variance in a data set in a small number of dimensions and thus plots here have 2 dimensions. Dimensions 1 and 2 are unitless and simply represent overall chemical differences based on the elements used to compare samples. Relationships between samples on a MDS diagram are determined from a matrix of sample-versus-sample Pearson correlation coefficients. Two samples plotting close together on the diagram would yield a sample-versus-sample, X–Y plot where all elements form a line yielding a high correlation coefficient. Two samples on opposite sides of the MDS plot would generate a comparatively scattered X–Y plot or a plot with a negative correlation. Because axes on MDS plots are unitless, it is not possible to plot new analyses on the diagram in the future without reprocessing all our data together with the new analyses. Said another way, it is not a classic 'discrimination diagram'.

The MDS diagrams were prepared by: 1) Z-scoring (= standardizing) to put all elements on the same scale so that concentration units do not impact comparisons of samples:

 $Z = (mean x - x)/σ$ 

Where:

mean x is the average trace element concentration

 $x =$  the sample's concentration

 $σ$  = the standard deviation.

2) Data were correlated using Pearson's correlation coefficient = *r*. 3) Matrices of sample-versus-sample *r* values were used to compare samples in Systat™ statistical software (Wilkinson et al. 1992). 4) All calculations used a Kruskal loss function and ≤ 50 iterations to converge input *r* values (measured object distances) with output MDS plot distances (Wilkinson et al. 1992).

# Petrography and Gold Grain Morphology

Gold grain characteristics are summarized below with details in Tetland (2015) Appendix A. Lambly Creek has the smallest average gold grain size (0.18 mm long dimension) with a range of 0.04 to 2 mm. Generally, grains are abraded with moderately smooth to well rounded edges. Many exhibit embayments and folded edges; most have fine grained detrital inclusions embedded in the surface. They are light yellow but range to slightly yellow-orange near the rim (Fig. 2a, 2b). The core of one grain contains < 10 µm, grey-pink anhedral sulphide inclusions (pyrrhotite; Fig. 2c, 2d). Several large primary or detrital quartz inclusions were observed.

Gold grains from Mission Creek were comparatively large, averaged 0.62 mm long, and several multi-millimetre flakes were collected. Grains are extremely flattened compared to Lambly Creek, with most being smooth and well-rounded. Detrital inclusions are limited and primary inclusions were not observed. Colour is mostly light yellow with some deeply coloured, Au-rich rims  $\leq 20$  µmthick (Fig. 2e, 2f).

The Winfield gold grains averaged 0.49 mm long but ranged from fine flour  $(< 200 \text{ }\mu\text{m})$  to flakes  $> 1 \text{ }\text{mm}$ . Edges are subrounded to smooth with evidence of folding and incorporation of detrital grains. Gold colour is light yellow with thin yellow-orange to rare red-orange rims (Fig. 2g, 2h). No definitive primary inclusions were found but one gold grain has a subhedral magnetite grain near the core. The gold pan heavy mineral concentrates contained little or no magnetite, but garnet was abundant.

#### RESULTS

# Precision and Accuracy

Table 2 gives sample element contents, isotopes used for LA-ICP-MS analysis (top row), precision (relative standard deviation, RSD; equation in Table 2 notes) and accuracy estimates. Silver and Au were determined by SEM-EDS analysis  $( \sim 0.1$ wt.% detection limit) and can be considered 'major elements'. Accuracy and precision for Au and Ag were calculated from replicate SEM-EDS analyses of the MAC 80Au–20Ag reference material and are 0.18% and 0.44% for Au and 0.72% and 1.74% for Ag (Table 2).

For trace elements, precision comes from 24 replicate analyses of AuRM2 made in association with the 'unknown' analyses. Silicon, Ca and Cr were added to AuRM2 but we do



Figure 2. Photomicrographs of gold grains from the study area; a), c), e), g) unpolished grains, and b), d), f), h) same grains (respectively) under reflected light after mounting and polishing. a) LAM2 gold grain from Lambly Creek showing in b) a faint Au enriched rim (darker yellow) under reflected light. c) LAM8 gold grain from Lambly Creek. d) Red arrow on polished LAM8 points to a primary sulphide inclusion of pyrrhotite. Note the thin, darker yellow Au-enriched rim. e) MIS2 gold grain from Mission Creek. f) MIS2 shows a deeply coloured Au-rich rim up to 80 µm thick, and the rim has an irregular 'coral-like' contact with the core of the grain. g) Unpolished WIN5 gold grain; note local red-orange tinge on grain surface. h) Polishing reveals a thin Au enriched rim on WIN5; arrow points to small (~ 0.01 mm), interior magnetite grain possibly of primary origin.

not report concentrations for them because low abundance isotopes had to be used during analysis to avoid mass interferences and this resulted in poor precision. Semi-quantitative Hg has an elevated RSD value (34%). Moderately elevated (15– 30%) elements include Mn, As, and Te. All other elements have precision better than 15% RSD (Table 2). Silver acted as an internal standard. Accuracy for elements other than Au and Ag is expressed as the percentage difference between the average  $(n = 24)$  predicted concentration of an element in AuRM2, using FAU 7 as an external standard (FAU 7 concentrations from Penney 2001) and the accepted concentrations in AuRM2 from Murray (2009; accuracy equation in Table 2). Low percentages reflect predicted concentrations close to the accepted concentrations. FAU 7 only contains 16 elements with known concentrations and for the accuracy calculations we assume element homogeneity in FAU 7. Sixty percent of elements (Mg, Ni, Cu, Sn, Pt, Pb, Ti, Mn, Zn) have accuracy between 1 and 10%; higher values were derived for Pb and Bi  $(10-15\%)$ , As  $(22\%)$  and Fe  $(> 40\%)$  (Table 2).

#### SEM-EDS Major Element Results

Only Au and Ag were quantitatively detected by SEM-EDS  $(\sim 0.1 \text{ wt.})$ % detection limit). Silver concentrations in grain cores vary from 5 to 26 wt.% yielding a fineness range of 950 to 740 (fineness =  $Au/(Au + Ag + Cu + Hg + trace$  elements)  $*$  1000); pure gold fineness = 1000). Gold-rich rims occur at each locality resulting in variations in major alloying element concentrations; see the line-scans (Fig. 3), and element maps (Fig. 4). Gold grain cores volumetrically dominate and tend to be homogeneous. Detrital inclusions of magnetite, quartz and possibly feldspars were observed and SEM-EDS analyses show that there are also primary (non-detrital) sulphide inclusions in Lambly Creek grains (Fig. 4b).

Mission Creek samples have an average grain core concentration of 83.4 wt.% Au. Three of five grains have rims with higher Au and lower Ag concentrations with some exhibiting thick  $(20 \mu m)$  Au-rich rims (Fig. 3a). These Au-rich rims follow cracks, crevices and embayments in and along gold grains. MIS2 shows two separate grain core compositions that may reflect the depth that the gold grain was sectioned (Fig. 4a).

Lambly Creek gold has an average core Au concentration of 84.8 wt.%. Rims with higher Au concentrations (up to 100 wt.%) are present in three out of six grains. Internally, the cores of individual grains have homogeneous major element compositions. Grains exhibiting Au-rich rims show relatively sharp core–rim compositional changes. However, not all grains had compositional changes at the rim (Fig. 3b) and are internally homogeneous. The SEM-EDS elemental map for LAM8, a composite grain, shows a very thin, 5 µm-wide Au-rich and Ag-poor rim together with detrital inclusions of quartz and feldspar(?) and a primary sulphide crystal (pyrrhotite; Fig. 4b).

Gold grains from the Winfield mine have an average core Au concentration of 84.0 wt.%. Three out of five grains have a Au-rich, Ag-poor rim with a maximum Au concentration of 98 wt.% and internally the gold grains are homogeneous (Fig. 3c).



**Figure 3**. SEM-EDS line-scans across representative Okanagan gold grains with backscatter images above the scans showing line location, grain boundaries and some internal features. Line-scans were created by measuring relative intensity of element-diagnostic K, L and M series X-ray signal peaks for detectable elements along the line. Grains tend to show Au-rich rims and Ag concentrations drop at grain edges. a) Gold grain MIS4 has Au-rich rims and an embayment with detrital material fill on the left side. In b) grain LAM7 shows internal homogeneity and no Au-rich rims. c) In WIN5 the Ag signal (green) dies off on the outer two microns of the grain. Note that the X-axis distance scale is very different on each graph.

#### LA-ICP-MS Trace Elements

Data and averages for each placer occurrence (Table 2) show that the most abundant trace elements (defined here as  $\leq 0.1\%$  $=$  < 1000 ppm) are Hg and Cu; they are over 10 times higher than all other trace elements except Fe. Mercury is particularly high with some analyses approaching 1000 ppm. The least abundant element, Rh, is consistently  $\sim$  50 ppb. All other elements fall between 0.1 and 10 ppm.

Mean Cu, As, Rh, Pd, Sn, Sb, and Te do not show large differences between localities though samples from Lambly Creek have lower average abundances for most trace elements, aside from Cu and Sb, which are higher in these samples (Table 2). Mission Creek samples are enriched in the lithophile ele-



**Figure 4.** SEM-EDS composite image element maps showing major element analyses for areas in a single gold grain. Colours represent proportional intensity of signal in cps for individual elements detected. a) Coloured map showing variations in major element concentrations in MIS2. Note very distinctive Au-rich and Ag-poor rim surrounding the grain's core. b) Coloured map of LAM8 gold grain which shows a less distinctive Au-rich rim and various mineral inclusions within the gold grain. Rectangles (e.g. Spectrum 68), lines and points provide an example of the spatial distribution of places in grains analyzed to determine major element variation and composition of grains.

ments Mg and Ti, as well as siderophile and chalcophile Fe, Ni, Zn, Se, Pt, Bi, and Hg, but have low Pb. Winfield gold grains have abundant Al, Mn, Pd and high Hg.

Probability plots (Fig. 5) illustrate differences in element concentrations between localities, and the distribution of concentrations between samples at one locality. Trends for Fe, Se, and Hg data are sub-parallel for all localities but Mission Creek is distinguished by higher concentration ranges. All Winfield analyses show very similar Cu values but Mission and Lambly creeks have variable Cu concentrations. In addition, Te concentrations are higher in Winfield samples. Rhodium and Pd values show similar trends for all three locations. Overall, Lambly Creek samples are perhaps most distinct with somewhat lower concentrations for a number of elements, particularly Bi, Hg and Pt, and Pt is also highly variable.

A MDS plot (Fig. 6), calculated using the quantitative trace element data, places samples/analyses with similar trace element signatures close together. The major elements Au and Ag were not used in preparing the graph, nor was semi-quantitative Hg, but inclusion of Hg in the calculations does not significantly change the relative positions of samples/analyses. Thus, the plot summarizes the relationships between the analyses of samples, based on 18 element chemical space, in only two dimensions. Mission Creek and Winfield analyses plot together although with some scatter. Lambly Creek analyses plot in two discrete fields with the smaller field containing two analyses from the same gold grain (LAM7).

#### **DISCUSSION**

#### Precision, Accuracy and Homogeneity

Precision and accuracy, and homogeneity of AuRM2 are assessed in Tetland et al. (2017) based on data collected while analyzing our Kelowna-area samples. Reproducibility of AuRM2 analyses (Table 2) reveals that, of the 18 LA-ICP-MS trace elements with certified homogeneity at a macroscopic scale, seven (39%) have precision (% RSD) better than 10% (Mg, Al, Ti, Ni, Cu, Zn, and Sn), nine (50%) are between 10 and 15% (Fe, As, Se, Rh, Pd, Sb, Pt, Pb, and Bi) and two (11%) fall between 15 and 20% (Mn and Te). Silver was added to AuRM2, but LA-ICP-MS precision cannot be estimated because it was used as the internal standard. Precision and accuracy for Ag and Au in Table 2 were calculated from replicate SEM-EDS analyses of the MAC 80Au–20Ag reference material and are excellent. Mercury is present in AuRM2 at detectable levels, but not intentionally added during manufacture, and therefore not certified for homogeneity at any scale. Precision on Hg is 34%. The precision estimates for half the elements (10 to 15%) reflect modest signal (background-corrected counts per second  $=$  cps) as a result of low concentrations in AuRM2 (Table 2; Tetland et al. 2017). The moderately elevated RSD values of Mn and Te are primarily due to low signal intensity, but are acceptable for the purposes of this study. The reproducibility of AuRM2 element concentrations provides a metric for expected reproducibility of duplicate sample analyses of natural gold. Most elements exhibit variation due to analytical precision that is negligible compared to natural geochemical variation in placer gold systems (Table 2).

Accuracy (Table 2; Tetland et al. 2017) was estimated by treating AuRM2 as an unknown, using the matrix-matched gold reference material FAU 7 as an external standard and comparing the mean  $(n = 24)$  calculated concentrations in



Figure 5. Probability plots of select trace elements (ppm) from Kelowna area samples. These plots order individual analyses from each locality from lowest to highest concentration for each element. A normal score of 0 (X-axis) represents the median value for an element from each locality, and element concentrations on the Y axis are in ppm.

AuRM2 with those determined by bulk solution ICP-MS (Murray 2009). The calculations assume FAU 7 is homogeneous and since it shows some heterogeneity the accuracy estimates represent minimum values (Tetland et al. 2017). For the 15 trace elements added to FAU 7 (excluding Ag, the internal standard), reasonable accuracy was confirmed with most elements showing less difference  $($  < 10%) from given values than variation associated with precision (generally better than 15%; Table 2). Iron shows the poorest accuracy.

Tetland et al. (2017) assessed homogeneity in AuRM2 and concluded that all added elements are suitably homogeneous for use in LA-ICP-MS fingerprinting studies of native gold. For Hg, which was not intentionally added to AuRM2, some component of the variability reflected in precision estimates (Table 2) is probably due to heterogeneity in the reference material.

#### Comments on Inferring Potential Sources of Gold

Sections below review potential bedrock sources of our native gold samples. The composition of gold from these sources is unknown but their geologic environment, and gold environmental discrimination diagrams from the literature can potenis that the major and trace element composition of bedrock gold may be modified by metamorphism and gold remobilization in low-melting point chalcophile element rich melts (Hg, Te, Sb, Bi) resulting in higher purity gold with lower silver, and elevated Hg (Hastie et al. 2020; Hastie et al. 2023; Melo-Gómez et al. 2021, 2022). The elemental signature of gold in a primary deposit may be lost or obscured and placer gold will reflect the impact of these secondary processes. Similarly, diffusion of trace elements in a weathering or near-surface environment might theoretically modify the composition of gold. There are gold-rich rims on some of our Winfield and Mission Creek grains, but replicate analyses of the interior of grains (e.g. MIS1, 1B, 1C; Table 2; Fig. 6) indicate homogeneous compositions and there are no gold-rich zones in the interior of grains that support amalgamation of grains with different sources and histories. Finally, mercury has been used to collect gold at surficial temperatures from ore during mining and so placer gold might scavenge Hg in the weathering environment. However, there is no evidence for detectable Hg in the SEM line scans across gold-rich rims of our Winfield and Mission Creek gold (Fig. 3).

tially narrow sources for the samples. A possible complication







**Figure 6.** MDS plot comparing the overall composition of Kelowna area samples based on all trace elements in Table 2 except semi-quantitative Hg and excluding major elements Au and Ag. Samples plotting close together tend to have similar geochemical compositions. Fields illustrate that Lambly Creek (LAM) analyses plot in two separate fields apart from Mission Creek (MIS) and Winfield (WIN) analyses. For more explanation of the MDS methods, see the earlier section on Exploratory Statistical Methods.

# Winfield and Mission Creek Gold

The cores of all placer gold grains from the three gold localities Winfield, Mission Creek and Lambly Creek show high Ag/Au and low Cu/(Au + Ag) ratios ( $> 0.08$  and  $< 0.0004$ , respectively) indicating they came from mesothermal/hypogene or Au porphyry bedrock sources (e.g. Townley et al. 2003). However, the Mission Creek and Winfield placer gold grains show cores with somewhat similar hypogene gold compositions which are mantled by Au-rich rims formed in a supergene environment. In contrast, the Lambly Creek gold grains largely lack supergene Au-rich rims and form two geochemical populations of gold, both distinct from Mission Creek and Winfield placer gold. Due to the modest number of samples, subjective descriptive grain morphology alone would be inadequate for distinguishing gold bedrock sources. However, when also examining quantitative geochemical analyses of grain compositions, discussed below, Lambly Creek gold appears distinct from Mission Creek and Winfield gold. We compare Mission Creek and Winfield placer gold and explore potential bedrock sources and travel history and then contrast them with Lambly Creek gold.

Major and trace element data support a similar bedrock environment of formation, and similarities in the transport history for Mission Creek and Winfield gold. Descriptive morphology and inclusion information supports these interpretations though the small number of grains would make conclusions based solely on this information unreliable. In addition to both Mission Creek and Winfield gold exhibiting Au-rich supergene rims, grains have a similar size distribution, from flour gold  $(< 200 \mu m)$  gold to millimetre-size flakes, and most show a flattened and rounded morphology. These properties indicate an extended transport distance (Grant et al. 1991) and prolonged exposure in weathering environments (see supergene text below). Individual Mission Creek and Winfield grains have variable compositions but exploratory statistical methods (MDS plot; Fig. 6), which simultaneously use all element data to portray relationships, indicate that overall the Mission Creek and Winfield gold grains have significantly overlapping compositions which are distinct from Lambly Creek gold. In addition, simple averages (Table 2) and ranked probability plots (Fig. 5) confirm that, for most elements, the gold grains from the two localities are similar. However, Fe, Se and possibly Hg appear higher in Mission Creek, compared to Winfield gold, but this may be misleading. It is not obvious that there is information available for Proterozoic or Phanerozoic Au deposits but Fe in Archean Abitibi mesothermal gold deposits (Greenough et al. 2021; Se and Hg data unavailable) is highly variable. The standard deviation on the mean divided by the mean  $*100$  is 116%, 256% and 109% for the Hollinger, McIntyre and Aunor deposits (respectively), whereas for all Mission Creek and Winfield analyses together it is only 66%. This indicates Mission Creek and Winfield gold was derived from distal, similar types of deposits, or possibly different portions of the same deposit. An assessment of whether element variability in the Okanagan gold samples reflects micro-inclusions, which would confound fingerprinting, is given in the section Trace Element "Fingerprinting" of Native Gold.

Various limitations can be placed on the potential original hypogene source or sources for Mission Creek and Winfield gold. In the case of Mission Creek gold, the extent of the current fluvial system does not appear to account for the extensive transport indicated by morphology. There are two Mo-Cu porphyry occurrences, Tick and Nova (White 1968; Osatenko 1980), close to the Winfield paleoplacer occurrence (Fig. 1) but they are unlikely sources because they are not Au or Au-Cu porphyry showings. Gold from Au-rich porphyries tends to exhibit a higher Cu content than that from orogenic settings (Morrison et al. 1991; Townley et al. 2003) though we note that metamorphic gold remobilization may result in higher purity gold with higher Cu and lower Ag (Hastie et al. 2020, 2023; Melo-Gómez et al. 2021, 2022). All our analyses have low Cu (Table 2). The proximity does not explain the morphological indications of significant transport distance. There are no known gold sources for either the Mission Creek or Winfield placer gold in the local Omineca belt plutonic and metamorphic rocks on the east side of the Okanagan Fault. The metamorphic rocks experienced amphibolite-facies conditions and contain < 5 cm-wide quartz veins and pods (Nesbitt and Muehlenbachs 1995) that are unlikely gold sources.

Boyle (1982) made paleohydrologic reconstructions, apparently based on present-day altitude of bedrock below stream channels and not on sedimentary structures, for Miocene to early Pliocene coarse-grained clastic sediments underlying plateau basalt east of Kelowna. The results suggest northwest to southeast water flow in Miocene to early Pliocene rivers that yielded the gravel deposits and placer gold at the Winfield Mine. The modern-day, geochemically and morphologically similar Mission Creek placer gold may have had a similar geographic origin to the Winfield Mine gold. Potential bedrock sources for the Mission Creek and Winfield placer gold are

extensive, uneconomic, quartz-carbonate vein gold occurrences predominantly in greenschist-facies rocks of the Omineca belt (Nesbitt and Muehlenbachs 1995). However, elsewhere in the Omineca belt there is significant orogenic gold mineralization (Zhang et al. 1989); vein fluid inclusions indicate  $H_2O$ -CO<sub>2</sub> fluids with minor CH<sub>4</sub> at 300–380 C (Nesbitt and Muehlenbachs 1995). This is the most likely source in the region for the hypogene portion of Mission Creek and Winfield placer gold, but we cannot eliminate the possibility that the actual source deposits have been completely or partially eroded away, or that the gold came from widespread, but small and/or low grade, uneconomic occurrences.

A supergene gold rim can be seen on Mission Creek and Winfield placer gold grains (Figs. 3 and 4). Major element analyses show significant Au-rich rims on grains indicating extended exposure to surficial or weathering environments. Variability in Mission Creek and Winfield gold trace element signatures is reflected in the Figure 6 MDS plot and may be related to grains containing a hypogene core and supergene rim. Although we attempted to avoid rims during LA-ICP-MS analysis any overlap of core and rim regions in the laser ablation pits could have led to intermediate trace element signatures.

Modes of supergene gold formation are not well established. Hypotheses include electro-refining (Groen et al. 1990; McCready et al. 2003), coupled dissolution and reprecipitation (Putnis 2009) and bacterial precipitation (Reith et al. 2010). The formation of supergene gold rims on these samples due to dissolution of Ag is unlikely, because as an incipient Au-rich rim forms it would shield the dissolution of additional Ag deeper within the grain. Diffusion rates of Ag in gold grains are extraordinarily low at low temperatures (Groen et al. 1990) and cannot account for the thickness of Au-rich supergene rims. This leaves the possibility that organic (bacterial) precipitation, inorganic precipitation, or electro-refining formed the supergene rim.

Microbially precipitated gold documented at the Prophet gold mine (Reith et al. 2010, 2013) is typified by the presence of biofilms containing nanoparticulate, biologically precipitated gold that aggregates to the placer gold grain and shows a reddish surface tinge. A similar reddish tinge occurs on some Winfield samples (Fig. 2g). Although reddish Fe-oxides could occur on gold grains in various sedimentary environments, the high gold content of Winfield rims is another feature resembling the biologically precipitated Prophet gold (Reith et al. 2010, 2013). Gold grains mobilized in an active fluvial placer system may have these surface films removed because they are not commonly observed on Mission Creek grains. It is likely that such films would be favoured on gold grains that are in an immobile position for a long period of time, or precipitation may occur after the placer system becomes dormant (e.g. Winfield). This is supported by a study at Rich Hill, Arizona, where films only occur on immobile gold grains (Kamenov et al. 2013). The Winfield and Mission Creek samples of this study support microbial precipitation even though they were not collected to best preserve films (cf. methods in Reith et al. 2010).

The U mineralization associated with sediments hosting the Winfield paleoplacer gold is significant as the redox-controlled U mineralization is epigenetic and related to circulation of post-depositional fluids (Boyle 1982). Fluid circulation for an extended period of time after deposition of the placer gold would provide an opportunity for precipitation of supergene gold. Unlike Mission Creek, and especially Lambly Creek, the heavy mineral concentrate at the Winfield site did not contain magnetite which is typically abundant in placer settings (Boyle 1979). It is possible magnetite was destroyed by oxidation to hematite from significant volumes of oxidized fluids. Oxidized settings may promote Au mobilization as a soluble uranoorgano-gold complex. This mode of transportation has been proposed to explain formation of secondary gold in the world class Witwatersrand gold deposits in South Africa (Large et al. 2013) and coprecipitation of Au and U has been noted in some Australian deposits (Wilde et al. 1989; Mernagh et al. 1994) although in these cases high gold mobility was ascribed to high Eh and chloride complexing.

In summary, Winfield and Mission Creek placer gold appears to have similar hypogene bedrock sources for the cores of grains. Mission Creek gold is modern (Holocene) and apparently derived from interglacial (Pleistocene?) sediments eroded from conglomerate at the base of the Rutland aquifer. Both sediments are younger than the coarse-grained Miocene river sediments that contain the Winfield gold. Both Mission Creek and Winfield gold grains show low-Ag supergene rims indicative of prolonged exposure to a weathering environment and the morphology of grains indicates extensive transport. These features suggest significant reworking and recycling of placer gold on the east side of Okanagan Lake. The Miocene age paleoplacer gold deposits (Winfield type) have been eroded and reworked in at least one, and possibly more, cycles of erosion into contemporary creeks such as Mission Creek.

# Lambly Creek Gold

Lambly Creek placer gold displays marked differences in composition compared to gold from the east side of the Okanagan Fault. Morphologically the grains are rougher, less flattened, smaller in size, and carry abundant primary mineral inclusions. The irregular shape and presence or preservation of primary mineral inclusions in small grains implies a proximal gold source. There is little variation in the major element chemistry of grain cores compared to other Kelowna samples, and Aurich rims are poorly developed to absent on Lambly Creek gold. This suggests very limited supergene precipitation and less time under surficial conditions.

The Lambly Creek gold carries two trace element signatures, both distinct from Mission Creek/Winfield fingerprints (Fig. 6). Two analyses had hundreds of ppm Cu, an order of magnitude more than the other Lambly Creek analyses (Table 2). A possible source is the porphyry Cu-Mo Brenda deposit 25 km southwest of Lambly Creek, but it is not known to contain native gold (Weeks et al. 1995). The Elk deposit, 55 km west of Okanagan Lake, contains free gold in intrusive-hosted quartz veins and represents another possible source containing

up to 301,000 oz of Au (Pooley et al. 2011) but Cu is not a significant metal in the deposit (Northcote 2022). The high Cu Lambly Creek analyses, and associated Ag concentrations, resemble some greenstone-hosted orogenic gold from the McIntyre and Aunor mines in the Abitibi Greenstone Belt, Timmins, Ontario, Canada (Greenough et al. 2021). Geologic mapping (Lenard 1987a) shows a small greenstone belt within the catchment basin which contains a vein hosted Au-Ag occurrence, the Bond showing (labelled 8 on Fig. 1), assaying up to 12  $g/t$  Au. Based on available information, this is perhaps the most likely source of the high-Cu gold grains.

The origin of the other type of Au is even less certain because there are several primary gold mineralization sources in the Lambly Creek catchment (see Geological Setting section). The Au mineralization could be related to emplacement of the Okanagan Batholith and possible sources include the stockwork Au-Ag-Pb-Zn veins of the Shear (Lenard 1987b) or Zumar occurrences (Murray 1991), skarn-related mineralization of the Lamb occurrence (Pautler 1988), or the low sulphidation Spod occurrence (Gourlay 1989). The Brenda Cu-Mo porphyry deposit (with Au-Ag as a by-product; Greenough et al. 2004) represents another possible source but as noted above it is not known for native gold (Weeks et al. 1995). In addition, the Elk deposit described above contains free gold and is a possible source (Pooley et al. 2011; Northcote 2022).

The dramatic differences in gold across the continent-scale Okanagan Fault appear to be related to tectonism and fault movement. Gold in Miocene to Recent placer gold deposits on the east side of the Okanagan Fault (Winfield and Mission Creek gold) has similar hypogene bedrock sources, supergene rims indicating prolonged exposure to weathering environments and external morphology consistent with extensive transportation. This indicates that continual movement on the upthrown side of Okanagan Fault over tens of millions of years led to continual recycling of placer gold, development of supergene rims, and gold morphology indicative of extensive transport as a result of recycling. In contrast, placer gold on the west side of the fault has not been recycled and shows hypogene gold compositions consistent with derivation from presently exposed bedrock sources. Compared to the west side of the Okanagan Fault the recycling of placer gold on the east side led to larger and higher grade placer 'deposits', compared to the west side over time (Garnett and Bassett 2005). Thus, these geological processes apparently had a major impact on the settlement and economic development of the BC interior and Kelowna area.

# Trace Element "Fingerprinting" of Native Gold

To use trace or minor elements to fingerprint native gold and determine if concentrations are representative of a deposit, it is important to know if an element is dissolved in gold or largely present in randomly distributed micro-inclusions. Selection of spots for analysis in individual BC gold grains avoided visible inclusions but sub-micron mineral inclusions might not be obvious in the one-minute signal used to calculate element concentrations. Exploratory statistical analysis (e.g. principal component analysis or multidimensional scaling) has been

used to compare element behaviour in multiple analyses of samples from one ore deposit and uncover element associations suggesting the presence of sub-micron mineral grains. The deposit origin of our BC gold samples is not known and so this approach cannot be used to assess the presence of micro-inclusions, but we review what was learned from previous studies. McInnes et al. (2008) studied Mesozoic mesothermal gold from a showing in central British Columbia and found that of the detected elements (V, Fe, Cu, As, Pd, Ag, Sb, Pt, Au and Bi) only Fe and As correlate indicating they may be controlled by arsenopyrite inclusions in the native gold. Greenough et al. (2021) evaluated element associations in three Archean, Abitibi greenstone belt deposits, Hollinger, McIntyre and Aunor. They noted chalcophile (Cu, Pb, Zn, Te, Sb, As, Bi, Sn) and siderophile (Ag, Pt, Pd, Rh, Fe?, Ni, Cr) trace or minor elements tend to fingerprint deposits and appear to be dissolved in Au. Lithophile elements (Si, Ti, Al, Mn, Mg, Ca) proved minimally useful for distinguishing deposits and some element concentrations may be controlled by micro-inclusions such as tourmaline. Liu et al. (2021) found that Fe, As, S and Hg can form lattice impurities or micro-inclusions in native gold but Liu and Beaudoin (2021) argued that Pd, Ag, Sb, Pb, Cu, Hg, and Te contents have a high potential to discriminate gold from different deposit types. The above information is supported by earlier experiments (Watling et al. 1994; McCandless et al. 1997; Miller et al. 2001; Penney 2001). As a generalization, the chalcophile and siderophile elements tend to be dissolved in gold, or occur as lattice impurities, and are useful for fingerprinting, but there are deposit-specific deviations from the norm where concentrations may largely reflect randomly distributed micro-inclusions.

Mean concentrations of elements by locality in Table 2 imply that Si, Ca and Cr should be important for fingerprinting native gold, but these elements have low precision and accuracy and we cannot eliminate the possibility that mean differences are related to the interception of silicate/oxide microinclusions by the laser. However, we saw no evidence of these in the time-resolved signal received by the ICP-MS. If present, the micro-inclusions were so small that mixing during sample cell wash-out prevented seeing anomalies in the signal. If these elements are impacted by micro-inclusions, the order-of-magnitude differences in Mg, Al and Ti could reflect intersection of silicate and/or oxide phases. Other elements with 2 to 45 times concentrations differences between mean Winfield, Mission and Lambly creeks analyses include Fe, Ni, Cu, As, Se, Rh, Pd, Te, Pt, Hg, Pb, and Bi (Table 2) with Hg concentration differences the largest. Of these, the probability plots show that Mission Creek samples have high Fe, Ni, Se and Hg but low As. Bismuth is similar in Mission Creek and Winfield samples and higher than in Lambly Creek. Winfield samples have the highest Te and Pb. Lambly Creek samples have the lowest Fe and Cu (except two have the highest Cu observed) and the lowest Pt, Bi and Hg. Overall, Winfield samples tend to have intermediate compositions that are closest to Mission Creek.

Over forty elements have been detected in native gold using various analytical techniques (e.g. Antweiler and Campbell 1977, 1982; Watling et al. 1994, 1995, 2014; McCandless et al. 1997; Outridge et al. 1998; Watling 1999; Penney 2001; Rasmussen et al. 2006; Brostoff et al. 2008); McInnes et al. 2008; Banks et al. 2018) but various analytical issues have compromised the determination of actual trace element concentrations. Confirmation of homogeneity in AuRM2 (Tetland et al. 2017) opened the door to the use of LA-ICP-MS to study the trace element composition of gold. Based on the results here (e.g. Figs. 5 and 6) the chalcophile trace elements Cu, As, Se, Sb, Te, Hg, Pb and Bi, and siderophile Fe, Ni, Pd and Pt are particularly useful for distinguishing Kelowna area gold samples. Of all these elements, Hg shows the largest range in concentrations indicating it could be particularly useful for fingerprinting. Our results corroborate studies of the composition of gold in numerous deposits across Ontario, Canada (Melo-Gómez et al. 2021, 2022) where Hg, Sb, Pd, and Cd concentrations are independent of gold content and apparently reflect geological factors. Copper concentrations tend to negatively correlate with Au due to closure; as Au goes up, other elements go down, but like us, these studies found that Cu fingerprints deposits. Future work should accurately determine Hg in AuRM2 using solution analytical methods and ascertain the degree of homogeneity in the reference material at the micro-analytical scale.

# **CONCLUSIONS**

- 1. Gold from Lambly Creek on the west side of Okanagan Fault has smaller grain sizes than from Mission Creek or the Winfield mine (east side). Lambly Creek grains show embayments, folded edges, are abraded and moderately smooth to rounded and contain primary and detrital inclusions. In contrast Mission Creek and Winfield grains are flatter, smooth and rounded, lack inclusions, and have deeply coloured, yellow-orange to rare reddish orange, < 20 µm Au-rich rims; characteristics suggesting distant transport and prolonged exposure to surface and supergene conditions
- 2. Placer gold in Mission Creek appears recycled from Miocene paleoplacer deposits such as at the Winfield Mine as a result of continual isostatic uplift of unearthed rocks on the east side of Okanagan Fault. There is no obvious local hypogene gold source for Mission Creek and Winfield gold. Future mineral exploration should focus on Miocene fluvial deposits.
- 3. Extended time (Miocene–present) under surficial conditions with post-depositional circulation of oxidized fluids (also related to U-mineralization) led to supergene gold precipitation on Kelowna area paleoplacer gold. Gold may have been carried as urano–organo–gold complexes, chloride complexes, or precipitated microbially as nanoparticles.
- 4. Two distinct trace element signatures were found for Lambly Creek gold supporting ≥ 2 hypogene sources for placer gold in the catchment. One group of grains has elevated Cu and could carry an orogenic gold signature sourced from the greenstone-hosted Bond occurrence. The low Cu group appears to have an intrusion-hosted gold signature.
- 5. Many trace elements show average concentration differ-

ences among the three sampling sites from 2 to over 45 times. The chalcophile elements Cu, As, Se, Sb, Te, Hg, Pb and Bi, and siderophile elements Fe, Ni, Pd and Pt are particularly useful for distinguishing Kelowna area gold samples. Of all these elements, Hg shows the largest range in concentrations indicating the element will be particularly useful for future fingerprinting studies.

6. Future work should confirm the concentration of Hg in AuRM2 using solution analytical methods and ascertain the degree of homogeneity in the reference material at the microanalytical scale.

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