Accepted Manuscript

Geological Society, London, Special Publications

Evaluation of the contributions of gold derived from hypogene, supergene and surficial processes in the formation of placer gold deposits

R. J. Chapman, D. Craw, N. R. Moles, D. A. Banks & M. R. Grimshaw

DOI: https://doi.org/10.1144/SP516-2020-260

To access the most recent version of this article, please click the DOI URL in the line above. When citing this article please include the above DOI.

Received 8 December 2020
Revised 23 April 2021
Accepted 18 June 2021

Evaluation of the contributions of gold derived from hypogene, supergene and surficial processes in the formation of placer gold deposits

R.J. Chapman[1*], D. Craw[2], N.R. Moles[3], D.A Banks[1], M.R. Grimshaw[4]

1. *Ores and Mineralization Group, School of Earth and Environment, University of Leeds, Leeds LS29JT*

2. *University of Otago, PO Box 56, Dunedin, New Zealand*

3. *School of Applied Sciences, University of Brighton, Lewes Road, Brighton BN2 4GJ, UK*

4. *RSC Mining and Mineral Exploration, Level 2, 109 Princes Street, Dunedin 9016, New Zealand *Corresponding Author (email: r.j.chapman@leeds.ac.uk),* ORCID: 0000-0003-3212-131X

ABSTRACT

Placer gold particles have traditionally been considered as either detrital products of weathering or authigenic minerals growing within placers. Recent advances in understanding of gold chemistry/bio-geochemistry demonstrate that gold growth in specific environments is plausible, but opinions differ on the importance of 'new' gold in the overall placer inventory. Here we draw upon visual inspection over 40,000 polished gold particle sections from locations worldwide to evaluate the implications of gold alloy composition and particle heterogeneity in determining the contributions of detrital and authigenic gold to fluvial placers. We conclude i. the detrital model of placer gold formation is widespread and demonstrable, ii. supergene gold may be a locally important constituent of fluvial placers, iii. gold-rich rims on placer gold particles comprise two distinct components: a surface micron-scale addition of pure Au and a tens- of- micron- scale inner rim formed by Ag depletion, iv. the importance to placer inventories of gold particle formation and modification by biogenic processes is considerably overstated.

KEYWORDS: *placer, gold, silver, mineral inclusions, nugget, supergene, hypogene, fluvial*

Gold particles are present in a variety of surficial sediments as a consequence of different chemical and/or physical processes. The origin of the gold is ultimately hypogene source(s) that have been exposed to weathering and erosion, but climatic and geomorphological factors govern the fate of gold in the surface environment. This paper is concerned with applying our understanding of the mineralogical nature of hypogene gold and subsequent modifications to the particle size, shape, (Fig. 1a-c) and chemical composition (Fig 1d-f) of individual gold particles in sedimentary systems. The aim is to gain a clear understanding of the origins of gold particles within placer deposits.

The various pathways that connect the gold source to expression in surface sediments has been the subject of considerable research, much of which has focussed on application in exploration (e.g. McClenaghan and Cabri 2011). The significance attached to gold values recorded during soil sampling campaigns has encouraged detailed studies of the behaviour of gold in weathering profiles (summarized in Freysinnet et al. 2005) and detailed studies of gold transport in glacial till (McClenaghan and Paulen 2018). In contrast, although placer deposits are the most easily accessible forms of gold concentrations they have not been utilized to the same extent in exploration campaigns, because the genetic relationships between source and placer may be clouded by the potential for chemical modification within the fluvial environment. The simplest placer deposit model involves hydrodynamic concentration of liberated gold particles as a consequence of their extreme density, and in this scenario it is straightforward to investigate compositional relationships between source and placer. This approach would be undermined if the gold particles were modified during residence in surficial environments. The potential for compositional modification has been discussed since the advent of systematic placer mining, and various commentators have suggested gold growth in surficial sediments as a likely cause of apparent replenishment (e.g. Boyle 1979; McCready *et al.* 2003). Boyle, (1979) considered the various arguments for contributions from detrital and authigenic gold and concluded that the relative importance of different models was site specific. Since Boyle's work, there have been various developments in our understanding of low temperature gold geochemistry (e.g. Craw and Lilly 2016), generic gold biogeochemistry (e.g. Shuster and Reith 2018; Rea *et al.* 2018) and the mineralogical nature of gold particles collected at various localities worldwide (e.g. Butt *et al.* 2020; Chapman *et al*. 2021). In addition, a large body of work focussing on New Zealand (e.g. Craw and Lilly 2016 and references therein) supports the formation of cm-scale gold nuggets in supergene environments overlying the hypogene ore. This paper updates the considerations of Boyle (1979) with a review of subsequent studies and their implications for our understanding of the origins of gold particles within placers. As a starting point, the refined models for the origins of gold particles in placers may be described as follows:

i. Detrital model: following erosion, gold particles from hypogene ore pass, unmodified, into the surficial sediment.

ii. Supergene model: gold mobility in solution at specific Eh-pH conditions results in the growth of particles in the supergene zone immediately above hypogene ore.

iii. Biogenetic model: biogenic activity in surficial environments results in accumulation of gold either *ab initio* or on pre-existing gold particle substrates to form new particles, and to enlarge and/or transform pre-existing gold particles.

iv. Inorganic model: inorganic processes which may variously deposit gold or modify pre-existing alloy composition through Ag removal.

The various models are not necessarily mutually exclusive in the context of a single gold particle. Detrital particles are subject to various processes that can modify their composition to generate heterogeneous internal textures such as gold-rich rims and internal gold-rich films (e.g. Chapman *et al*. 2021 and references therein). Gold nuggets formed in the supergene environment are subject to the same subsequent chemical and physical influences that affect detrital particles (Craw and Lilly 2016). Advocates of the biogenic model have suggested that detrital particles may 'seed' gold growth (e.g. Reith *et al.* 2010).

An understanding of the origins of gold particles in surficial sediments is important for several reasons. From a scientific perspective it is important to understand the implications of both inorganic and organic process which influence gold particle size and abundance in the surficial environment. The potential for authigenic gold to form within the placer environment, or ubiquitous modification of alloy textures that eradicate primary features clearly have implications for developing exploration methods that utilise characteristics of particulate gold as a vector to source. Lastly, placer mining strategies could be influenced if natural replenishment of mined areas occurs on a suitable timescale.

Natural gold is often regarded as an inert material comprising homogeneous alloy. Recent studies have demonstrated marked heterogeneity within gold particles that may result from changing conditions within the ore forming stage, the weathering environment and in fluvial settings during the protracted evolution of placer deposits (Chapman et al. 2021 and references therein). Each of these stages yields distinctive features within placer gold particles (Fig. 1g-j) and this consideration of the nature and abundance of compositional features within placer gold particles permits an evaluation of their origins. This contribution draws upon the wide range of literature available together with the authors' experiences from the examination of over 40,000 gold particle sections from hypogene and placer localities worldwide and large collections of supergene particles from New Zealand. Our focus is specifically gold present in fluvial (or palaeo-fluvial) settings, and we include discussions of the chemical behaviour of gold in weathering profiles only where those particles may subsequently pass into fluvial systems, and where their mineralogical characteristics permit correlation with genesis.

TERMINOLOGY

This contribution has adopted a standard terminology to ensure clarity and remove the potential for ambiguity. Definitions of various terms are presented below:

i. Nugget: we have adopted the definition of Hough *et al.* (2009) which uses either a size characteristic (>4mm longest dimension) or a mass of >1g.

ii. Gold grain: the domain of a continuous gold crystal, of which particles may comprise one, several, or many.

iii. Gold particle: a single physical entity commonly comprising several gold grains.

iv. Gold alloy: the chemical composition of gold and associated metals. Many studies adopt the term 'fineness' (wt% Au x 1000)/(wt% Au + wt% Ag), excluding other minor metals whose concentration may be significant and informative. The term 'electrum' is used in various contexts, often without definition, but we prefer the term 'gold alloy' because it is unambiguous and encompasses all concentration ranges of all the alloying metals. The term 'gold' is employed in the context of the mineral whereas 'Au' is used when referring specifically to the element: e.g. 'the wt% Au content of a gold particle'.

v. Hypogene gold: gold formed in the original mineralizing event, i.e. a hydrothermal or orthomagmatic system.

vi. Authigenic gold: gold particles and particle overgrowths formed in situ from chemical dissolution and re-precipitation. This includes supergene gold, formed in the weathering zone of hypogene deposits (including laterite) prior to erosion, and gold that is re-precipitated in situ within placer and palaeoplacer deposits.

vii. Proximal detrital: implies a direct genetic link between gold particles in the surficial environment and their source. This may be used in the context of 'proximal primary detrital', in relation to a local unoxidised hypogene source (dominantly mechanically weathered?) or 'proximal secondary detrital' in relation to local supergene gold (chemically and mechanically weathered?). The term 'proximal detrital' is used unqualified where the text applies to both categories.

viii. Evolved detrital: implies a gold particle has a more complex transport/residence history that may involve recycling from older sediments.

ix. Core: the main central zone of a detrital gold particle and may include gold of differing grain textures and inclusions of various other minerals.

x. Outer rim: Gold encrustations: c 1 µm scale amorphous and/or crystalline pure gold coatings attached to the inner rim.

xi. Inner rim: the outer zone of a detrital gold particle that is typically < 20 µm thick and has low Ag content.

xii. Eluvial gold particles: gold particles in weathered and disaggregated bedrock and nearby colluvium. Some of this gold is essentially in situ within the scapolite and some has moved downslope short distances (typically <200 m).

xiii. Placer: a concentration of primary and/or evolved detrital gold particles in an active transport and depositional system. In this study we discuss only alluvial placers.

xiv. Palaeoplacer: a detrital gold concentration in an older sedimentary system (Pleistocene-Archaean) that is no longer in an active sedimentary system, typically because of uplift, burial, or river drainage re-orientation.

xv. Sample population: gold particles collected from a specific locality.

GOLD IN HYPOGENE SETTINGS

The precipitation of gold from hydrothermal solution is a consequence of changes in P-T-X at the point of mineral precipitation, but the controls on the particle size of gold remain unclear. Particle size may be constrained by accommodation space during precipitation although this factor is unlikely to account for the micron-sized particles found in many economically important deposits. The size of gold particles may be a function of paragenetic stage, for example in porphyry Cu-Au deposits within the potassic alteration stage, gold of c. 1-20µm size has exsolved from chalcopyrite and bornite (Simon et al. 2000). Coarser gold particles may be formed in later-stage mineralization within the evolving hydrothermal system (Chapman *et al.* 2017). Generic classification of gold particle size into smaller (early-formed) and coarser (later-formed) was reported in a study by Harris (1990) of 57 Canadian ores. In some cases, coarse gold particles are attributed to a specific genesis. The cm-scale nuggets from the placer of Mechanic Creek, Yukon, exhibit a coating of Bi-telluride (Fig. 1d), indicative of the Bi-Te collector model in which Au exsolves from a Au-Bi ± Te melt (Chapman *et al.* 2018). Conversely, in the highly localised, bonanza style mineralization hosted in black shales in North Wales, the precipitation mechanism involved gold partitioning to water -immiscible organic phases (Bottrell *et al.* 1990). Finally, hypogene gold masses commensurate with the size of placer nuggets have been recorded in a number of important placer districts in Australia and Canada (Butt *et al*. 2020; Hughes *et al.* 1999; Grimshaw, 2018).

Generic features of hypogene gold particles

Hypogene gold particles have been studied in two ways; firstly by observing native gold in ore sections, and more commonly by recovering gold particles from ore by crushing and panning or another gravity separation method. Populations of liberated gold particles are studied in the same way as populations of placer gold particles. The large majority of gold particles are Au-Ag alloys, sometimes with Hg and/or Cu and/or Pd detectable by the electron probe micro analyser (EPMA). Hypogene gold comprising near pure (99.9 wt %Au) have been recorded from a few settings (Chapman et al 2009, 2021). Optical microscopy and back scattered electron (BSE) imaging using scanning electron microscopy (SEM) has revealed alloy and mineralogical heterogeneity within individual particles in numerous studies worldwide. Alloy heterogeneity mostly relates to variation in Au/Ag ratio, although in some cases heterogeneity observable in BSE imaging may result from variation in concentration of Cu, Hg or Pd within Au-Ag alloys (Chapman *et al.* 2021). Ag-rich alloy may either augment (Fig. 2a) or replace relatively Au-rich alloy (Figs. 2b, c).

Inclusions of other minerals are commonly encountered in hypogene gold particles (Fig. 1h, 2d) irrespective of source deposit type (Chapman et al. 2021). Inclusions of sulphides, sulpharsenides, sulphosalts, tellurides and selenides > 1 µm diameter are readily observed in backscatter (BSE) mode of SEM imaging. Their elemental compositions are determined by energy dispersive X-ray spectroscopy (EDS), and the mineralogy inferred either from peak heights or the semi-quantitative analysis afforded by the system. Abundances of inclusions of specific minerals within a population of gold particles is broadly comparable to their abundances in hypogene ore and hence pyrite is the most common. However, less common minerals may be valuable in identifying the style of source mineralization (e.g. Chapman et al. 2017; 2018).

In situ trace element mapping of gold particle sections, using laser-ablation–ICP-time-of-flight (ToF) mass spectrometry is achieved by rastering a pre-defined target using single ablations (Banks et a. 2018). Figure 3a shows the Hg response from a gold particle recovered from in situ mineralization in the Lone Star area, Klondike, Yukon. Higher concentrations are present at the particle edge, and along the grain boundaries revealed in the EBSD image in Figure 3b. A similar enhancement of Hg at the particle edge is observed in a placer particle from the Similkameen River, BC. The majority of ToF LA-ICP-MS data available to the study relates to placer particles, such as that illustrated in Figures 3d-i. The presence of pyrite inclusions (Fig. 3d) demonstrates a hypogene origin for this particle and on this basis we have utilized these images to illustrate a range of trace element features present within hypogene gold.

Simultaneous analysis of the trace element suites has revealed not only strong co-variance of elements within inclusions, but also high degrees of heterogeneity within individual gold particles (Chapman et al. 2021). Figure 3c shows the relatively high intensity response from Fe associated with pyrite inclusions identified during SEM imaging. The distribution of Bi and La is sympathetic, (Figs. 3d, e) but Pb is present only in one of the inclusions (Fig. 3f). The distribution of both Pt and Sb (Figs 3 g, h) is highly heterogeneous but unrelated to that of Fe. The intensities of the response for Pt and Sb are very low, and such features were termed ‘clusters’ by Chapman et al. (2021). The reasons for the presence of clusters are currently unclear; however, their presence provides an explanation for the ephemeral recording of many elements during gold ablation using quadrupole LA-ICP-MS systems (Chapman et al. 2021). The elemental components of clusters are often unrelated to the inclusion suite observable by SEM.

GOLD AND SILVER MOBILITY IN THE SURFICIAL ENVIRONMENT

The principal inorganic ligands that bind to Au and facilitate the dissolution and re-precipitation of gold are chloride (acid oxidised environments), thiosulphate (oxidising sulphides at circumneutral pH), and bisulphide (reducing sulphate at circumneutral pH (Webster and Mann 1984; Webster 1986; Craw and Lilly 2016; Shuster and Reith 2018). Some organic ligands, including cyanide, can contribute to Au mobility in organic-rich environments (Shuster and Reith 2018). These potential ligands are abundant in many surficial environments, including supergene zones overlying hypogene gold deposits, gold placers, and gold palaeoplacers (Webster and Mann 1984; Craw and Lilly 2016; Craw and Kerr 2017; Shuster and Reith 2018). Hence, normal surficial geochemical processes can lead to gold dissolution and re-precipitation at many stages during translation of hypogene gold to placer deposits.

At the same time, biological processes, especially those involving bacteria, can facilitate and even enhance the development of geochemical conditions that lead to Au mobilisation in these settings. Bacterially-mediated oxidation of sulphide minerals by sulphur- and iron-oxidising bacteria almost inevitably leads to localised acidification (Dockrey et al. 2014; Shuster et al. 2016), so Au mobility can be facilitated by the combination of this acidification and the availability of dissolved chloride (Webster and Mann 1984). Likewise, at circumneutral pH, bacteria can facilitate oxidation of sulphide minerals leading to formation of metastable thiosulphate ions, and/or can cause reduction of dissolved sulphate ions to bisulphide ions (Lengke and Southam 2007; Zammit et al. 2015; Kerr and Craw 2017a).

Purely inorganic geochemical variations in the surficial are highly inhomogeneous, and the proximal (metres to tens of metres) re-precipitation of Au is almost inevitable (Webster and Mann 1984; Craw et al. 2015; Craw and Lilly 2016). Au mobilisation that has been facilitated by bacterial processes is typically localised at the micron to centimetre scales, and Au re-precipitation nearby is probable (Dockrey et al. 2014; Lengke and Southam 2007; Zammit et al. 2015; Kerr and Craw 2017a). In these bacterially-mediated situations, Au mobilisation and re-precipitation are merely by-products of normal inorganic geochemical processes that have been catalysed by bacteria.

Gold dissolution is an undesirable process from the biological perspective, and the bacteria sequester the gold either within their cell walls or externally as amorphous masses and microcrystals (Johnston et al. 2013; Reith et al. 2020). These bacterial authigenic Au deposits are therefore typically microns to tens of microns in size (Johnston et al. 2013; Shuster et al. 2016; Kerr and Craw 2017a).

The results of the last increments of this process are commonly observed on the surfaces of placer gold particles as vermiform and crystalline coatings at the 1-10 micron scale (Figs 4a, b), and as micron-scale gold inclusions in authigenic clay coatings on gold particles (Reith et al. 2010; 2012; Shuster et al 2015; Rea et al. 2016; Kerr and Craw 2017a).

GOLD IN WEATHERING PROFILES

A comprehensive account of the chemical mobility of gold in soil profiles was provided by Freyssinet et al. (2005), and the reader is referred to that work for analysis of the relationship between climate, geomorphological control on groundwater geochemistry and gold composition. The present contribution focusses on gold found within fluvial placers and involves interpretation of composition features and alloy microfabrics in terms of the preceding history of individual particles. We consider gold formed in surficial environments only where the particle size facilitates subsequent concentration in fluvial placers.

Generic process affecting gold stability in weathering profiles

As discussed above, in the environs of an individual gold deposit, remobilization of gold may occur through complexing with reduced sulphur or thiosulphate, depending upon the prevailing pH. In some cases, 'invisible gold' in sulphide ore is mobilized by fluids in the supergene environment that contain reduced sulphur and re-precipitates as micron-scale gold particles that retain the Au/Ag ratio of the fluid (e.g., Stoffregren 1987, MacKenzie *et al.* 2015). This process does not necessarily result in gold of the requisite size to accumulate in fluvial settings to form placers. For example, large scale Au remobilization in the supergene environment resulting in size enhancement from 'invisible' gold to micron size was reported at the Coffee orogenic gold deposit, Yukon (MacKenzie *et al.* 2015). Evidence for this process is occasionally observed in larger gold particles where clouds of micron-sized gold dust fills Fe oxides or clays in embayments on the gold surface (Butt et al. 2020; Chapman et al. 2021). Gold transport by a thiosulphate complex in weakly alkaline environments provides a mechanism by which Au-Ag alloys form (Webster and Mann 1984; Webster 1986; Freyssinet 2005; Craw et al. 2015; Craw and Lilly 2016; Dunn et al. 2019). These conditions are prevalent in the upper 10-100 m of some hypogene gold deposits in New Zealand and result in the development of a supergene alteration zone (Fig. 5), similar to that found on copper deposits worldwide (Sillitoe, 2005; Craw *et al.* 2015; Craw and Lilley 2016; Craw and Kerr 2017). Historically, workers preferentially mined these supergene zones for their relatively high-grade (10-100 g/tonne) coarse gold, and such mining ceased once the refractory hypogene gold was reached (Fig. 5a-c; Craw *et al.* 2015).

Supergene zones are typified by steep redox gradients, from relatively reduced alteration processes at the base to fully oxidising processes at the top (Fig. 5a). Hypogene sulphide minerals have been extensively altered within this profile, contributing to the chemical complexity of the supergene processes. As a result, hypogene gold can be dissolved and redeposited, locally causing enrichment and enhanced gold particle sizes. Similar processes can occur within colluvium immediately adjacent to an eroding hypogene deposit, and the distinction between disaggregating weathered hypogene rocks and colluvium derived from them is often obscure.

The effects of supergene processes are most apparent in terranes with orogenic gold deposits that are dominated by refractory gold: typically micro-particulate gold intimately intergrown with, or fully encapsulated by, sulphide minerals. Most hypogene gold in the Otago Schist of New Zealand, for example, is of this type (Fig. 5a,b), and in particular the Macraes mine produced 5 million ounces of gold from low-grade (typically ~1 g/tonne) refractory ore (Fig. 4b) with negligible larger gold particles. Supergene processes have been suggested for the gold precipitation both at Amani, Tanzania, (Dunn et al. 2019) and in Arizona (Kamenov et al. 2013). Dunn et al. (2019) correlated seasonal fluctuations in the water table with redox variation to explain augmentation of pre-existing gold particles with arborescent growths. Whilst Kamenov et al. (2013) do not specify the chemical system responsible for gold mobility, they present evidence for the growth of cm-scale nuggets based on comparative studies of Pb isotopes in gold, in surficial sediments and in the assumed hypogene source. Hughes *et al.* (1999) invoked gold transport by chloride media to explain the origin of some gold nuggets in the Victorian gold province, Australia. These authors did not report any investigations of the internal features of the gold and consequently it remains possible that the apparent abundance of coarse gold near surface is simply a consequence of overburden wasting.

Generic features of gold particles formed in weathering profiles

Gold masses formed in the supergene environment overlying orogenic gold occurrences in New Zealand are typically intimately intergrown with clay minerals and oxidised minerals such as ferrihydrite and/or ferric sulphates (Fig. 5d-g) at the top of the supergene zone, where sulphide minerals have decomposed. Clay minerals were reported within a few microns of particle surfaces in cross sections of gold from Tanzania (Dunn et al. 2019). Under intermediate redox conditions, arsenolite (As_4O_6) can form from decomposing arsenopyrite and become intergrown with the supergene gold (Fig. 4e). The base of the supergene zone, below the water table, is relatively reduced, and sulphide minerals are stable, but these are mineralogically and texturally different from the hypogene sulphides. For example, pyrite is fine-grained and locally framboidal (Fig. 4h) and contains no As. Likewise, As sulphides form as micron-scale realgar (AsS) and related minerals, rather than arsenopyrite (Craw and Kerr 2017; Kerr *et al.* 2019).

Chemical modification to gold particles within the weathering profile comprises the formation of gold-rich areas sympathetic to grain boundaries (Fig. 4c and Hough et al. 2007, 2009 and Butt el al.

2020). Hough *et al.* (2009) noted that gold crystallography was unaffected by the compositional transition from grain core to the film of Au enrichment and concluded that formation occurred through Ag removal as opposed to Au addition. The presence of porosity commonly associated with Au films supports this hypothesis, and confirms that the features are a result of a surficial process (Chapman et al. 2021). The feature has also been observed in gold particles from hypogene settings from Yukon (Knight et al. 1999a) and in various Australian nuggets (Hancock and Thorne, 2011, Butt et al. 2020).

GOLD IN FLUVIAL SYSTEMS

Once eroded from either hypogene or supergene settings, gold particles enter a fluvial system where the subsequent extent of transport is a function of both fluvial environment and particle size. Coarse gold particles in first-order upland streams may form a lag, proximal to the point of influx. Smaller particles are transported downstream to a site of deposition controlled by fluvial sedimentology. In the following discussion, we consider gold in placers according to several headings each linked to source and transport history

Proximal placers

The proximal primary detrital model of placer formation predominates in terranes where the source has been exposed with minimal weathering and the gold particles have been transported in an active river system. This type of setting is common in mountainous regions, especially those with active tectonic uplift and high rates of erosion (Craw *et al.* 1999, 2010; Roy *et al.* 2018). Similarly, glaciated areas such as large parts of the mid-high latitude Northern Hemisphere have abundant exposed fresh bedrock that has shed hypogene gold either into local diamict, subsequently reworked by fluvial systems, or in some cases directly into the watercourse itself.

The relationships between hypogene setting and primary detrital gold particles in a proximal placer are often evident through observation of whole particles (Fig 1a-c; 6a-c) or their sections (Fig. 7a-d). Other minerals from the hypogene setting may be attached to gold, which itself often exhibits rough and irregular surfaces. The progressive shape modification of gold (Fig 1a-c, Fig. 6) has been reported previously by several workers (e.g., Youngson and Craw 1999, Townley et al. 2003) and had underpinned various studies that aim to quantify morphological change as a function of transport distance (e.g. Crawford 2007, Wrighton 2013, Masson et al. 2021). Internal features of hypogene gold are all represented in gold from the proximal detrital expression. The degree to which gold–rich rims (Fig. 1g) have developed varies between localities, and is a function of particle history prior to residence in the fluvial system, and/or time of residence in the fluvial system, and this subject is discussed below.

Various investigations of gold particle surface by SEM techniques have revealed the widespread occurrence of submicron- to micron-scale encrustations of pure gold in the form of crystal overgrowths and budding textures (Figs. 4a, b). These features appear to be ubiquitous irrespective of the maturity of the placer environment and it appears likely that they may form both in the weathering zone and within the fluvial environment. They have been variously ascribed to inorganic processes (e.g., Craw et al. 2015) or biogenic activity (e.g., Fairbrother et al. 2012, Reith et al. 2018) and have been observed on placer gold particles worldwide; e.g., South America (McCready *et al.* 2003), New Zealand (Craw *et al.* 2017, Stewart et al. 2017), Turkey (Chapman et al. 2021), Scandinavia (Reith *et al*. 2018) and Poland (Wierchoweic et al. 2021).

The presence of inclusions of ore minerals within placer gold particles provides clear evidence for a hypogene source (Figs 1 h-j, 2d). Consideration of inclusion abundance in polished sections of around 40,000 gold particles from different localities, styles of mineralization and surficial environments worldwide undertaken by Chapman *et al.* (2021) showed that on average, inclusions are recorded in around 10% of polished gold particles. Gold from Precambrian orogenic sources tends to exhibit fewer inclusions whereas gold particles from some Phanerozoic orogenic and epithermal mineralization show far higher proportions. It is important to note that these data relate to particle sections, and therefore represent absolute minimum value for the abundance of inclusions within whole particles. Within individual populations, comparisons of alloy compositions between those gold particles containing inclusions and not containing inclusions do not reveal separate ranges of Ag (e.g., Chapman et al. 2000a), which supports a hypothesis that all particles are of hypogene origin. There are two implications of these data sets. Firstly, populations of placer gold particles that contain inclusions of minerals unstable in the surficial environment cannot be entirely derived from either supergene or biogenic/chemical models. Secondly, the proportion of gold particles which are undoubtedly detrital is almost certainly higher than the proportion in which inclusions are observed in a single section.

Evolved detrital placers

Formation

Terranes with low relief, slow uplift rates, slow erosion rates, and an absence of widespread glaciation, have more complex histories of gold particle evolution, transport, and deposition. Gold particles are subject to substantial chemical and physical modifications after entering a fluvial system. Recognition of features caused by modification aids discrimination between gold particles with a history of fluvial transport and those exhibiting features that could be interpreted as indicative of in situ supergene formation. Evolved detrital placers result either from a single ongoing transport history along a major fluvial system, or through a process of transport followed by long-term residence in bench sediments prior to release into fluvial systems following surficial erosion. These gold particle recycling processes can be repeated many times in the history of such terranes, ultimately leading to a complex of fluvial deposits that constitute giant placers on a regional scale (Henley and Adams 1979). In addition, individual palaeoplacers have been important loci of gold mining activity (Boyle 1979).

The Otago Schist terrane of New Zealand is one such giant palaeoplacer system in which evidence for numerous stages of gold concentration, recycling, and re-concentration has been preserved during the past 100 million years (Fig. 6a-d). As well as recycling of previously formed palaeoplacer gold, each stage of gold accumulation has also incorporated newly eroded gold particles from the underlying hypogene and supergene zones (Fig. 6a-c). Hence, most palaeoplacers of all ages contain gold particles with a range of shapes and sizes, from rough angular nuggets to thin flakes (Fig. 6a-c). Similarly, a mixture of gold particle morphologies can also occur in modern placers where gold particles from different sources are represented.

Modification of placer gold particles in evolved placers

Physical deformation of the particles during fluvial transport results in progressive modification of the surfaces and also to the shapes of the particles (Townley et a. 2003; Crawford 2007; Stewart et al. 2017; McLachlan et al. 2018, Masson et al. 2021). Internal grain boundaries become distorted, and the gold crystal structure deforms within grains (Fig. 7a, b; Stewart et al. 2017; Kerr et al. 2017b; McLachlan et al. 2018). Locally the surface gold becomes smeared into thin mylonitic lamellae at the micron- or sub-micron-scale (Fig. 7c, d; Kerr et al. 2017b). All these processes accompany the general flattening of particles into flakes with deformed interiors (Fig 6a-c; Craw et al. 2017). The progressive nature of gold particle deformation has been studied in the context of transport distance both qualitatively (Townley *et al.* 2003) and quantitatively (e.g. Knight *et al.* 1999a; Youngson and Craw 1999, Crawford 2007; Wrighton 2013, Masson et al. 2021). Other studies have correlated gold particle morphology with composition in order to constrain the location of sources (Youngson et al. 2002; Crawford 2007; Wrighton 2013).

High grain boundary energies associated with crystallographic deformation encourage annealing of the internal grain structure to reduce that strain energy (Doherty et al. 1997; Stewart et al. 2017). For the mylonitic exterior zones, grain size increases as annealing progresses, and in the interior of particles the grain size typically decreases (Fig. 7a-f; Kerr et al. 2017b). The deformed particles often develop low-Ag zones as part of this annealing process (Fig. 7e, g, h). Post-depositional encrustations of low-Ag gold commonly form on particle surfaces at the micron scale (Fig. 7i), and these can merge with the annealed rims. With further transport and physical deformation, gold particles become progressively flattened and their interior structure becomes progressively finer grained and eventually becomes fully annealed (Fig. 7j; Stewart et al. 2017; Craw et al. 2017).

Annealing of gold in response to stress is also enhanced by time, such that gold particles in old palaeoplacers tend to have larger recrystallisation domains affecting both cores and rims (Fig.7g, h and Kerr et al. 2017b). In a terrane with normal or low heat flow and only shallow (<500 m) burial of palaeoplacers, temperatures are unlikely to exceed ~40°C for annealing processes, for example over >40 my (Stewart et al. 2017) or >60 my (Kerr et al. 2017b). Some leaching of Ag from core regions can occur during this process, with development of what appears to be a relatively large rim (Fig. 7h).

Inclusions are preserved within gold particles unless deformation permits ingress of oxidizing fluids. In general, they become less common with increasing fluvial transport (Loen 1995; Melchiorre *et al.* 2019), but some survive despite particle and inclusion deformation (Fig 1j; 7f).

Biogenically-driven transformation of gold within placers has been proposed as an influence on both gold size (e.g. Reith et al. 2010, Shuster et al. 2015) and composition (Rea *et al.* 2018, Reith *et al.* 2018). The potential for these processes to substantially influence the overall nature of gold in placer deposits is discussed in the following section.

PARTICLE SIZE ENHANCEMENT AND ALLOY MODIFICATION IN THE FLUVIAL ENVIRONMENT

Contemporary researchers of gold in placer environments, and exploration geologists tracing detrital gold back to source(s), face the challenge of establishing the degree to which detrital gold has changed in its passage from hypogene source to the point of collection within a fluvial environment. The potential effects of gold formed in situ to the overall placer gold particle size distribution and gold compositional variations are of particular relevance. There is little or no evidence for significant chemical addition of gold to the placer environment from outside the immediate area, so any transformations within a placer are related to redistribution of gold and other elements amongst the detrital gold particles and the associated groundwater. Some of these transformational processes are a result of linked physical and inorganic geochemical effects, as outlined above. In addition, several recent studies have focussed on biogenic processes in the placer environment (Kamenov et al. 2013; Shuster et al. 2015; Rea et al. 2016).

The features of hypogene gold particles such as microfabrics and inclusions can be recognised in placer gold and are diagnostic for the detrital model. Such features may be apparently absent either because the original hypogene (or indeed supergene) particle was itself featureless, or because they have been eradicated by processes active in the surficial environment. The following subsections focus on aspects of placer gold mineralogy where views differ regarding the nature or relative importance of the processes responsible for genesis and/or modification of the Au alloy.

Origin of rims

Gold-rich rims are a global feature of placer gold particles (Boyle 1979) and in our experience their absence is unusual. A rim usually surrounds each gold particle and is typically 10-100 µm thick outside a core zone which is typically texturally, compositionally, and mineralogically different from the rim (Fig 1g). The rims also commonly have discontinuous overgrowths of authigenic gold (Figs 4a, b) that have been variably bacterially mediated, as outlined above. However, the rims (Fig 1g) are texturally distinct from the clearly authigenic overgrowths on the particles (Figs 4a, b), and the origin of rims has been subject to abundant scientific discussion. At the simplest level, rim formation may be ascribed to either gold addition or silver depletion. It is important to establish the relative importance of these processes because acceptance of gold addition provides a platform for hypotheses that advocate larger changes to gold in the fluvial environment.

Proponents of rim formation by processes of gold addition consider the authigenic overgrowths to represent the last additional layer of ongoing gold accumulation that formed the rim (e.g. McCready et al. 2003; Fairbrother et al. 2012; Reith et al. 2018). Rea (2019) cites the presence of rims to 'several hundred microns' and refers to various other studies. On inspection, the evidence is not so robust. In papers advocating biogenic accumulation of rims, only Reith (2012) provides an image of a c 200 µm thick rim in a particle of maximum diameter c 700 µm. No information is provided on the orientation of the sectioned particle, such that the true thickness is unclear. Stewart et al. (2017) report 'wide' (c 100 µm) rims but specifically ascribe their formation to strain-induced annealing, not to biogenic processes. In all cases the rims comprise near–pure Au that exhibit a sharp boundary with the underlying Au-Ag substrate. Whilst Reith et al. (2018) acknowledge that Ag-depletion may generate rims in some other cases, there was no consideration of why one process should be favoured in any particular situation. In our own studies, we have not identified different alloy textures within gold rims in different particles that suggest different mechanisms of formation.

Models of rim formation by Ag depletion point to various lines of evidence revealed in studies of large numbers of polished sections (Knight et al. 1999b: Craw et al. 2017). In the majority of cases, there is a limit to the true thickness of rims, which appears inconsistent with a model of gold addition. The range of rim thickness reported in a variety of studies appears very similar irrespective of whether that study advocates rim formation by gold addition (Kamenov *et al.* 2013; Dunn *et al.* 2019; Reith et al 2018) or Ag removal (e.g., Groen et al. 1990, Knight *et al.* 1999b). Groen et al. (1990) proposed a generic process of electroless plating of rim formation by Ag-removal. The degree of Ag removal could be expected to be vary slightly between particles, as observed by Knight et al. (1999b), whereas the potential for biogenic processes to generate Ag-bearing gold alloys remains unclear. For rim formation by Ag depletion, removal of Ag from an Au-Ag alloy comprising 10% Ag could be expected to generate a passivating Au layer after alteration of only 10 monolayers of alloy (Erlebacher et al. 2001). These authors applied a combination of experimental and modelling approaches to Ag dissolution from Au-Ag alloys and showed redistribution of gold atoms at the alloy–fluid interface maintained nanoporosity and permitted an ongoing reaction.

Nevertheless, even following consideration of difficulties in measuring the true thicknesses of rims of flattened particles by sectioning, rims of true thickness up to 100µm have been reported by Stewart *et al.* (2017). Their formation was ascribed to recycling of gold particles into successive fluvial regimes, each of which caused the deformation required to induce further annealing and associated compositional modification. According to this hypothesis, residence time between cycles is a critical factor to facilitate compositional change (Stewart et al. 2017; Kerr et al. 2017b). Similarly thick rims have been observed in gold particles from Yukon (Knight *et al.* 1999a) and examples are provided in Figures 8b and c. In both cases the rims contain remnants of the primary alloy. One explanation for this microfabric (observed in 2 dimensions) is that the Ag-rich alloy is continuous with the core (in 3 dimensions). However, the relative positions of core and Ag-rich gold outliers appears incompatible with this hypothesis, and we prefer a model in which the original core alloy is incompletely replaced.

Pristine inclusions of sulphide and telluride minerals have been observed at the rim/core interface (Chapman et al. 2010b, 2021 and Fig. 8a-c). The spatial relationship of these inclusions to both core and rim alloys attests to rim formation by Ag removal. Similarly, some rims contain relics of original core composition (Figs 8a, d, e). The particle illustrated in Figure 8a shows both relic core within the rim and an inclusion at the core-rim interface. Figures 8 d and e show part of a sections of gold particles from two other Yukon localities where an island of unaltered core is surrounded by the inner rim; a microfabric clearly incompatible with gold addition.

To date there have not been any systematic studies of trace elements within rim alloy. The elevated levels of Hg at the edges of a placer gold particle from the Similkameen River (Fig 3c) indicate that some particle-edge heterogeneity may be caused by processes active in the hypogene environment. Presently the mechanisms by which such features form are unclear, but such relationships must be considered in any future studies that seek to establish the mechanism of rim formation through trace element profiles.

In summary, rim formation by Ag depletion in the fluvial environment provides the best fit for the overwhelming majority of observations of detrital particle sections. Hence, we suggest that biologically facilitated gold re-precipitation occurs at the 1-10 micron scale and is unlikely to dramatically alter placer gold particle shapes except for the smallest particles (<50 µm). Nevertheless, supergene oxidation of sulphide minerals containing nanoparticulate or solid solution Au can yield microparticulate gold (e.g., MacKenzie et al 2015), which is >100-fold increase in particle size, and this supergene oxidation process almost certainly has a biological input as demonstrated experimentally by Shuster and Southam (2015) and Shuster et al. (2016).

Alteration of core alloy composition

Chemical alteration to gold particle cores can occur during annealing following deformation as described above (Stewart et al. 2017; McLachlan et al. 2017; Kerr et al. 2017b), and in our view is the most common origin of gold particles which appear to have multiple cores, such as illustrated by Knight et al. (1999a). Some researchers view the addition of a gold rim to pre-existing particles as the first stage in a process of biologically mediated 'transformation'. This hypothesis proposes the progressive replacement of the detrital particle with pure gold, and has been advocated in relation to populations of gold particles from Finland (Reith et al. 2018), the UK, (Rea et al. 2018) and Switzerland (Rea et al 2019). Progressive eradication of the original Au-Ag alloy by pure gold was described in terms of biogenic-induced formation of thin, penetrating Au-rich zones as a precursor to larger Au-rich patches and ultimately complete replacement. Both contributions adopted the premise that transformation occurs, and that identification of specific heterogeneous textures in different particles, sometimes from different localities in the study area, constituted the requisite evidence. We disagree with this hypothesis for the following reasons. Firstly, we are strong advocates of inner rim formation by Ag depletion for the reasons described above. Secondly various workers have identified penetrating gold films within gold liberated from weathering in situ occurrences (Knight et al. 1999b, Chapman et al. 2021) or lateritic profiles (Larizatti et al. 2008), and Figure 5c shows well developed Au-rich zones parallel to grain boundaries, but the particle exhibits only a very minor partial rim. Thus, rim formation and generation of interior gold-rich zones are not necessarily genetically related. Finally, pure gold is compatible with the deformation- recrystallization process described by Stewart et al. (2017), and can also in some cases reflect the hypogene gold composition (Chapman et al. 2021).

Addition of gold to substantially enhance particle size

Boyle (1979) noted the presence of filigree gold within sediments from various localities and proposed that the alloy had formed in situ. Gold growth during residence in fluvial systems by either biogenic or inorganic models could be expected to generate particles exhibiting internal textures and compositions compatible with that hypothesis. A homogeneous alloy would result from growth in chemically stable environments, with permissible Ag contents governed by the chemistry of the immediate environment. If large gold particles were generated, common minerals within the sediment matrix would inevitably be incorporated and rounded quartz particles and clays could be expected to be common inclusions. Augmentation of pre-existing detrital particles would generate internal microfabrics reflecting gold addition to the substrate, with outer layers of greater thickness than that normally associated with the inner rim. Fluctuations in the conditions of deposition (e.g. changes in Eh, $aS_2^{-}{}_{(aq)}$) on burial in sediments might influence alloy composition according to the equilibrium relationships established by Gammons and Williams-Jones (1995) to generate concentric or colloform textures similar to those observed in some hypogene particles and their detrital expression (Chapman et al. 2009). The presence of gold crystals has been cited as evidence for gold growth within sediments, in the small number of cases investigated to date the alloy composition of gold crystals is compatible with other particles in the same sample population. For example, the 4.2g nugget from Last Chance Creek, Yukon that exhibits multiple crystal surfaces (Fig. 1d) comprises alloy of 29 wt% Ag, comparable to the mean value of 100 particles form the same location of 32 wt% Ag (data from Chapman et a. 2010b). Delicate dendritic crystals of palladian gold have been collected from small drainages in Devon, England, where the locally exposed hypogene mineralization (Hope's Nose, near Torquay) contains gold of the same composition and morphology (Chapman *et al.* 2009).

Historically, there has been an emphasis on consideration of the origin of large (>10 cm) nuggets, as summarised in Butt et al. (2020). There is no doubt some such nuggets have formed in hypogene environments, but the relative contributions of hypogene and secondary (authigenic) processes to nugget formation have been the subject of much debate (Butt et al. 2020). However, such large nuggets are unlikely to travel far, if at all, in a fluvial environment, and are beyond the scope of this paper. Some centimetre-scale eluvial nuggets have similar 1-10 micron scale authigenic vermiform and crystalline gold overgrowths to those seen on fluvial placer particles (previous subsection; Craw and Lilly 2016; Kerr and Craw 2017a), although these authigenic additions are volumetrically minor. Laminated rims (up to 50 μm) on centimetre scale nuggets have also been observed and attributed to biologically mediated authigenic processes (Henne et al. 2021), but the cores of such nuggets do not retain evidence of cumulative growth processes.

Within the fluvial environment, nuggets are clearly an end member of the gold particle size distribution and it seems reasonable to assume that if gold growth occurs, smaller particles should be generated too, and mass gain to nugget status is not inevitable. Studies of smaller particles should reveal compositional and textural evidence for lower degrees of augmentation if gold addition is ongoing. The majority of gold particle studies examine particles of between 100 μm and 2mm, both because this size range is often the most common, and practical considerations of mounting permits study of sufficient particles. Thus it is probable that any textural features commensurate with particle growth would have been observed during the routine screening of our collections. Evidence for episodic gold particle growth in hypogene settings is relatively easy to identify (Chapman et al. 2009; Chapman et al. 2021). A small study of large (0.2-0.5g) particles from various localities in the UK and Ireland was undertaken to compare both internal composition and microfabrics with those observed in much larger populations of smaller particles from the same site. In this way, any ubiquitous gold growth could be established.

Figure 9a shows sections of these large gold particles, and Figures 9 b-d show various features within those particles that are also commonly observed in smaller counterparts, e.g. a rim of the comparable thickness (Fig. 9b), an inclusion (Fig. 9c), and relics of shale which is the local country rock and therefore presumably the vein matrix (Fig. 9d). In Fig. 9e, the average Ag content of multiple spot analyses by EMP is compared to the compositional range of a population of smaller particles from the same location. Any differences in the environment or mode of formation of the coarse particles could be expected to be reflected in extreme compositions with respect to the larger population, but no such differences were observed. Some particles illustrated in Figure 9 were collected from the same area where Rea et al. (2018) proposed gold transformation by biogenic processes. The microfabrics observed in the large particles reported in the present study are indicative of a hypogene origin and also consistent with those observed in the many thousands of gold particles from southern Scotland and other comparable regions in upland areas of Great Britain and Ireland

Regional variation of the Au-Ag ratio within natural gold alloy has long been recognised from analyses of doré bullion produced at different placer mining operations. Various authors have reported the phenomenon of increased bulk gold fineness in placers with transport distance (e.g. Boyle 1979) and some (e.g. Marquez-Zavalia *et al.* 2004) have invoked addition of authigenic gold as an explanation. On the basis of various arguments provided above, we prefer explanations which centre on the inner rim/core volume ratio, which is governed by gold particle size and shape (Craw *et al.* 2017). Flattening of gold results both in a higher proportion of Au-rich rim, and increased transportation in fluvial regimes as a consequence of reduced settling velocity such that bulk compositions inevitably change with locality along a drainage.

FUTURE DIRECTIONS

Future clarification of various aspects of gold composition and behaviour in the weathering and fluvial settings will prove insightful in further evaluating the relative importance of biogenic, supergene and detrital models of placer gold genesis both at specific localities and more widely. In this section we identify specific areas where new studies could yield valuable outcomes.

The majority of discussions on genesis of placer gold particles focus on the Ag content of the alloy because other metals are often below detection limits of EMPA. The application of more sensitive analytical techniques will permit interrogation of data sets according to other elemental components. For example, Banks *et al*. (2018) report immobile elements such as Cr and W in placer gold associated with both orogenic and magmatic hydrothermal systems, and these geochemical features would be difficult to reconcile with gold formation through low temperature processes. The limited amount of information currently available from ToF-LA-ICP-MS analyses of hypogene gold particles (Chapman et al. 2021) has shown that particles may be heterogeneous in various respects, and the origins of some features remain unclear. Far more work of this kind is needed to map trace elements in gold particle sections to facilitate consideration in the context of particle genesis, and correlation of hypogene and placer particle features. Trace element characterization of gold ascribed to low temperature formation would be extremely helpful, and in particular, it would be useful to have available SEM and EBSD images of sections of synthetic gold particles formed through the biogenic processes as described by Shuster et al. (2015), but presently none have been published. This information would facilitate direct comparison with placer gold of hypogene origin and provide an additional means to evaluate the contribution of the biogenic model in specific placers.

Crystallographic considerations have also contributed to discussions of both nugget origin and alloy microfabrics. Hough *et al.* (2007) cited the presence of twinned crystal domains revealed by EBSD in large Australian nuggets as indicative of annealing at elevated temperature and therefore incompatible with a supergene genesis. These authors argued strongly for a hypogene origin for nuggets, a conclusion reiterated in Hough *et al.* (2009) and Butt et al (2020). Conversely Craw and co-workers argue that annealing can take place at lower temperatures over long periods of geological time (e.g. Stewart et al. 2017). Synthesis of crystallographic information with major and trace element compositions will provide a generic approach ultimately capable of classifying gold particles, or parts thereof, to their genetic origins.

CONCLUSIONS

Characterization of gold from hypogene settings has identified features such as internal alloy microfabrics and inclusions of other minerals, and observation of these features in gold particles from placer environments confirms a detrital origin. Features diagnostic for hypogene gold have been observed within some gold particles in the overwhelming majority of populations of placer gold particles. We make this assertion following visual inspection of SEM images of over 40,000 gold particle sections from various localities in different climatic zones worldwide. Nevertheless, compositional studies focussing on Au-Ag ratios, consistently reveal overlaps in features observed in gold derived from hypogene and supergene sources. Particles of both types subsequently develop the same array of features caused by transport-related deformation, subsequent annealing, and inorganic and organic authigenic gold mobility. Separating these effects is not easy and commonly equivocal, but an understanding of the range of microfabrics and compositional features of hypogene gold provides a starting point to consider various models of placer gold formation.

Gold–rich rims are a near ubiquitous feature of placer gold particles, and understanding their origins is of great importance because they could potentially represent evidence for the widespread addition of gold to pre-existing alloy. Rims usually comprise two distinct components, both formed in the surficial environment. The inner feature comprises an Ag depleted zone, normally to c 20 µm maximum depth (occasionally to 100 µm), whose geometry is broadly sympathetic to the particle edge. Inner rims result from Ag removal, not Au addition. The outer rim feature comprises micron-sized overgrowths of pure gold on the inner rim substrate, whose origins may be biogenic or chemical. Conflation of these two separate features has encouraged acceptance of a biogenically-driven process for gold particle augmentation, ultimately leading to either nugget genesis or complete transformation of pre-existing gold particles. We have yet to observe any internal microfabrics (with the exception of the micron-scale outer rims) within placer gold particles of any size that could be ascribed to gold deposition in the fluvial environment. Similarly, we reject the model of biogenic transformation of placer gold particles because we consider the hypothesis to conflate unrelated generic alloy microfabrics that have their origins elsewhere. We conclude that claims for the potential importance of biogenic processes in both generating and modifying gold particles in fluvial environments are commonly overstated. Nevertheless, we acknowledge that biogenic gold growth is feasible, and a review of the internal characteristics of gold grown biogenically under laboratory conditions would facilitate comparison with those of natural gold.

Many of the outstanding questions regarding gold particle genesis may ultimately be answered by the application of new approaches to compositional and crystallographic analysis. In particular, descriptions of the internal distribution of variation of trace elements within individual Au particles formed in different environments using LA-ICP- ToF-MS for gold alloys would add considerable clarity.

ACKNOWLEDGEMENTS

We are greatly indebted to Dr Erin Marsh and Dr Charles Butt, whose diligent and constructive reviews greatly improved the original manuscript.

REFERENCES

Bottrell, S.H. & Miller, M.F. 1990. The geochemical behaviour of nitrogen compounds during the formation of black shale hosted quartz-vein gold deposits, north Wales. *Applied Geochemistry*. **5,** 289-96.

Banks, D.A., Chapman, R.J. & Spence-Jones, C.P. 2018. Detrital gold as a deposit-specific indicator mineral by LA-ICP-MS analysis. *Geoscience BC report 2018-21*. Available at: http://www.geosciencebc.com/s/2016-006.asp

Boyle, R.W. 1979. The geochemistry of gold and its deposits. *Geol Surv Can Bull* 280p

Butt, C.R.M., Hough, R.M & Verrall, M. 2020. Gold Nuggets: The Inside Story. *Ore And Energy Resource Geology.* 4-5, 100009. https://doi.org/10.1016/j.oreoa.2020.100009

Chapman, R. J., Leake, R. C., Moles, N. R., Earls, G., Cooper, C., Harrington, K. & Berzins, R. 2000a. The application of microchemical analysis of gold grains to the understanding of complex local and regional gold mineralization: a case study in Ireland and Scotland. *Economic Geology*, **95**, 1753–1773.

Chapman, R. J., Leake, R. C. & Moles, N. R. 2000b. The use of microchemical analysis of alluvial gold grains in mineral exploration: experiences in Britain and Ireland. *Journal of Geochemical Exploration*, **71**, 241–268.

Chapman, R. J., Leake, R. C., & Floyd, D. J. 2000c. Regional gold mineralization in the vicinity of the Glengaber Burn, Scottish Borders. *Scottish Journal of Geology*, **36**, 165-176.

Chapman, R. J., Leake, R. C., Bond, D. P. G., Stedra, V. & Fairgrieve, B. 2009. Chemical and mineralogical signatures of gold formed in oxidizing chloride hydrothermal systems and their significance within populations of placer gold grains collected during reconnaissance. *Economic Geology,* **104,** 563–585.

Chapman, R. J., Mortensen, J. K., Crawford, E. C. & LeBarge, W. 2010a. Microchemical studies of placer and lode gold in the Klondike District, Yukon, Canada: 2. Constraints on the nature and location of regional lode sources. *Economic Geology*, **105**, 1369–1392.

Chapman, R. J., Mortensen, J. K., Crawford, E. C. & LeBarge, W. 2010b. Microchemical studies of placer and lode gold in Bonanza and Eldorado creeks, Klondike District, Yukon, Canada: evidence for a small, gold-rich, orogenic hydrothermal system. *Economic Geology*, **105**, 1393–1410.p.165-176.

Chapman, R.J., Mileham, T.J, Allan, M.M. & Mortensen, J.K . 2017. A distinctive Pd-Hg signature in detrital gold derived from alkalic Cu-Au porphyry systems. *Ore Geology Reviews* **83,** 84-102.

Chapman, R.J., Allan, M.M., Mortensen, J.K., Wrighton, T.M. & Grimshaw, M,.R. 2018 A New Indicator Mineral Methodology Based On A Generic Bi-Pb-Te-S Mineral Inclusion Signature In Detrital Gold From Porphyry And Low/Intermediate Sulfidation Epithermal Environments In Yukon Territory, Canada. *Mineralium Deposita*, **53,** 815-834.

Chapman, R.J., Banks, D.A, Styles, M.T, Walshaw, R.D., Piazolo, S., Morgan, D.J., Grimshaw, M.R., Spence-Jones, C.P., Matthews, T.J. & Borovinskaya, O. 2021. Chemical and physical heterogeneity within native gold: implications for the design of gold particle studies. Mineralium Deposita

Craw, D., & Kerr, G. 2017. Geochemistry and mineralogy of contrasting supergene gold alteration zones, southern New Zealand. *Applied Geochemistry*, **85**, 19-34.

Craw, D., Windle, S. J. & Angus, P. V. 1999. Gold mineralization without quartz veins in a ductile-brittle shear zone, Macraes Mine, Otago Schist, New Zealand. *Mineralium Deposita*, **34**, 382-394.

Craw, D., Upton, P., Yu, B. S., Horton, T. & Chen, Y. G. 2010. Young orogenic gold mineralisation in active collisional mountains, Taiwan. *Mineralium Deposita*, **45**, 631-646.

Craw, D., Mackenzie, D. & Grieve, P. 2015. Supergene gold mobility in orogenic gold deposits, Otago Schist, New Zealand. *New Zealand Journal of Geology and Geophysics*, **58**, 123-136.

Craw, D. & Lilly, K. 2016 Gold nugget morphology and geochemical environments of nugget formation, southern New Zealand. *Ore Geology Reviews,* **79**, 301-15.

Craw, D., Mclachlan, C., Negrini, M. & Becker, N. 2017. Quantification and Prediction of Bulk Gold Fineness at Placer Gold Mines: A New Zealand example. *Minerals*, **7**, 226.

Crawford, E.C. 2007. Klondike placer gold: New tools for examining morphology, composition and crystallinity: Unpublished M.Sc. thesis, The University of British Columbia, 151 p.

Dockrey, J.M., Lindsay, K. Mayer, R. Beckie, K. Norlund, L.Warren, G. Southam, 2014. Acidic microenvironments in waste rock characterized by neutral drainage: Bacteria–mineral interactions at sulphide surfaces Minerals, 4, pp. 170-190.

Doherty, R.D., Hughes, D.A., Humphreys, F.J., Jonas, J.J., Juul Jenson, D., Kassner, M.E., King, W.E., Mcnelley, T.R., Mcqueen, H.J.& Rollett, A.D. 1997. Current issues in recrystallisation: a review. *Materials Science and Engineering*, A238, 219–274.

Dunn, S. C., Bjorn, P., Rozendaal, A. & Taljaard, R. 2019. Secondary gold mineralization in the Amani Placer Gold Deposit, Tanzania. *Ore Geology Reviews*, **107**, 87-107.

ERLEBACHER, J., AZIZ, M.J., KARMA, A., DIMITROV, N.& SIERADZKI, K.2001 Evolution of nanoporosity in dealloying. Nature. 410, 450-3.

Fairbrother L, Brugger J, Shapter J, Laird JS, Southam G, Reith F. Supergene gold transformation: Biogenic secondary and nano-particulate gold from arid Australia. Chemical Geology. 2012 Aug 6;320:17-31.

Freyssinet P. , Butt C. R, Morris R.C, Piantone P. 2005. Ore-forming processes related to lateritic weathering. Economic Geology 100th Anniversary Volume, Hedenquist J.W., Thompson, J.H., Goldfarb, R.W and Richards, J.P. Eds. Society of Economic Geologists, Littleton, Colorado

Gammons, C. H. & Williams-Jones, A. E. 1995. Hydrothermal geochemistry of electrum: Thermodynamic constraints: *Economic Geology*, **90**, 420-432.

Grimshaw, M.R. 2018. Gold mineralisation in the Lone Star area of the Klondike gold District, Yukon, Canada. PhD Thesis, University Of Leeds.

Groen, J. C., Craig, J. R. & Rimstidt, J. D. 1990. Gold–rich rim formation on electrum grains in placers. *Canadian Mineralogist*, **28**, 207–228.

Frevsinnet 2005

Hancock, E.A. & Thorne, E.M. 2011. Mineralogy of lode and alluvial gold from the Western Capricorn Orogen, Western Australia. *Australian Journal of Earth Sciences*, **58**, 793-801.

Harris 1990

Henley, R. W. & Adams, J. 1979. On the evolution of giant gold placers. *Transactions of the Institution of Mining and Metallurgy, Section B*, **88**, 41-50.

Henne, A., Craw, D., Hamilton J., Paz A., Kerr G, Paterson, D., Shuster, J. & Southam, G. 2021. Biogeochemical formation of metalliferous laminations in surficial environments. Mineralogical Magazine 85 (1) Frank Reith Memorial Issue (on-line February 2021).

Hough, R.M, Butt, C.R., Reddy, S.M. &Verrall M. 2007. Gold nuggets: supergene or hypogene? *Aus J Earth Sci* **54**, 959-64.

Hough, R. M., Butt, C. R. M. & Fischer-Buhner, J. 2009. The crystallography, metallography and composition of gold. *Elements*, **5**, 297-302.

Hughes, M.J., Carey, S.P. & Kotsonis, A.N. 1999.Lateritic weathering and secondary gold in the Victorian Gold Province. *Regolith*, **98**, 155-172.

Kamenov, G. D., Melchiorre, E. B., Ricker, F. N. & Dewitt, E. 2013. Insights from Pb isotopes for native gold formation during hypogene and supergene processes at Rich Hill, Arizona. *Economic Geology*, **108**, 1577-1589.

Johnston, C.W., Wyatt, M.A., Li, X., Ibrahim, A., Shuster, J., Southam, G. & Magarvey, N. 2013. Gold biomineralization by a metallophore from a gold-associated microbe. *Nature Chem Biol* **9**, 241-243.

Knight, J. B., Morison, S. R. & Mortensen, J. K. 1999a. The relationship between placer gold particle shape, rimming and distance of fluvial transport; as exemplified by gold from the Klondike District, Yukon Territory, Canada. *Economic Geology*, **94**, 635–648.

Knight, J. B., Mortensen, J. K., & Morison, S. R. 1999b. Lode and placer gold composition in the Klondike district, Yukon Territory, Canada: Implications for the nature and genesis of Klondike placer and lode gold deposits: *Economic Geology,* **94**, 649–664.

Kerr G, Craw D 2017a. Mineralogy and geochemistry of biologically-mediated gold mobilisation and redeposition in a semiarid climate, southern New Zealand. in: Reith F; Shuster J (eds), Special Issue

"Geomicrobiology and biogeochemistry of precious metals", Minerals 7, 147, doi:10.3390/min7080147

Kerr, G., Malloch, K., Lilly, K. & Craw, D. 2017a. Diagenetic alteration of a Mesozoic fluvial gold placer deposit, southern New Zealand. *Ore Geology Reviews,* **83**, 14-29.

Kerr G, Falconer D, Reith F, Craw D 2017b. Transport-related mylonitic ductile deformation and shape change of alluvial gold, southern New Zealand. *Sedimentary Geology* 361: 52-63.

Larizzatti, J.H., Oliveira, S.M. & Butt Cr. 2008.Morphology and composition of gold in a lateritic profile, Fazenda Pison "Garimpo", Amazon, Brazil. *J. of South American Earth Sciences.* 2008 **25**, 359-76.

Loen, J.S. 1995 Use of placer gold characteristics to locate bedrock gold mineralization. *Exporation and Mining Geology,* **4***:* 335–339

Lengke, M. & Southam, G. 2007. The deposition of elemental gold from gold (I) thiosulfate complexes mediated by sulfate-reducing bacterial conditions: *Econ Geol*, ***102*,** 109–126.

Mackenzie, D., Craw, D. & Finnigan, C. 2015. Lithologically controlled invisible gold, Yukon, Canada. *Mineralium Deposita*, **50**, 141-157.

McLachlan, C., Negrini, M. & Craw D. 2018. Gold and associated minerals in the Waikaia placer gold mine, Northern Southland, New Zealand, *New Zealand Journal of Geology and Geophysics* **61**: 164-179.

McClenaghan, M.B, &, Cabri, L.J. 2011Review of gold and platinum group element (PGE) indicator minerals methods for surficial sediment sampling.

McClenaghan M.B & Paulen, R.C. 2018. Application of till mineralogy and geochemistry to mineral exploration. In; Past glacial environments 2018 Jan 1 (pp. 689-751). Elsevier.

McCready, A. J., Parnell, J. & Castro, L. 2003. Crystalline placer gold from the Rio Neuquen, Argentina; implications for the gold budget in placer gold formation. *Economic Geology*, **98**, 623–633.

Márquez-Zavalía, M. F., Southam, G., Craig, J. R. & Galliski, M. A. 2004. Morphological and chemical study of placer gold from the San Luis Range, Argentina. *The Canadian Mineralogist*, ***42***, 169-182.

Masson, F-X, Beaudoin, G & Laurendau D. 2021 Multi-method 2D and 3D reconstruction of gold grains morphology in alluvial deposits: a review and an application to the Rivière du Moulin (Québec, Canada) in: Recent Advances in Understanding Gold Deposits: from Orogeny to Alluvium Geological Society, London, Special Publication 516.

Melchiorre, E. B. & Henderson, J. 2019. Topographic gradients and lode gold sourcing recorded by placer gold morphology, geochemistry, and mineral inclusions in the east fork San Gabriel River, California, USA. *Ore Geology Reviews*, **109**, 348-357.

Rea, M.A., Zammit, C.M. & Reith, F. 2016. Bacterial biofilms on gold grains—implications for geomicrobial transformations of gold. *FEMS microbiology ecology*, **92,** 6.

Rea, M.A., Standish, C.D., Shuster, J., Bissett, A. & Reith, F. 2018. Progressive biogeochemical transformation of placer gold particles drives compositional changes in associated biofilm communities. *FEMS microbiology ecology*, **94** fiy080.

Rea MA, Wulser PA, Brugger J, Etschmann B, Bissett A, Shuster J, Reith F. Effect of physical and biogeochemical factors on placer gold transformation in mountainous landscapes of Switzerland. Gondwana Research. 2019 Feb 1;66:77-92.

Reith, F., Fairbrother, L., Noize, G., Wilhelmi, O., Clode, P. L., Gregg, A., Parsons, J. E., Wakelin, S. A., Pring, A., Hough, R., Southam, G. & Brugger, G. 2010. Nanoparticle factories: biofilms hold the key to gold dispersion and nugget formation. *Geology,* **38**, 843-846.

Reith F, Stewart L, Wakelin SA. Supergene gold transformation: Secondary and nano-particulate gold from southern New Zealand. Chemical Geology. 2012 Aug 6;320:32-45.

Reith, F., Rea, M.A., Sawley, P., Zammit, C.M., Nolze, G., Reith, T., Rantanen, K., Bissett, A. 2018. Biogeochemical cycling of gold: Transforming gold particles from arctic Finland. *Chem Geol* **483**, 511-29.

Reith F, Falconer DM, Van Nostrand J, Craw D, Shuster J, Wakelin S 2020. Functional capabilities of bacterial biofilms on gold particles. *FEMS Microbiology and Ecology* 96, https://doi.org/10.1093/femsec/fiz196.

Roy, S., Upton, P. & Craw, D. 2018. Gold in the hills: patterns of placer gold accumulation under dynamic tectonic and climatic conditions. *Mineralium Deposita*, **53**, 981-995.

Shuster, J.& Southam, G. 2015The in-vitro “growth” of gold grains. Geology. Jan 1;43(1):79-82.

Shuster, J., Lengke, M., Marquez-Zavalia, M.F.& Southam, G. 2016. Floating gold grains and nanophase particles produced from the biogeochemical weathering of a gold-bearing ore. *Econ Geol*, **111**, 1485-1494.

Shuster, J. & Reith, F. 2018. Reflecting on gold geomicrobiology research: thoughts and considerations for future endeavors. *Minerals*, **8**, 401.

Shuster, J., Johnston, C.W., Magarvey, N.A., Gordon, R.A., Barron, K., Banerjee, N.R. & Southam, G. 2015 Structural and chemical characterization of placer gold grains: implications for bacterial contributions to grain formation. *Geomicrobiology Journal,* **7**, 158-69.

Sillitoe, R.H. 2005. Supergene oxidized and enriched porphyry copper and related depoits. In: Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J., Richards, J.P. *Economic Geology 100 Anniversary Volume*, Society of Economic Geologists, Littleton, Colorado, 723–768.

Simon, G., Kesler, S.E., Essene, E.J., Chryssoulis, S.L., 2000. Gold in porphyry copper deposits: experimental determination of the distribution of gold in the Cu-Fe-S system at 400 to 700 C, Econ Geol. 95, 259–270.

Stewart. J., Kerr, G., Prior, D., Halfpenny, A., Pearce, M., Hough R., & Craw, D. 2017 Low temperature recrystallisation of alluvial gold in paleoplacer deposits. *Ore Geology Reviews,* **88**, 43-56.

Stoffregen, R.E. Genesis of acid-sulfate alteration and Au-Cu-Ag mineralization at Summitville, Colorado. 1987. Economic Geology. **82**, 1575-91.

Townley, B.K., Hérail, G., Maksaev, V., Palacios, C., De Parseval, P., Sepulveda, F., Orellana R., Rivas, P. & Ulloa, C. 2003. Gold grain morphology and composition as an exploration tool: application to gold exploration in covered areas. *Geochemistry, Exploration, Environment, Analysis,* **3**, 29-38

Webster, J.G. & Mann, A.W. 1984. The influence of climate, geomorphology and primary geology on the supergene migration of Au and Ag. *J. Geochemical Exploration,* **22**, 21-42.

Webster, J. G. 1986. The solubility of gold and silver in the system Au-Ag-S-O_2-H_2O at 25° C and 1 atm. *Geochimica et Cosmochimica Acta*, **50**, 1837-1845.

Wierchowiec J, Mikulski SZ, Zieliński K. Supergene gold mineralization from exploited placer deposits at Dziwiszów in the Sudetes (NE Bohemian Massif, SW Poland). Ore Geology Reviews. 2021 Feb 10:104049.

Wrighton, T.M. 2013 Placer gold microchemical characterization and shape analysis applied as an exploration tool in western Yukon. Unpublished MSc Thesis, University of British Columbia.140p

Youngson, J. H. & Craw, D. 1999. Variation in placer style, gold morphology, and gold particle behavior down gravel bed-load rivers; an example from the Shotover/Arrow-Kawarau-Clutha River system, Otago, New Zealand. *Economic Geology*, **94**, 615-633.

Youngson, J. H., Woperies, P., Kerr, L. C. & Craw, D. 2002. Au-Ag-Hg and Au-Ag alloys in Nokomai and Nevis valley placers, northern Southland, and Central Otago, New Zealand, and implications for placer-source relationships. *New Zealand Journal of Geology and Geophysics*, **45**, 53–69.

Zammit, C.M., Schuster, J.P., Gagen, E.J., Southam, G., 2015. The geomicrobiology of supergene metal deposits. Elements, 11, 305-310.

Figure Captions

Figure 1. Examples of external and internal features of placer gold particles that underpin this study. Black and white scale bars are 1mm intervals. (a)-(c) examples of progressive physical modification of gold particles associated with transport in the fluvial environment.(a) Eldorado Creek, Yukon, (b) Last Chance Creek, Yukon, (c) Carie Burn, central Scotland. (d)-(f) Placer gold nuggets with minerals attached: (d) Nugget with silver coating of Bi telluride, Mechanic Creek, Yukon, Canada. (e) Rough gold particle from Kildonan Burn, Scotland with attachment of quartz. (f) Nugget of gold (29 wt % Ag) exhibiting triangular crystal faces, with coating of Pb-As-bearing secondary minerals. (g-j) internal heterogeneity within placer gold particles revealed in BSE images (g) Homogeneous Au-Ag particle core surrounded by continuous Au rim, Co. Wexford, Ireland. (h)-(j) Examples of mineral inclusions in placer gold particles. (h) Pyrite inclusions, with Fe oxide pseudomorph after pyrite at gold particle edge, Sperrin Mountains, N. Ireland. (SE image). (i) Molybdenite inclusion, within pure gold alloy, eluvial deposit, Kivu, Rwanda (SE image). (j) Galena inclusion deformed sympathetic to gold particle flattening. River Almond, Scotland (BSE image).

Figure 2. Examples of features of gold formed in hypogene settings, all BSE images unless otherwise stated. (a) Ag-rich alloy surrounding Au-Ag core, hypogene particle, Violet Mine, Klondike, Yukon, Canada. (b) Ag-rich alloy within gold particle from the oxidized cap of the Casino Cu-Mo-Au porphyry, Yukon (c) Thin Ag-rich zones sympathetic to grain boundaries, veronica vein, Lone Star, Yukon, (d) Sphalerite inclusion in hypogene gold, Hunker Dome lode, Klondike, Yukon, Canada, (SE image).

Figure 3. Trace element distribution in hypogene particles and placer particles of hypogene origin. (a), (b) Images of the same part of hypogene particle, Buckland Zone, Lone Star, Yukon. (c)-(h) Tof –LA-ICP-MS maps showing intensities of Fe, Bi, La, Pb, Pt, and Sb.

Figure 4. Features formed in the weathering profile (a) Vermiform and platy authigenic gold overgrowths on a 1 cm nugget from Pleistocene colluvium, Otago, New Zealand (b) micron sized gold crystals on surface of a gold particle from a palaeo placer, Sardis, Turkey. (c) Gold zones

sympathetic to grain boundaries, in placer particle which exhibits only a thin discontinuous Au rim, Orange R. Namibia.

Figure 5. Textures associated with refractory hypogene gold deposits in Otago Schist, New Zealand, and associated supergene features in basement and nearby colluvium. (a) Sketch section through the transition from hypogene to supergene zones. (b) Typical refractory microparticulate gold encapsulated in hypogene arsenopyrite. (c) Coarse crystalline gold from in situ supergene zone. (d) Coarse gold particle, intergrown with ferrihydrite, from colluvium resting on a supergene zone. (e) Surface of supergene gold that has grown around an octahedral crystal of arsenolite (partially dissolved). (f) Close view of the surface of a supergene gold particle from colluvium resting on a supergene zone, showing late-stage supergene gold deposited in and around desiccation cracks in a Fe-sulphate coating. (g) Supergene gold partially enclosed a Fe-sulphate crystal on the outside of a small supergene nugget. (h) Edge of a colluvial gold particle from reduced zone below the water table, with authigenic pyrite, clay and microparticulate authigenic gold.

Figure 6. Gold recycling history in paleoplacers on the Otago Schist, New Zealand. (a) Schematic recycling pathways. (b) Angular nugget incorporated into a Pleistocene paleoplacer with recycled flakes. (c) Nugget and flake coexisting in a Cretaceous paleoplacer. (d) Micron-scale gold cementation of host sediment in Cretaceous paleoplacer.

Figure 7. Internal recrystallisation of evolved detrital gold particles from paleoplacers from Otago Schist, New Zealand, shown clearly in EBSD images (coloured grains). (a) Distorted single grain inside a transported small nugget. (b) Interior and rim of a deformed flake, showing distortion of core grain boundaries and grains, and an annealed rim. (c) Smeared margin of a particle. (d) Mylonitic grain structure inside the smeared zone in c. (e) Contrasting grain sizes of coarse-grained core and fine-grained rim. (f) Etched particle, showing that some of the coarse-grained core has recrystallised, around arsenopyrite inclusions. (g) Recrystallised grain structure of the outer edge of a particle from a Cretaceous paleoplacer. (h) Section from core to rim of a particle from same paleoplacer as g. (i) Authigenic gold encrustation adhering to the rim of a flake. (j) Interior of a fully annealed flake.

Figure 8. Characteristics of the core- rim interface (a)-(e) BSE images (a) and (b) particle from Hunker creek Yukon, showing islands of unaltered core within over- thickened rim, and an inclusion of arsenopyrite at the core- rim interface (b) enlargement of inclusion – rim relationship shown in (a). (c) chalcocite inclusion in placer particle form the Orange River, Namibia (d) Over-thickened rim in particles from Stowe Creek (Yukon) showing relict core within rim, (e) same feature in particle from Eldorado Creek, Yukon. (f) ToF LA-ICP-MS image of placer gold particle from the Similkameen R. BC, showing elevated Hg at particles edges.

Figure 9. Coarse gold particles examined in this study. (a) 1-4: Glengaber Burn, S. Scotland, 5-8: Shortcleugh Water Leadhills, Scotland, 9-11, Afon Mawdach, N. Wales, 12-14: Croagh Patrick stream in Mayo, Ireland. (b) c 5µm thick rim on particle 5, Shortcleugh Water (BSE image). (c) Chalcopyrite inclusion in particle 6, Shortcleugh Water (BSE image). (d) fragments of shale host in particle 4 , Glengaber Burn (SE image). (e) Average of 10 analyses for each particle superimposed on cumulative percentile vs increasing Ag plot describing Ag contents of smaller particles from the same locality (Data from Chapman *et al.* 2000a, b, c).

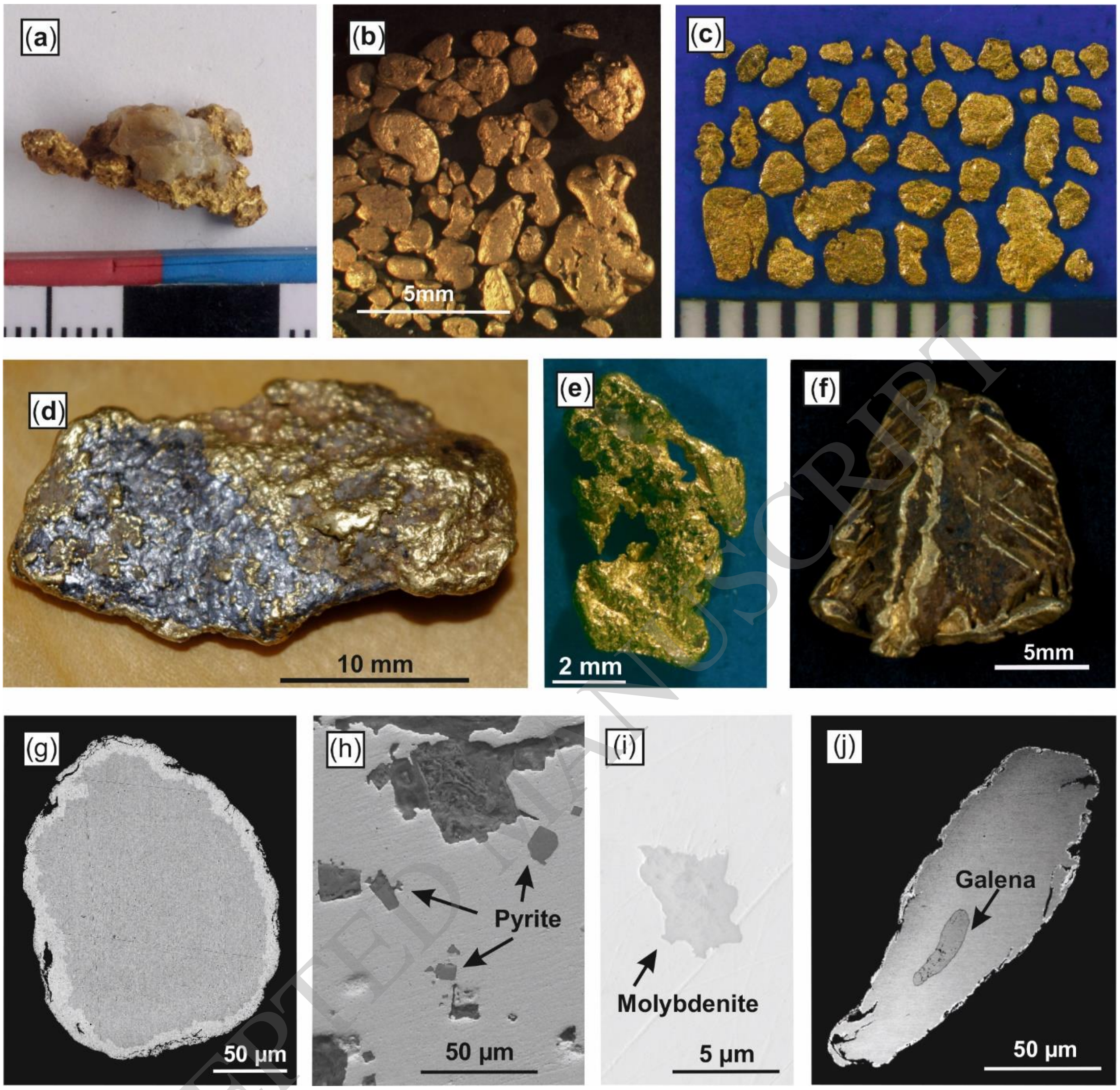

(a)
(b)
5mm
(c)
(d)
10 mm
(e)
2 mm
(f)
5mm
(g)
50 µm
(h)
Pyrite
50 µm
(i)
Molybdenite
5 µm
(j)
Galena
50 µm

Figure 1

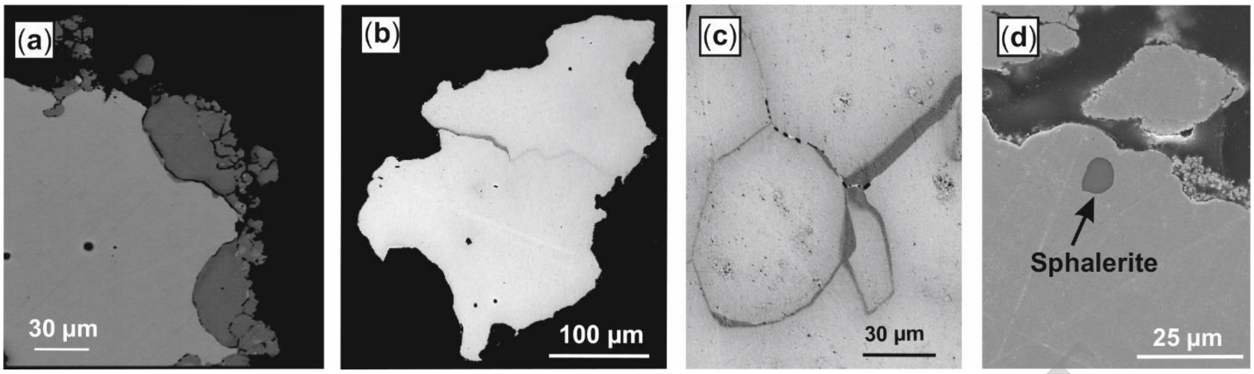


Figure 2

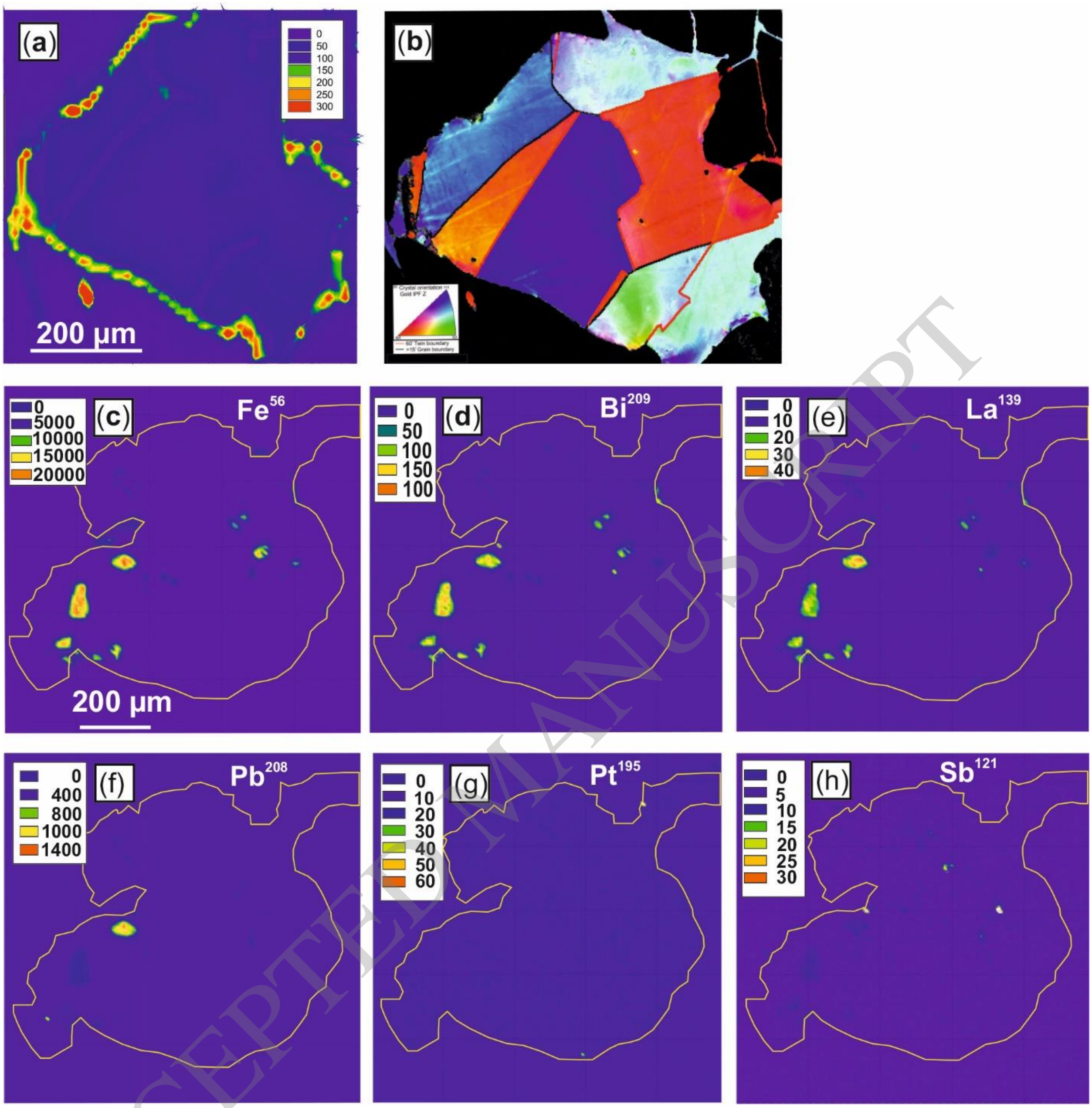

(a)
0
50
100
150
200
250
300
200 µm
(b)
(c)
Fe56
0
5000
10000
15000
20000
200 µm
(d)
Bi209
0
50
100
150
100
(e)
La139
0
10
20
30
40
(f)
Pb208
0
400
800
1000
1400
(g)
Pt195
0
10
20
30
40
50
60
(h)
Sb121
0
5
10
15
20
25
30

Figure 3

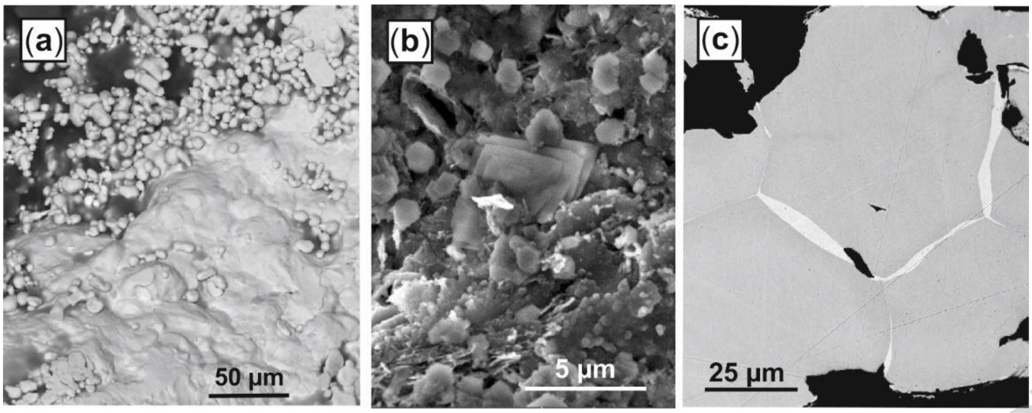
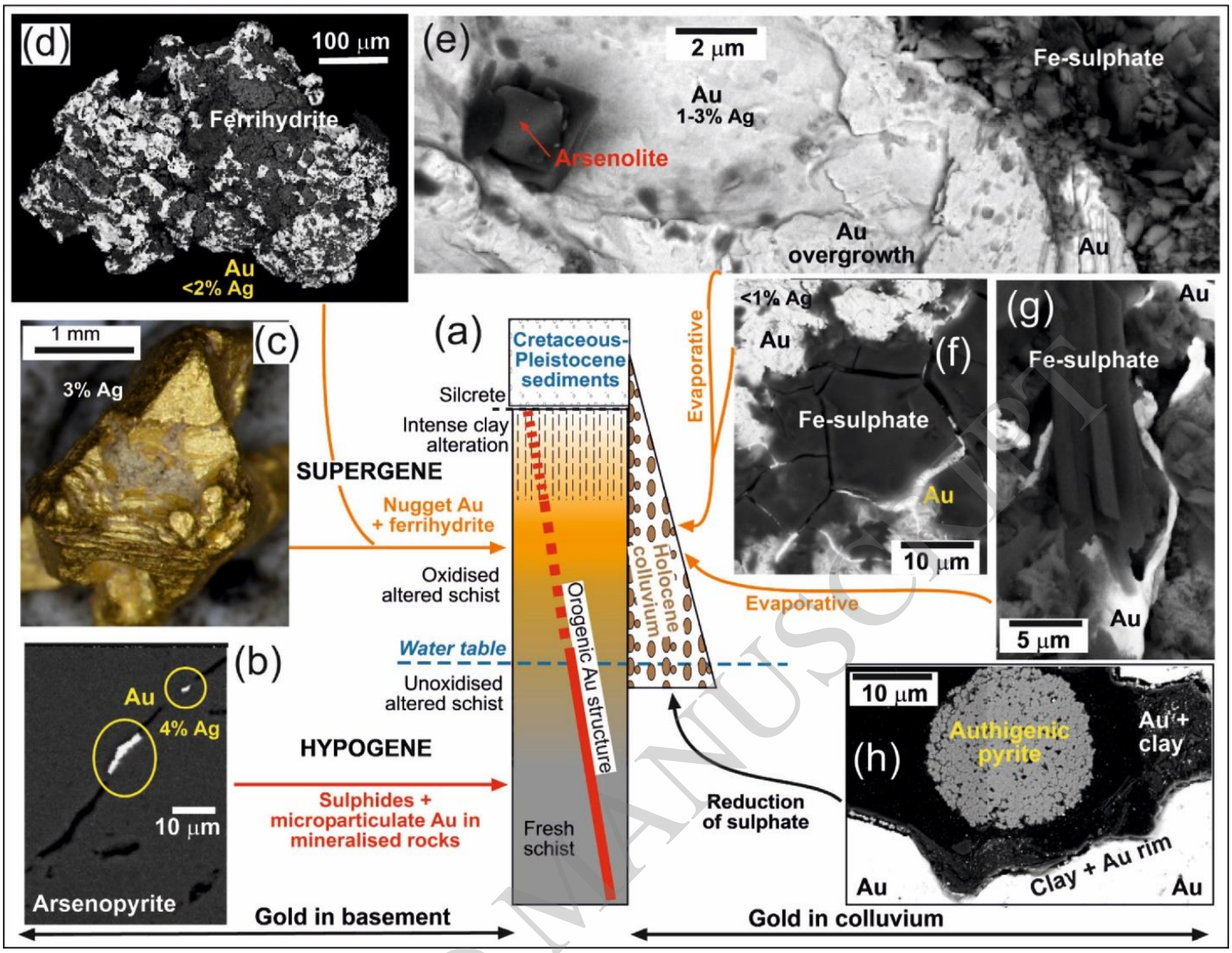


Figure 4



(d)
100 µm
Ferrihydrite
Au
<2% Ag
(e)
2 µm
Au
1-3% Ag
Arsenolite
Fe-sulphate
Au
overgrowth
Au
(c)
1 mm
3% Ag
(a)
Cretaceous-
Pleistocene
sediments
Silcrete
Intense clay
alteration
SUPERGENE
Nugget Au
+ ferrihydrite
Oxidised
altered schist
Water table
Unoxidised
altered schist
HYPOGENE
Sulphides +
microparticulate Au in
mineralised rocks
Fresh
schist
Orogenic Au structure
Holocene
colluvium
Evaporative
Evaporative
Reduction
of sulphate
(b)
Au
4% Ag
10 µm
Arsenopyrite
(f)
<1% Ag
Au
Fe-sulphate
Au
10 µm
(g)
Au
Fe-sulphate
Au
5 µm
(h)
10 µm
Authigenic
pyrite
Au +
clay
Au
Clay + Au rim
Au
Gold in basement
Gold in colluvium

Figure 5

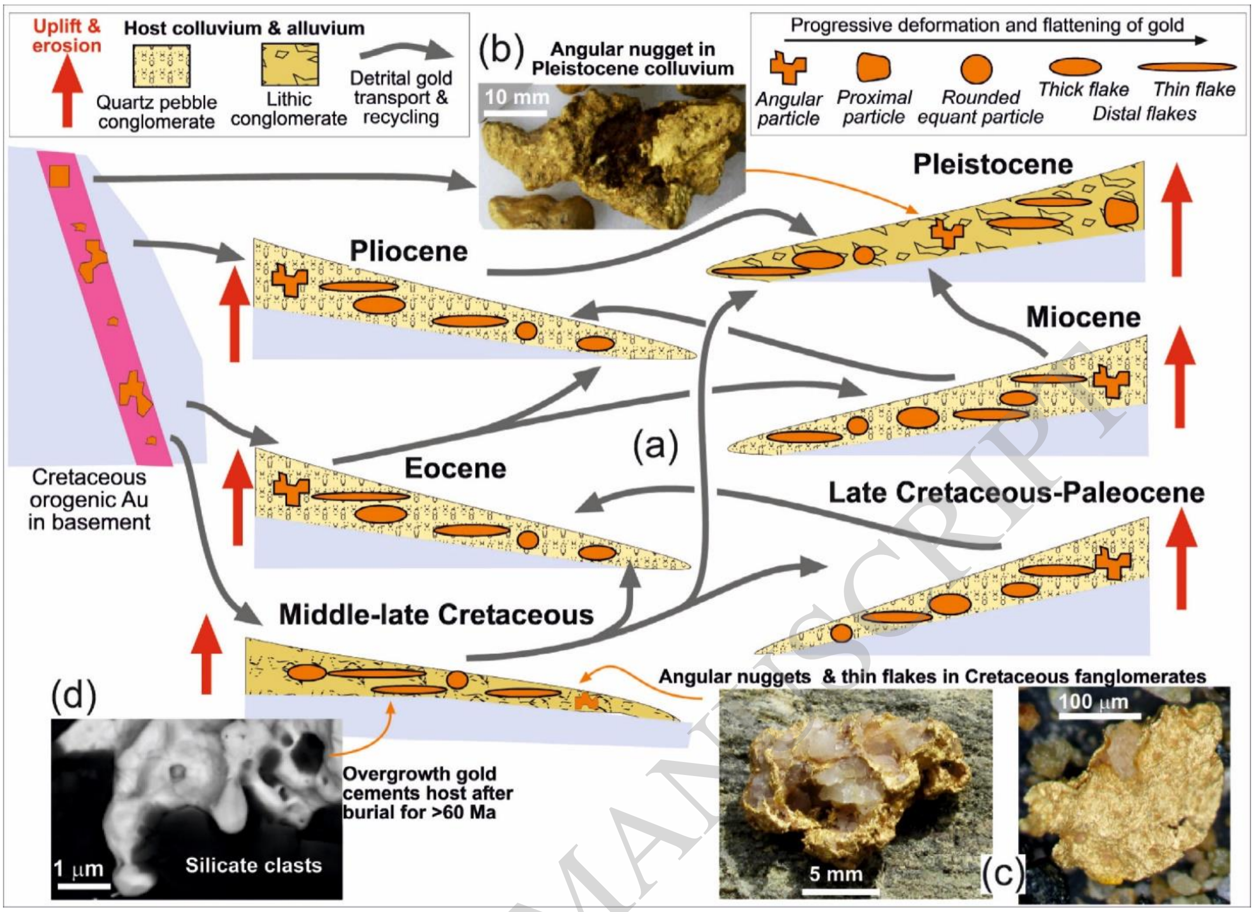
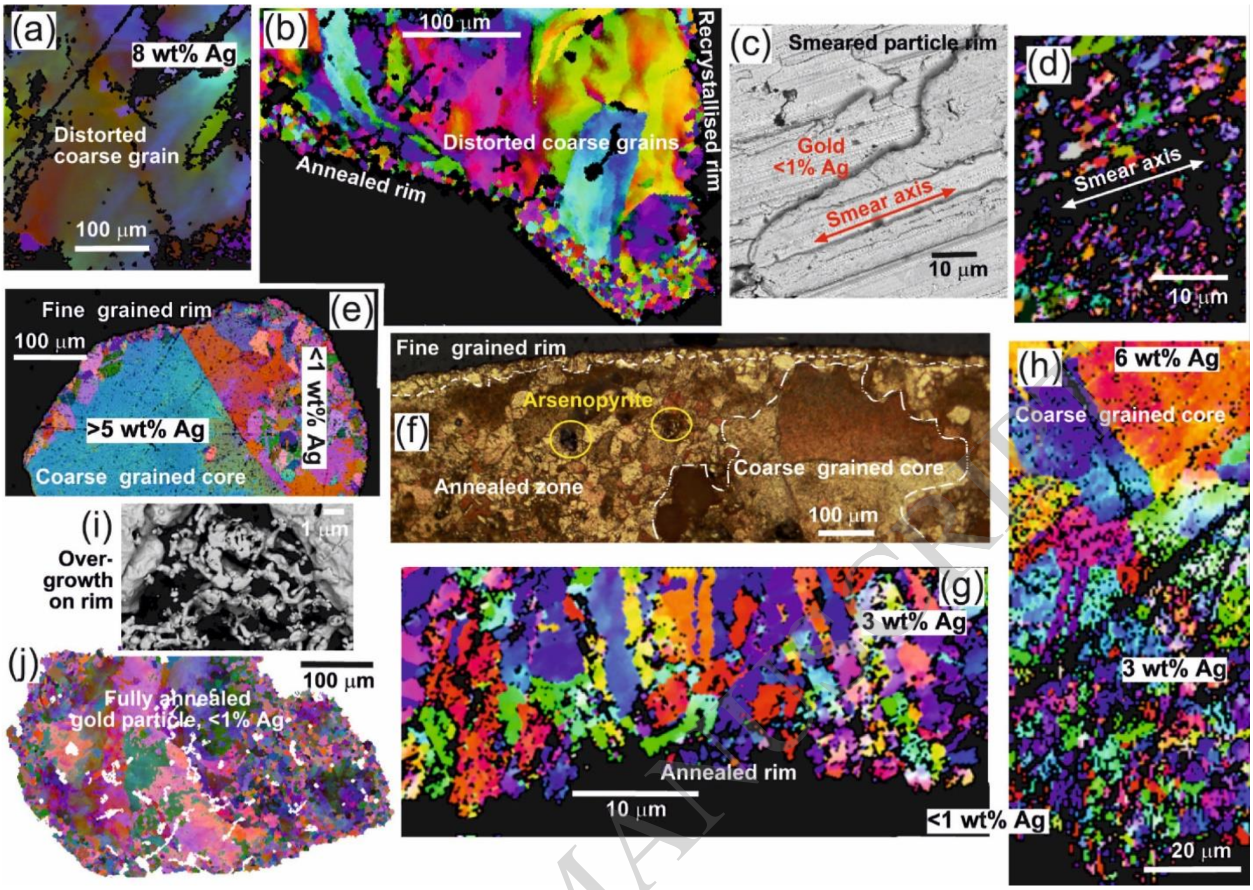

Uplift & erosion
Host colluvium & alluvium
Quartz pebble conglomerate
Lithic conglomerate
Detrital gold transport & recycling
(b)
Angular nugget in Pleistocene colluvium
10 mm
Progressive deformation and flattening of gold
Angular particle
Proximal particle
Rounded equant particle
Thick flake
Thin flake
Distal flakes
Pleistocene
Pliocene
Miocene
Eocene
(a)
Late Cretaceous-Paleocene
Cretaceous orogenic Au in basement
Middle-late Cretaceous
(d)
Angular nuggets & thin flakes in Cretaceous fanglomerates
100 µm
Overgrowth gold cements host after burial for >60 Ma
1 µm
Silicate clasts
5 mm
(c)

Figure 6



(a)
8 wt% Ag
Distorted coarse grain
100 µm
(b)
100 µm
Recrystallised rim
Distorted coarse grains
Annealed rim
(c)
Smeared particle rim
Gold <1% Ag
Smear axis
10 µm
(d)
Smear axis
10 µm
(e)
Fine grained rim
100 µm
>5 wt% Ag
<1 wt% Ag
Coarse grained core
(f)
Fine grained rim
Arsenopyrite
Coarse grained core
Annealed zone
100 µm
(h)
6 wt% Ag
Coarse grained core
3 wt% Ag
20 µm
(i)
Over-growth on rim
1 µm
(j)
100 µm
Fully annealed gold particle, <1% Ag
(g)
3 wt% Ag
Annealed rim
10 µm
<1 wt% Ag

Figure 7

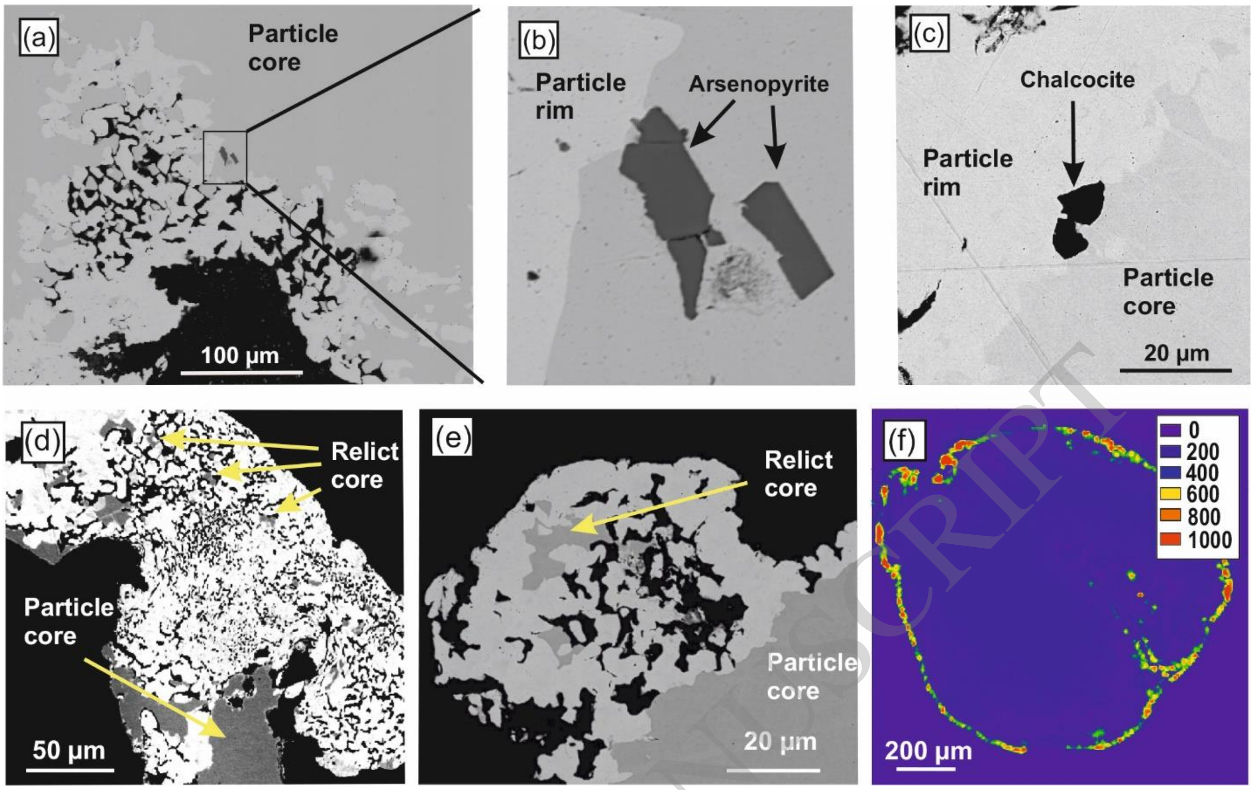

(a)
Particle core
100 µm
(b)
Particle rim
Arsenopyrite
(c)
Chalcocite
Particle rim
Particle core
20 µm
(d)
Relict core
Particle core
50 µm
(e)
Relict core
Particle core
20 µm
(f)
0
200
400
600
800
1000
200 µm

Figure 8

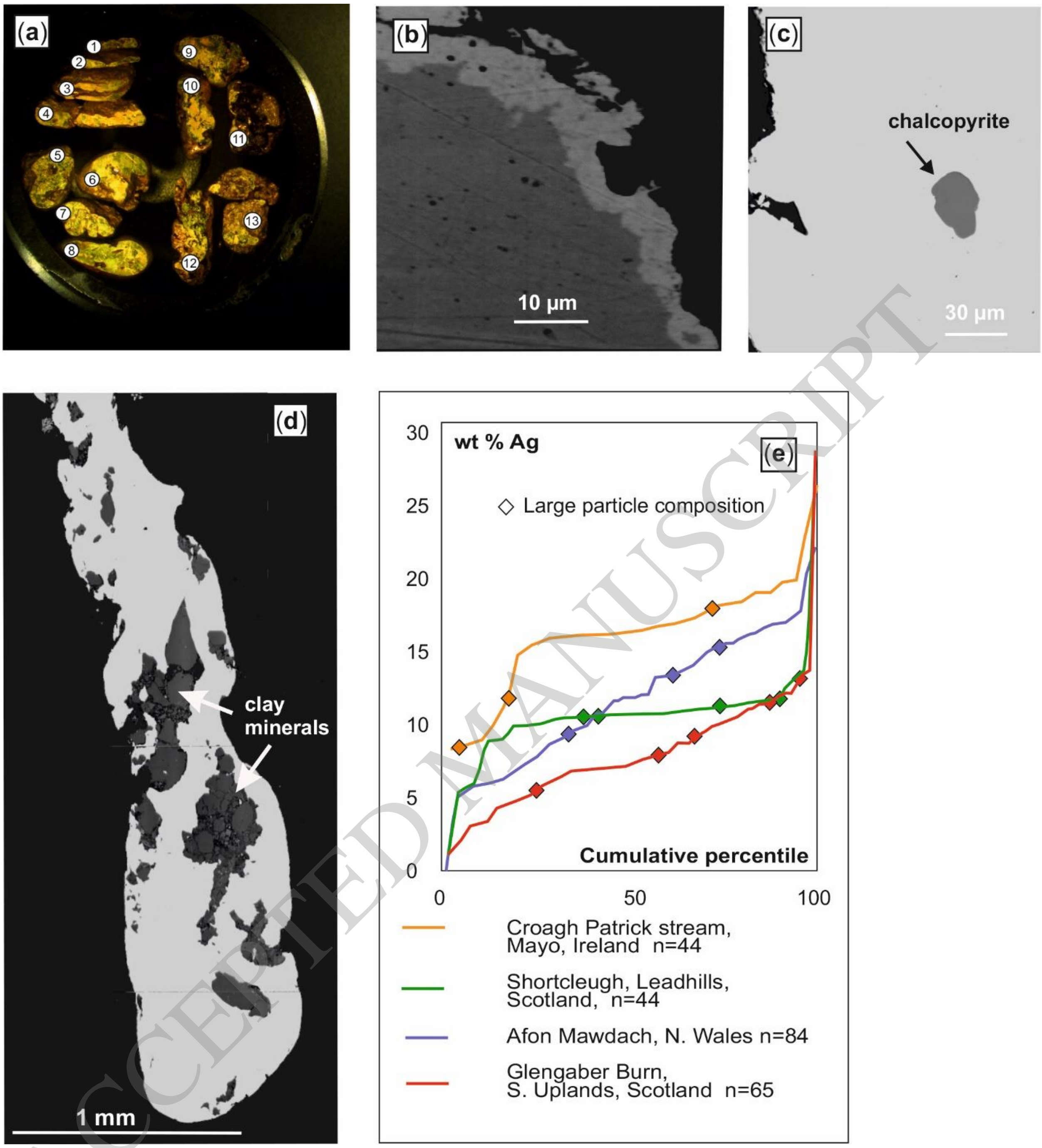

(a)
1
2
3
4
5
6
7
8
9
10
11
12
13
(b)
10 µm
(c)
chalcopyrite
30 µm
(d)
clay
minerals
1 mm
(e)
wt % Ag
Large particle composition
Cumulative percentile
30
25
20
15
10
5
0
0
50
100
Croagh Patrick stream, Mayo, Ireland n=44
Shortcleugh, Leadhills, Scotland, n=44
Afon Mawdach, N. Wales n=84
Glengaber Burn, S. Uplands, Scotland n=65

Figure 9