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Article:

Standish, CD, Chapman, RJ, Moles, NR et al. (2 more authors) (2022) Archaeological applications of natural gold analyses. Geological Society Special Publications, 516. pp. 401-424. ISSN 0305-8719

https://doi.org/10.1144/sp516-2021-59

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Geological Society, London, Special Publications

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C. D. Standish, R. J. Chapman, N. R. Moles, R. D. Walshaw & J. A. Sheridan

DOI: https://doi.org/10.1144/SP516-2021-59

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Received 27 March 2021
Revised 3 August 2021
Accepted 7 September 2021

Archaeological applications of natural gold analyses

Standish C.D.[1*], Chapman R.J.[2], Moles N.R.[3], Walshaw, R.D.[2] and Sheridan J.A.[4]

[1] *School of Ocean and Earth Science, University of Southampton, Waterfront Campus, National Oceanography Centre Southampton, European Way, Southampton, SO14 3ZH, UK*
[2] *Ores and Mineralization Group, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK*
[3] *School of Applied Sciences, University of Brighton, Lewes Road, Brighton BN2 4GJ, UK*
[4] *c/o Department of Scottish History & Archaeology, National Museums Scotland, Chambers Street, Edinburgh EH1 1JF*
*Corresponding author (email: C.D.Standish@soton.ac.uk)

Abstract: Compositional studies of natural gold usually have a geological focus, but are also important in archaeological provenancing. Both methodologies rely on compositional comparison of two sets of samples, one of which is geographically constrained. Here we describe how experiences in gold characterization resulting from geological studies are relevant to archaeology. Microchemical characterization of polished sections of natural gold identifies alloy compositions, alloy heterogeneity and mineral inclusions. Gold from all deposit types shows Cu and Sn values much lower than those recorded during numerous studies of artefacts. Inclusions in artefact gold include various Cu- and Sn-bearing compounds which indicate specific high temperature reactions that could ultimately illuminate the conditions of (s)melting. The use of LA-ICP-MS to generate a wide range of elemental discriminants for provenance studies may be compromised by alloy adulteration and/or unrepresentative analysis of natural/artefact alloys, which are commonly highly heterogeneous at the micron scale. Geological studies normally characterize only the earliest-formed (hypogene) alloy, whereas archaeology-focussed studies should entail analyses of bulk alloy compositions and impurities that may be incorporated during (s)melting. Isotopic-based provenancing alleviates many of these problems but, to date, generates regional rather than locality specific targets. A dual isotopic-compositional approach is recommended.

Characterization of ore systems via mineralogical studies involving compositional and isotopic analyses is a standard approach to deduce the ore-forming processes involved in gold mineralization, and to determine its age and geological setting (e.g. Simmons et al. 2005; Goldfarb and Groves 2015). An understanding of the relationships between the chemical composition of ore minerals and their geological environment of formation is also of benefit to other academic disciplines, and the key aim of this publication is to alert geologists to how this information can find application elsewhere. This contribution focusses on archaeological provenance studies which provide an excellent example of the application of geological knowledge to illuminate prehistoric technological capabilities and ancient networks of exchange or trade.

Archaeological provenance studies aim to link objects, including those made from metals (Northover et al. 2001; Desaulty et al. 2011), stone (Bevins et al. 2012), glass (Henderson et al. 2005) and amber (Beck and Shennan 1991), to their geological source(s). Not only do such studies strive to identify where the raw material used in the manufacture of an object may have originated, they can also inform on the presence and extent of raw material circulation pools, on patterns of exchange or trade with their associated social and political connections, on past economies, and on extraction processes. They can even allow exploration of the social meaning of an object or material. While it is highly challenging to link an artefact categorically to a single source, the strength of these provenance studies lie in their ability to allow hypotheses to be tested. With its perceived high status value in prehistory, and its high preservation potential, gold is commonly the subject of such studies (e.g. Chapman et al. 2006; Bendall et al. 2009; Ehser et al. 2011; Standish et al. 2014a; 2015).

Geological studies, which identify geochemical characteristics of gold that may act as discriminators between different sources, are key both in identifying discriminators that may be of use to archaeological provenance studies and in generating detailed compositional datasets of gold and associated minerals which, at the simplest level, permit comparison of artefact and potential source on a 'same or different' basis. Major element characterization of the artefact alloy, often through non-destructive analytical techniques, forms the backbone of the majority of such studies. This is variously supplemented with investigations into the minor and/or trace element composition of the artefact alloy, its Pb isotope composition, and the elemental or isotopic composition of any mineral inclusions (e.g. Meeks and Tite 1980; Chapman et al. 2006; Constantinescu et al. 2008; Warner et al. 2009; Ehser et al. 2011; Nocete et al. 2014; Standish et al. 2014a; 2015; Borg et al. 2019; Borg and Pernicka 2020). A summary of influences on the source-artefact compositional relationship is provided in Figure 1.

The chemical and mineralogical characteristics of gold particles liberated by erosional processes are inherited by the resulting placer deposit (Chapman et al. 2021a). This principle has underpinned numerous studies of the relationship between placer and lode gold (e.g. Knight et al. 1999; Chapman and Mortensen 2016, and references therein). The discovery and recovery of placer gold by prehistoric people is entirely plausible and probably preceded the requisite technology for recovery of gold from most, if not all, *in situ* gold ores. Therefore, the principle that compositional features of placer gold are those of their bedrock source is important, because it provides the means to link a potential site of gold winning to a local geological setting with the associated constraints on gold compositional range. In recent years, compositional studies of placer gold have become more sophisticated and have sought to identify diagnostic features of gold from specific geological settings (e.g. Chapman et al. 2017; 2018). Consequently, there is no longer a need for archaeological provenance studies to identify a single source, but instead to narrow the search area according to fundamental geological criteria (e.g. Standish et al. 2015) whilst acknowledging considerations of the practical feasibility of gold recovery from a particular area at a particular period in the past.

The geochemical signature of an ore may not match that of an object produced directly from it because of compositional changes induced by factors including the different stages of the object's manufacture; by alloying, recycling and mixing of gold from different sources; and by the object's use-life and post-depositional history (Fig. 1). Modern metal processing technologies such as bulk smelting and electro-refining all but eradicate these features and produce a homogeneous alloy of the desired composition. However, in prehistory gold extraction and working probably involved small batches of material and different technology, and it is possible that some characteristics of natural gold would persist into the archaeological artefacts. Ancient goldworking methods have been the subject of much research (e.g. Needham 2000; Armbruster 2019; 2021), as archaeologists have sought to understand emergent technologies and their transfer between societies. Speculation on the technological development of goldworking techniques is in part informed by the alloy composition of the artefacts. For example, Early Bronze Age (EBA) Irish goldwork appears simpler than that of Late Bronze Age (LBA) objects, not only in terms of its design, but also in that the alloy is chemically simpler: whilst gold in EBA artefacts is broadly compatible with the compositional range of natural gold (as discussed below), that of LBA artefacts is typically richer in Cu and Sn (Chapman et al. 2006). This suggests deliberate alloying to achieve the desired qualities of hardness and colour, and/or possibly to render the alloy more amenable to working. More complex metallurgical/goldworking processes might be expected to result in different types of micro-features within the gold artefacts, and the presence of the latter may be used to inform on the former.

With prior knowledge of discriminators in natural gold, it is possible to predict the signature that would have been generated according to different goldworking conditions, and it will become apparent which discriminants are of use in comparing artefact to ore. Furthermore, by understanding why discriminants vary geologically, it becomes possible to interpret the geochemical signatures of artefacts as if they were natural samples themselves, and hypothesise the style/s or geological period/s from which the source material may originate. As it is impossible to characterize every potential archaeological source, such interpretive knowledge is highly valuable.

The overriding aim of this paper is to provide an unambiguous account of the nature of the compositional information that is required to underpin archaeological provenance studies of gold, to identify what information is not useful, and to explain how such studies can generate robust conclusions based on sound geological principles. Firstly, we address the mineralogical nature of gold, including its microfabric and mineral associations, and discuss the relevance to characterizing natural gold from localities of archaeological interest. Secondly, we show how techniques developed for characterization of gold in various geological pursuits are relevant to archaeological study. With an archaeological focus on the British and Irish Bronze Age, we illustrate this by presenting new data describing the internal features of four gold artefacts created over the course of ~1,300 years.

Geochemical discriminants in natural gold

Elemental composition and heterogeneous microfabrics

Consideration of Au-Ag ratios. Gold is usually found in nature as an alloy, with Ag typically ranging from ~5–25 wt% sometimes alongside relatively minor amounts of Cu, Hg and Pd, whilst other elements may be present at trace concentrations (Table 1; Chapman et al. 2021b). The nature of the various geological settings in which gold forms controls the depositional environment, such that it may be possible to link gold compositions to deposit type (see Chapman et al. 2021c). The Au-Ag ratio in natural gold is sensitive to a number of parameters that vary within a mineralizing system (Gammons and Williams-Jones 1995), so it is usual for individual gold particles from one bedrock occurrence to exhibit different compositions (Fig. 2A). Consequently, characterization of gold from a particular locality requires studies of populations of particles (Fig. 1) such that the compositional range may be established (e.g. Chapman et al. 2021c and references therein). Graphical representations of Ag composition of individual particles efficiently display the complexity of the population, and permit identification of mutually exclusive subpopulations, indicative of multiple contributions.

Whilst Ag is the obvious metal discriminant for archaeological provenance studies, it is rarely diagnostic of gold deposit type (Fig.3, Chapman et al. 2021b), although extreme values may prove useful. For example, characteristically pure gold is associated with low temperature oxidizing chloride systems (although in this instance Pd would also be expected), and some high-Ag alloys are formed in epithermal systems (Table 1; Morisson et al. 1991). Nevertheless, Ag concentrations in artefact gold inconsistent with naturally occurring gold alloys, e.g. less than ~2 % or greater than ~30 % (Fig. 3), are likely an indication of specific metallurgical processes during fabrication (e.g. Rehren et al. 1996; Ramage and Craddock 2000), and in archaeological contexts where silver was not an available commodity, the Ag content of an artefact alloy provides an upper limit for potential sources.

Gold associated with different geomorphological settings, such as placer and lateritic environments, do not have distinct geochemical properties and are therefore not a 'type'. This is the case for Au-Ag ratios, as gold grains inherit the compositional features of the gold in the hypogene source. However, Au/Ag may be modified to a small extent through the formation of gold-rich rims (e.g. dos Santos Alves et al. 2020; Chapman et al. 2021a; Combes et al. 2021), as discussed in the following section. The composition of artefacts is itself a weighted average of the component gold particles, and to gain meaningful comparison with natural gold, notwithstanding the potential complicating factors mentioned above, it is necessary to replicate the outcomes of fabrication processes by either melting or dissolution of an appropriate quantity of particles.

Heterogeneous microfabrics. Compositional heterogeneity with respect to Au and Ag is indicative of distinct episodes of gold particle development. These may be a consequence of either an evolving hydrothermal system, or residence of the particles in the surficial environment, or both. An appreciation of the nature of these microfabrics is necessary to interpret the outcomes of some analytical methods.

The most commonly encountered heterogeneous feature in detrital gold particles is a gold-enriched rim, typically of 5–20 µm true thickness (Fig. 2B). Rim formation has been ascribed both to Ag depletion (e.g. Groen et al. 1990) and Au augmentation (e.g. McCready et al. 2003). The subject is discussed in detail in Chapman et al. (2021a). The reader is referred to that text for a more detailed evaluation that leads to the conclusion that the outer portions of gold particles comprise alloy with two different origins. The micron to sub-micron thicknesses of pure Au are a near ubiquitous feature on the surface of most detrital gold particles, and are a consequence of additions of gold either via chemical precipitation or biogenic action. These accumulations are distinct from rim formation, which is a consequence of Ag removal. The observation of well developed (c. 20 µm) rims on placer gold particles is evidence of considerable residence in a fluvial setting. Rim thicknesses are usually fixed, such that the proportion of rim gold is greater in small or flaky particles that are more mobile in fluvial settings. This relationship explains both the observation that distal placer gold is relatively Au rich with respect to that in proximal placers in the same drainage, and the assertion that gold from placers exhibits a higher Au/Ag ratio with respect to that of the source (Boyle 1979; Chapman et al. 2021a). Studies that have a focus on mineral exploration and/or geological characterization of the bedrock source of detrital gold (Fig. 1) normally seek to obtain the core composition, as this relates to the original environment of mineralization. Consequently, it is necessary to section gold particles, or to ablate the rim, in order to expose the core. In such studies, normally each particle is analysed in a sample set (a 'population') from a locality, rather than melting or dissolving the gold to obtain a bulk analysis. A bulk alloy composition for the locality, disregarding particle rim formation, is approximated by taking the mean or median value of the individual analyses.

Compositional heterogeneity of the gold alloys within individual particles is another important feature with implications for the choice of analytical approach. Localised areas of relatively Ag-rich alloys are not uncommon (e.g. Fig. 2C,D) and have been related to post-depositional equilibration with either cooler or relatively Au-impoverished fluids (Chapman et al. 2021b). The textural relationship between volumes of different alloy compositions revealed in polished section indicates both a paragenetic sequence and whether alloy modification occurred in a hypogene or surficial setting (see discussion in Chapman et al. 2021b).

Minor alloying metals. Copper, mercury and palladium concentrations may be more useful than silver as diagnostic indicators of deposit type (Table 1; Chapman et al. 2021b and references therein). Two types of anomalous concentration pattern may be present within a population of gold particles, and these are best described by considering the two possible end members. Firstly, a minor metal may be present in all or most particles at detectable, but low, levels. The concentrations of Cu in gold from porphyry settings provides an example (e.g. Morisson et al. 1991, Chapman et al. 2018). Alternatively, a small proportion of the population of gold particles may exhibit highly elevated concentrations of a minor metal: e.g. the Hg contents of some gold particles from some orogenic settings (Cavanacaw, N. Ireland: Chapman et al. 2000b; Lone Star District Klondike, Yukon, Canada: Chapman et al. 2010; some localities in the Cariboo Gold District, British Columbia, Canada: Chapman and Mortensen 2016). Similarly, occasional high Hg and Pd values have provided a generic discriminant for gold from alkalic porphyry systems (Chapman et al. 2017) and Pd and low/absent Ag is a generic marker for gold from oxidizing chloride hydrothermal systems (Chapman et al. 2009). Gold associated with ultramafic rocks in the Coquihalla River catchment, British Columbia, exhibited a wide range of Cu contents to a maximum of around 25 wt% (Knight and Leitch 2001).

Copper concentrations in artefact gold have provided an important criterion by which to classify the alloy. As copper was readily available in antiquity, deliberate or accidental additions of metal genetically unrelated to the gold are plausible and could greatly influence the approach to provenancing. Consequently, it is important to establish both the range of Cu concentrations in natural gold and to identify any generic relationships between Cu content and deposit type. Figure 4A presents the Cu contents of 4474 gold particles from 9 auriferous regions of the UK. Gold from one of the regions (Ochil Hills) is inferred to be low sulphidation (LS) epithermal and potentially associated porphyry mineralization (Chapman et al. 2005), whereas orogenic gold mineralization is present elsewhere. Analysis by electron probe micro-analysis (EPMA) showed that around 94% of all data points are below LOD, but many of the relatively high values derive from gold particles from the Ochil Hills. Identification of deposit-specific compositional criteria could provide important information in the context of provenancing, and it is important to establish general compositional features. As the processes which form different gold deposit types are generic, it is appropriate to invoke the best data sets that we have at our disposal despite geographical location. Quantitative Cu data derived from laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) analyses of gold from a range of Canadian deposit styles (Banks et al. 2018) is illustrated in Figure 4B. Cu values in gold from magmatic hydrothermal systems (Fig. 4B) generally exhibit higher Cu values than gold from epithermal or orogenic settings, a result consistent with the study of Cu contents of British and Irish gold reported above. In almost every instance, Cu values in natural gold alloys are over 2 orders of magnitude smaller than commonly observed in LBA British and Irish gold artefacts (Warner 2004; Chapman et al. 2006; Standish 2012).

A parallel exercise was undertaken investigating Sn levels in natural gold. Systematic screening of gold particles for Sn using EPMA was undertaken on many particles from the UK Caledonides. Figure 4C shows that over 90% of analysis values are below LOD. Quantitative data derived from LA-ICP-MS analysis of gold from different deposit styles (Figure 4D) shows all values to be less than 10ppm (0.001 wt%). Although gold from calc-alkalic porphyries appears to contain more Sn than gold from other deposit types, and elevated concentrations have been recorded for some placer deposits in certain ore-fields (e.g. Ehser et al. 2011), values are generally 3 orders of magnitude less than those regularly recorded in artefact gold.

Trace elements in natural gold. Trace element analysis, both of natural gold and of artefact gold using LA systems linked to quadrupole ICP mass spectrometers, have become increasingly common over the last 25 years, aiming to take advantage of the extremely low limits of detection of all elements (e.g. Watling et al. 1994, 1999; Taylor et al. 1995; Ehser et al. 2011; Banks et al. 2018). Boyle (1979) reported that numerous metals were present in natural gold, and subsequent application of LA-ICP-MS studies in geological and archaeological contexts aimed to take advantage of the larger suite of elemental discriminants so generated.

The only published large-scale study of individual gold particles (1,100) using LA-ICP-MS revealed that only Au, Ag Cu and Hg are almost always detectable (Banks et al. 2018 summarised in Chapman et al. 2021b), and of the remaining elements only Sb, Bi and Pd were detectable in >50% of the particles studied. Thus the premise that the range of generic discriminants would be extended has not been realized. Nevertheless, quantitative data are generated for Cu and Hg, and other elements may be present in sufficient gold particles within deposit-specific or geographically-specific studies to fulfil the role of a discriminant. Ablation of the polished gold particle surface inevitably samples sub-surface material where compositional heterogeneity cannot be observed. The time analysis of elemental responses from quadrupole ICP-MS systems easily detects ablation of heterogeneous features such as inclusions (see description below) because the Au-Ag response falls sympathetically with the rise in elements present in the inclusion. However, in addition to these major responses there are often fleeting lower elemental signals. Some of these may be a consequence of partial or tangential ablation of inclusions, but in other cases the responses are of extremely low intensity.

The facility to generate trace element maps of gold particle sections using a Time of Flight (ToF)-MS system has for the first time revealed striking heterogeneity, which may occur in alloys homogenous with respect to Ag at wt% levels (Fig. 2E–G) (Banks et al. 2018; Chapman et al. 2021b). The new understanding of the nature of heterogeneity in gold particles provided by the ToF-MS systems shows these features to comprise localised and low concentrations of elements within gold alloy, defined as 'clusters' by Chapman et al. (2021b). The heterogeneity revealed by these trace element maps provides a robust explanation for the variation in elemental responses that are very commonly recorded using standard ablation processes linked to a quadrupole ICP-MS system. The heterogeneity is so pronounced (e.g. Fig. 2G) that sub-sampling of a 1mm gold particle using a relatively large laser diameter of 50µm diameter could generate a wholly unrepresentative value for specific trace elements. The realization that element distribution within natural gold is far from uniform has profound implications for studies that are designed to generate an array of discriminants to permit confident correlation of artefact to source. The degree of heterogeneity observed in natural gold, together with the range of elements recorded in particles from single localities, negates the rationale that fewer particles are required for robust characterization.

Mineral inclusions. Inclusions of other minerals are commonly encountered within natural gold (e.g. Fig. 2H,I). The abundance of different inclusions species within a population of gold particles is a consequence of ore mineralogy, and gangue minerals such as quartz and calcite are the most common. Correlation of gold deposit type with associated mineralogy is well established (Table 1), and inclusions provide a route to reconstruction of the hypogene ore (and hence deposit type) through the study of detrital gold particles. Inclusions are readily identified using the imaging facilities of a scanning electron microscope (SEM) in conjunction with an energy dispersive spectroscopy (EDS) system, and their systematic recording has become routine in many studies. Inclusion suites preserved in detrital gold particles may be diagnostic for specific deposit types (e.g. Chapman et al. 2017; 2018; 2021c) and are an important route to classifying gold from different localities within regions of complex geology (Moles and Chapman 2019; Chapman et al. in press). A standard approach to characterization of the compositional features of a population of gold particles involves synthesis of the alloy and inclusion data to generate a 'microchemical signature' (e.g. Chapman et al. 2000a) and this approach may prove to be transferrable to the study of fabricated artefact gold, as we discuss below. PGE inclusions have been reported in artefact gold, however they are not found in native gold and therefore likely derive from a smelt charge containing both metals. The origin of the mixture is most probably the co-occurrence of Au and Pt in placers derived from different host rocks in the same drainage (Meeks and Tite 1980; Jansen et al. 2016).

Isotopic Analysis

Pb Isotope Analysis. The Pb isotope signature of an ore mineral, typically expressed as a series of ratios, is controlled by the composition and age of the geological source of the Pb incorporated (Faure and Mensing 2005), and can therefore be employed to link ore deposits to geochemical source regions or provide the deposits with a broad chronology. Lead isotope analysis is frequently used in studies of gold mineralization with most studies analysing the associated sulphide minerals. For example, analysis by Curti (1987) of sulphides associated gold by from the Monte Rosa deposit of the Western Alps suggested ore deposition from at least two hydrothermal systems with Pb deriving primarily from Caledonian metapelites, whilst analysis by Mortensen et al. (2010) of sulphides associated with gold from the Otago Schist Belt indicated two distinct mineralizing events derived from essentially the same crustal source. It is also now possible to analyse gold particles directly (Standish et al. 2013), and in a study of Irish gold mineralization, Standish et al. (2014b) demonstrated that placer gold, lode gold, and associated sulphides from the same deposit or locality inherit Pb from the same source(s) (Fig. 5). This highlighted placer-lode relationships, and demonstrated that the analyses of one sample type can be used as a proxy for others. It also showed how the Pb isotope signature of the gold hosted by orogenic belts was largely structurally controlled, with signatures primarily reflecting that of the basement terranes that host them. In addition, the study identified a distinct, more radiogenic, source of Pb, hypothesised to be linked to magmatic processes. The Pb isotope ratio signature of gold therefore acts as a useful discriminant relating to both the geological source and age of the Pb incorporated into gold mineralization.

Ag Isotope Analysis. During the past decade, Ag isotope ratio analysis (^{109}Ag/^{107}Ag) by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is increasingly being used to study gold mineralization (e.g. Chugaev and Chernyshev 2012; Argapadmi et al. 2018; Brügmann et al. 2019). These studies have demonstrated that both primary deposits in the same ore field, and particles/nuggets with the same placer deposit, can vary isotopically. For example, gold samples from two mines at the Barberton Greenstone Belt, South Africa, are characterized by ε^{109}Ag values ranging from -4.2 ± 0.4 to 3.6 ± 0.4 (Argapadmi et al. 2018). Yet they also show that the isotope ratios of single gold particles or 'nuggets' can be internally isotopically homogeneous (Brügmann et al. 2019), thus Ag isotope ratios may have some potential as a discriminant for correlating placer gold with bedrock mineralization (Fig. 6). No study has identified a correlation between Ag isotope ratios and either age of the deposit or composition of their host rocks. Instead the silver isotope ratios are likely to constrain the physicochemical environment of gold deposition or supergene alteration (e.g. Chugaev and Chernyshev 2012; Argapadmi et al. 2018; Brügmann et al. 2019).

Whilst there are limited Ag isotope data relating to gold alloy, parallel studies of Ag isotope ratios in metallic silver and other ore mineral samples have suggested similar isotopic controls. Arribas et al. (2020) concluded that there is no evidence for systematic Ag isotope variation associated with deposit type, source rock, mineralization age or temperature, suggesting that this technique has a limited use as a tracer in archaeological provenance studies. Indeed, Ag isotope ratio variation in native silver has instead been linked to both redox reactions in low-temperature environments (epigenetic, gossan) and temperature effects and variable abundances of S, Sb, and As in hydrothermal fluids (Fujii and Alberède 2018; Marthur et al. 2018). However, as Arribas et al. (2020) point out, variations within and between certain deposits and ore fields may exist, even though detailed ore deposit studies would be needed to understand them. Furthermore, the approach has potential to act as a complimentary discriminator to Pb isotope ratios because it is able to discriminate sources in the same ore field and at a smaller geographical scale due to isotopic variations relating to hydrothermal fluid evolution (e.g. Argapadmi et al. 2018).

Mineral associations of gold in surficial environments

Compositional characteristics of natural gold are clearly an important influence on those of the resulting artefact, at least as far as Chalcolithic and Early Bronze Age objects are concerned since they were made before deliberate alloying became commonplace. However, a charge to a smelter is unlikely to have comprised only gold alloy particles, as rudimentary mineral separation processes could not generate a ‘clean’ concentrate. Techniques which depend upon trace element analyses of artefacts must take into account the possible contaminants in a smelting charge and consider whether these could influence the artefact alloy composition. To some extent it is possible to evaluate what such contaminants could be, according to the geological setting of the gold source. Comminution of gold-bearing ores often yield mixed particles of gold alloy and other minerals. The bulk composition of a (s)melting charge depends on the degree to which specific mineral species remain attached to the gold. For hypogene ores, the full elemental inventory of the ore may be represented, whereas during weathering some components may be removed in solution (e.g. Cu).

In situ weathering of pyrite-bearing ores generates a gossan comprising Fe hydroxy-oxides (Fig. 7a) and this can render gold visually distinct. Weathered sulphide ores are typically soft and friable, and liberation of gold is relatively straightforward. The abundance of sulphides would be dependent on degree of weathering, but overall it seems likely that Fe (III) compounds would be the major contaminant. The formation of soluble gold species has been invoked in several contexts globally as a mechanism for authigenic growth. In New Zealand, circum-neutral groundwaters facilitate dissolution of microscopic gold from primary sulphides. Sulphide decomposition generates thiosulphate ions that form aqueous complexes with both Au and Ag (Craw et al. 2015). Both Au and Ag are solubilized by thiosulphate and respond to the same precipitation triggers such that the supergene Au particles exhibit similar Au/Ag ratios to primary alloy. The relationship of the trace element profiles to those of hypogene Au have yet to be established. Advocates of biogenic gold growth in surficial conditions promote the hypothesis of gold particle formation and enlargement through progressive addition of gold precipitated through bacterial action (e.g. Shuster and Reith 2018). Whilst the overall importance of this process is contentious (Chapman et al. 2021a), it is the case that Ag is absent from biogenically-precipitated gold.

In placer environments, gold is generally associated with other dense minerals and with clays, although other minerals may be entrained (Fig. 7B) and decomposition products of the original host mineralization may remain (Fig. 7C). Clay minerals often infill voids within the lower strata of fluvial sediments which is also where the heavy minerals accumulate. Embayments in gold particles may be filled with clays to an extent governed by both gold particle morphology and specific fluvial contexts. For example, in upland Britain and Ireland, crevices in bedrock are often filled by compact clays and the main gold concentrations occur at the interface between clay and the overlying sediment. Clay minerals themselves adsorb heavy metals so that they become repositories for metallic elements ultimately derived from chemical degradation of local materials. The influence of small amounts of clay on a gold smelting charge would probably be small but also unpredictable. Residence in sediments may also lead to the precipitation of Mn oxide (Figs 7D,E) or Fe II oxide directly onto Au alloy (Fig. 7F).

Co-collection of heavy minerals together with gold provides a more likely mechanism for strongly influencing artefact composition (Fig. 7G). The range of heavy mineral species present in gold placers varies both according to deposit type and erosional history. Ore minerals such as sulphides are rare because they are unstable in the surficial environment, and softer gangue minerals such as carbonates or barytes physically degrade, whereas resistates such as zircon, garnet, monazite and xenotime are not uncommon (e.g. Moles and Chapman 2019). The ratio of gold to heavy mineral(s) is a function of the particle size of gold, the particle size of associated heavy minerals, and the ratio of the two. In prehistory, whilst it is feasible that nuggets could have been collected individually by hand, it seems equally or more likely that gold collection would have involved some form of gravity and/or selective attachment separation process, e.g. with the aid of animal skins or plants (Neesse 2014). The relative settling rates of gold and common heavy minerals such as magnetite and cassiterite are governed by their relative specific gravities, particle size and shape. Malleable gold becomes progressively flattened with fluvial transport such that distal placer deposits contain gold flakes which are very difficult to separate from granular, but less dense minerals. Consequently, it is highly probable that heavy minerals co-collected with the gold reported to a (s)melting charge, and that the degree to which this occurred varied between (s)melting operations. The presence of both PGE inclusions and elevated PGE concentrations, including Pt, in artefact gold relate to the exploitation of placer deposits where gold co-collects with PGMs (e.g. Meeks and Tite 1980; Junk and Pernicka 2003; Jansen et al. 2016; Borg et al. 2019); a scenario that is not uncommon worldwide (see also Nixon et al. 1990; Barkov et al. 2018). However, although the heavy mineral species may provide information on provenance in some cases, this is not always the case. For example, whilst the low abundance of Sn in native gold (Figs. 4C,D) favours co-collected cassiterite as the most probable source of Sn in artefact gold, it could also be present as a consequence of deliberate contamination during (s)melting and fabrication.

Characterizing artefact gold with geological approaches

Materials and Methods

Our understanding of natural gold has advanced considerably as a consequence of the range of analytical techniques employed and the evolution of approaches to data interrogation. These methodologies may be applied to the study of artefacts, both individually and collectively, although with respect to artefacts there is the additional consideration of the necessity to avoid or minimise destructive sampling. Populations of artefacts, defined by an archaeological criterion such as chronology or typology, can be characterized in the same way as populations of gold particles, using alloy compositions, inclusions of other materials, and heterogeneous alloy microfabrics. In studies of natural gold, the compositional data sets may be applied to exploration or ore deposit studies (e.g. Knight et al. 1999; Chapman et al. 2017), whereas in the case of artefactual gold they may be used to consider compatibility with a particular source and to illuminate the gold-working processes.

In this section we describe an example of artefact gold characterization by SEM and EPMA. Millimetre sized samples from four Bronze Age artefacts in the collections of National Museums Scotland were studied (Fig. 8, Table 2) — namely two Early Bronze Age dagger hilt bands, from Gask Hill, Collessie, Fife (NMS X.EQ 53) and Skateraw, East Lothian (NMS X.EQ 238) respectively, along with a Late Bronze Age ‘cuff fastener’, presumed to be an Irish find (NMS X.FF 3), and a Late Bronze Age ‘lock [hair] ring’ found near Gogarburn House, City of Edinburgh (NMS X.FE 7; n.b. this artefact is very likely to have been made in Ireland). They span ~1,300 years of the British and Irish Bronze Age. All four samples had previously been analysed by Axel Hartmann and colleagues during the 1960s as part of the *Studien zu den Anfängen der Metallurgie* (SAM) project (Hartmann 1970; Raftery 1971) and had been included by Joan Taylor in her *corpus* of British and Irish Bronze Age goldwork (Taylor 1980). Their SAM sample numbers and Taylor Catalogue numbers are as follows, respectively: Collessie: 2364, Fi1; Skateraw, 2365, El 2; ‘Ireland’ 2342, NLI 19; Nr Gogarburn House: 2337, Ml1. The results of the SAM analyses are listed in Taylor’s *corpus* (1980, 140).

Results of microchemical characterization

The two Early Bronze Age (EBA) hilt bands date from a period when goldworking processes were relatively simple; objects were produced from sheet gold worked from an ingot/former that could theoretically have been formed by sintering of gold particles at temperatures below the melting point (e.g. Raub 1995; Guerra and Calligaro 2003), or else by melting the gold into some kind of former (n.b. these are sheet gold artefacts, not cast gold; for further details of EBA goldworking technology, see Taylor 1980; Eogan 1994; Needham 2000; Needham and Sheridan 2014). The two Late Bronze Age (LBA) objects date from a time when a range of goldworking techniques were practised, including casting, and a more diverse range of artefact types were produced (Taylor 1980; Eogan 1994; Cahill 2014). Study of this group of artefacts permits consideration of their microchemistry in terms both of potential gold sources and also of goldworking techniques and processes. Table 2 summarises the new analytical data for the artefact samples investigated, and Figure 9 shows back scattered electron (BSE) SEM images of the artefact sample cross-sections and examples of the internal features observed.

The two Scottish EBA artefacts studied here differ in their Ag contents (8.75 and 15.46 wt%), but lie within the range typical for comparable artefacts from this period (e.g. Standish et al. 2015). The EBA hilt band from Collessie, NMS X.EQ 53, shown in Figure 9A, comprised a homogenous Au alloy containing 8.75 ± 0.07 wt% Ag, 0.16 ± 0.03 wt% Cu, and 0.19 ± 0.01 wt% Sn (n=10, uncertainties are 1SD of the repeat analyses). An inclusion of calcium sulphate in this artefact is depicted in Figure 9B. Gypsum mineral inclusions are extremely rare in natural gold and where present appear related to magmatic hydrothermal systems (e.g. gold from the calc-alkalic porphyry at Casino, Yukon; RJC unpublished data). However, gypsum inclusions were not observed in any of the 1246 gold particles form the low sulphidation epithermal mineralization from the Ochil Hills, Scotland described by Chapman et al. (2005). The implications of inclusion species such as this are discussed in Section 5.3.

Figure 9C shows a fragment of LBA artefact NMS X.FE 7, the 'lock ring' found near Gogarburn House, Edinburgh (Table 2), with the trace of a traverse of 6 EPMA analyses. The alloy is homogenous, with mean values of 13.49 ± 0.08 wt% Ag, 5.31 ± 0.05 wt% Cu, and 0.21 ± 0.01 wt% Sn (uncertainties are 1SD of the repeat analyses). The dataset describing the alloy compositions of a second fragment of the same artefact (Fig. 9D) can be viewed as two separate populations; one relating to the core of the particle, and the others to relatively rich alloy compositions of a few microns' width, all situated at the fragment edges (apparent in the centre of the image). The core appears to be a broadly homogenous Au alloy containing 13.59 ± 0.09 wt% Ag, 5.45 ± 0.10 wt% Cu, and 0.19 ± 0.02 wt% Sn (n=10). The Au-rich areas at the fragment edges are compositionally variable, comprising Au alloys containing 1.8–2.4 wt% Ag, 0.3–0.5 wt % Cu, and 0.05–0.1wt % Sn (n=4) (Table 2).

Figures 9E–I show a third fragment of LBA artefact NMS X.FE7, with an overview provided in Figure 9E. This fragment was not analysed by EPMA for its alloy composition. Pronounced Au-rich areas are, however, visible (Fig. 9F), together with tiny (typically 1 µm) inclusions of Sn±Cu±Fe-bearing compounds that often occur in clusters or stringers as illustrated both in BSE imaging (Fig. 9F-H) and in a Sn X-ray map (Fig. 9I). None of these inclusion compositions correspond to natural minerals. However, Chapman et al. (2006) and Standish (2012) have reported natural mineral inclusions of Cu-sulphide within Irish LBA artefacts.

The other LBA artefact studied, the 'cuff fastener' probably found in Ireland, NMS X.FF 3, shows very similar compositional values to that of NMS X.FE 7 (13.18 ± 0.197 wt% Ag, 3.75 ± 0.063 wt% Cu, and 0.18 ± 0.06 wt% Sn; n=10, uncertainties are 1SD of the repeat analyses). The alloy compositions of both NMS X.FE 7 and NMS X.FF 3 are within the range reported for Irish LBA artefacts: ~11–15 wt%

Ag coupled with ~4–8 wt% Cu and up to ~0.2 wt% Sn (e.g. Warner 2004; Chapman et al. 2006; Warner et al. 2009; Standish et al. 2015).

The compositional data for this small sample set suggests that inclusion suites in LBA gold artefacts are more complex than those in their EBA counterparts, as previously recorded for other artefacts by Chapman et al. (2006) and Standish (2012).

Discussion: implications for archaeological provenance studies

Gold provenance

Considerations on the provenance of gold used in earlier periods, such as the EBA, is likely to be more straightforward than for later periods because of the lower likelihood of metal recycling — although this practice cannot altogether be ruled out (e.g. evidence for recycling of gold in EBA Ireland in presented in Standish et al. 2015). Since Ag does not seem to have been exploited in Britain during the EBA — the one silver artefact found in Britain, a sheet silver bead cover from Gussage Cow Down, Dorset, is believed to be a Continental import (Needham and Sheridan 2014, 915 and Fig. 18f) — the Ag content of the gold artefacts constrains the localities that could have acted as a source. For example, the Ag values of the two EBA artefacts studied here (8.8 wt% Ag for NMS X.EQ 53 and 15.5 wt% Ag for NMS X.EQ 238) invalidate the Kildonan goldfield of Sutherland, Scotland, as a sole source because melts produced from this gold returned Ag values over 20 wt % (Chapman et al. 2006). Few Scottish auriferous localities yield gold of around 16 wt% (Leake et al. 1998), thus ruling out the majority as possible sources of sample NMS X.EQ 238. However, several localities both in the Southern Uplands and the Angus Glens could generate alloy compositions of 8.8 wt% Ag, consistent with that documented for sample NMS X.EQ 53 (Leake et al. 1998; Chapman et al. 2000c). In addition, gold mineralization hosted by Devonian volcanic rocks in the Ochil Hills also has a compatible alloy % Ag composition, but in this case trace element artefact alloy analyses should be able to identify elevated Bi associated with the low sulphidation epithermal source. Therefore, whilst the Ag data permit some (well-characterized) potential gold sources to be ruled out, further discriminators are needed if provenance is to be investigated further.

Satisfactory characterization of natural gold for provenance studies

Various challenges face archaeological provenance studies where the focus is to characterize the auriferous material that comprised the feedstock for fabrication. Obtaining sufficient samples of natural gold itself is often very difficult, particularly where museums or donations provide the sole option, as the quantity of gold available for analysis may be limited. The approaches adopted to gold characterization by exploration geologists — whose principal aim is to illuminate geological relationships — generate data sets of alloy compositions which do not fully acknowledge the potential mineralogical complexity of gold won from either placer, eluvial or *in situ* environments because the analytical protocols specifically exclude surface materials and surface alloy heterogeneity such as gold-rich rims. The true thickness of gold-rich rims on placer gold particles is normally limited to around 20 µm (Knight et al. 1999b) unless the history of the particle has included multiple deformation events and associated recrystallization (Stewart et al. 2017). Following liberation from source, fluvial winnowing of populations of detrital gold particles result in longer distance transport of smaller particles. Progressive flattening of malleable gold particles also influences hydrodynamic properties, such that flakes are also more mobile. Both smaller particles and flaky particles comprise higher proportions of rims than their larger, equant counterparts. This results in an apparent increase in Au:Ag ratio of the bulk composition with transport distance (e.g.

Boyle 1979). For example, a comparison of spherical gold particles of 1000µm and 100µm diameter, with a core composition of 20% Ag, each with a 2µm rim of 2 wt% Ag, yields bulk compositions of 19.7 wt% Ag and 17.6 wt% Ag respectively. This difference would be amplified by increasing differentials in particle size, rim thickness, and increased flattening accompanying fluvial transport.

The heterogeneous microfabrics present within natural gold pose a fundamental challenge to characterizing these gold alloys for the purpose of archaeological provenance studies, with the choice of analytical technique controlling which component or components of the gold alloys are being measured. This is particularly so for methodologies that rely on analysis of a small part of the alloy, particularly when analysis is confined to surface layers (influenced by the rim) or subsurface where the degree of heterogeneity is unproven. Neither analyses by EPMA nor LA-ICP-MS result in an alloy composition representative of a (s)melt charge because both approaches specifically exclude inclusion species. For EPMA analyses, site selection is manual and inclusions are avoided. LA-ICP-MS analyses generate time-resolved signals from which inclusions may be identified and their influence removed. Initial studies of trace element partitioning to inclusions using both quadrupole ICP-MS and ToF-MS systems indicate that specific inclusions may be very effective sinks for elements absent in the surrounding alloy (Chapman et al. 2021b).

The characterization of natural gold particles using LA-ICP-MS systems must be informed by an understanding of the mineralogical nature of the gold alloy. Generation of highly spurious results is likely when small sample sets are used, but may be mitigated by studying larger sample sets where available. Currently it is not possible to provide guidelines for the sample size required to generate robust data sets because we have limited understanding of the degree of heterogeneity within and between gold particles from the same locality. However, it is clear that the adoption of LA-ICP-MS systems for analysis does not increase the number of discriminants available over those already obtained by EPMA, although the quality of quantitative data for the minor elements is far superior.

These problems may be overcome using gold collection exercises which simultaneously permit characterisation of associated materials such as other heavy minerals and the clay fraction, and analytical programmes which are tailored to the needs of provenance studies. Imaging of natural gold particles, and samples of artefact gold, by SEM and the use of ToF-MS in conjunction with LA systems, provide a route to evaluate the nature of major and trace element heterogeneity within gold, and also to evaluate the reliability of analyses derived using other techniques. Application of ToF-MS systems to artefact gold would permit quantification of heterogeneity (both at the surface and at depth within the artefact body) and would greatly aid interpretation of existing datasets. Finally, correlating natural gold compositions with artefact composition requires an understanding of (*inter alia*) the chemical behaviour of melt components under the actual goldworking conditions. Whilst there has been some speculation on the fates of various elements according to the prevailing redox conditions (e.g. Hauptmann et al. 1995; Schmiderer 2009), it is also possible to gain some insights from the nature of inclusions identified within artefacts, which we discuss next.

Implications of features observed in natural and artefactual gold

It is apparent, from the inclusions identified here in artefact gold, that the value of such an approach lies in the clues they give relating to the goldworking techniques, rather than acting as a match for inclusions in natural gold. The mineralogical simplicity of inclusions reported in EBA gold studied here and elsewhere (Chapman et al. 2006; Standish 2012) are consistent with the simple fabrication processes associated with the sheet-working techniques that were employed in this period (e.g. Taylor 1980; Eogan 1994; Needham 2000; Needham and Sheridan 2014). Chapman et al. (2006) speculated on the implications of Ca-bearing compounds, which could derive ultimately from a gold-carbonate association in the raw material. With regard to the presence of calcium sulphate illustrated in Figure 9B, the most plausible cause is sulphation of calcium carbonate by sulphur dioxide generated during fabrication. This reaction can take place via two pathways, but both require the presence of oxygen (Tullin and Ljungstroem 1989). Silica (quartz) was also commonly observed, but it is difficult to demonstrate a clear link to source for such a common material.

In contrast, LBA artefacts exhibit a wide range of chemical compounds as inclusions. In this study, very local enrichments of Cu, Fe and Sn (Fig. 9F–I), in conjunction with bulk alloy Cu values far in excess of plausible natural gold sources, prove that additions have been made to the smelting charge. The chemical nature of inclusions is often difficult to establish because of their small size, but there are sufficient data to permit the following consideration of the implications of Cu-sulphide inclusions in some Irish LBA artefacts reported by Chapman et al. (2006) and to evaluate whether chalcopyrite was a component of the feed. According to Mitovski et al. (2017), chalcopyrite decomposes at 385°C to yield copper sulphide (Cu_2S) and iron sulphide (FeS) but these appear to exist only in a limited temperature range to around 405°C. The absence of FeS inclusions in artefactual gold suggests that chalcopyrite is not the source of Cu in the alloy, and that (decreasing?) fabrication temperature profiles eventually permitted formation of Cu_2S. The potential nature of Cu additives may instead relate to deliberate additions of metallic Cu or bronze (Northover 1989; Warner et al. 2004), thus the combination of Cu values in artefact gold and the nature of the inclusion suite together suggest deliberate or accidental addition of Cu-bearing metal. Future studies that take into account both overall Cu:Sn ratios and the composition of Sn-rich inclusions should help to resolve whether the metal addition was Cu or bronze.

Calcium stannate (CaO_3Sn) inclusions were also identified in LBA gold by Chapman et al. (2006) and the presence of this compound may also ultimately help to constrain conditions of goldworking. Synthetic calcium stannate is generated by the reaction of cassiterite with calcium carbonate at temperatures around 1000°C (Zhang et al. 2018). More work is required in this area to establish the thermodynamic properties of such compounds as a basis for constraining both redox conditions and temperature during goldworking.

Characterization of the LBA samples also demonstrates that Au-rich zones are present in the microfabric of artefact gold alloys. Spatially focussed on the sample edges and along cracks/fissures within, such features likely relate to the depletion of elements such as Ag through surface treatment, use-wear, and/or from post-depositional leaching (Scott 1983; Rapson 1996; Troalen et al. 2014).

The outcomes of considering the compositional characteristics of artefact gold in this way have implications both for our understanding of ancient goldworking processes, and the validity of various approaches to archaeological provenance studies of gold. Although these studies are at an early stage, it is clear that compositional features and bulk compositions of LBA gold artefacts are incompatible with a simple source-melt-artefact process relationship. Given the clear evidence for the deliberate addition of Cu in some of these artefacts, commonly to levels of around 5 wt%, methodologies dependent upon trace element matching of LBA artefact and natural gold face serious challenges.

Methodological considerations of gold provenance studies

Implications for previous studies. The discussion above has highlighted the implications of gold heterogeneity in the context of archaeological provenance studies. The first issue relates to sub-sampling particulate natural gold using approaches which take no account of potential heterogeneity, with the reliability of datasets generated by the partial ablation of a relatively small number of particles being particularly questionable. Furthermore, analyses of unpolished surfaces of detrital particles are almost certain to generate compositional data unrepresentative of the whole particle, due to surface heterogeneities. LA-ICP-MS approaches, such as those used by Taylor et al. (1995), Watling et al. (1999) and Ehser et al. (2011), may or may not generate data representative of the alloy depending upon the location of the ablated material. Similarly, methodologies developed for geological purposes whose focus is placer-lode relationships and mineralization paragenesis usually analyse only the core compositions of gold particles, because only these relate to the conditions of gold precipitation in the source. In each case, the databases are only partially suitable for purposes of archaeological provenancing as unrepresentative sampling of the bulk composition is inevitable. Neither approach accommodates the presence of other minerals entrained within a population of gold particles and which may be incorporated in the (s)melt charge.

Recommendations for future studies. The nature of both natural and artefact gold alloys is complex, with the presence of heterogeneous microfabrics, mineral inclusions, and other phases raising a number of issues for archaeological provenance studies that have to be considered alongside other complicating factors, including the mixing of gold from different sources to make an artefact. However, despite this, such studies still have great potential, and if planned and executed appropriately they can provide valuable information on the provenance of raw materials used and fabrication processes employed. On the basis of the factors discussed above, we have developed a series of recommendations regarding how future provenance studies of archaeological gold can offer a scientifically robust approach.

Isotopic approaches, only recently adopted for studies of natural gold, provide important additional geochemical discriminators that bring with them certain advantages. Characterization of the Pb isotope signature of Irish gold mineralization (Standish et al. 2014b) demonstrated its ability to discriminate gold sources on a regional scale, highlighting its potential as a primary discriminant for a given study area. Consistency between placer gold, lode gold, and associated sulphide minerals from the same locations indicate that signatures survive weathering and demonstrate that analysis of mineral inclusions or associated minerals is unlikely to be an issue — unless multiple mineralization styles with very different Pb sources contribute to the same deposit. Furthermore, in contrast to elemental ratios which can change according to the prevailing redox conditions, fractionation of Pb isotope ratios during (s)melting has, for the most part, been ruled out (e.g. Barnes et al. 1978; Baron et al. 2009; Stos-Gale and Gale 2009), although Cui and Wu (2011) did detect Pb isotope fractionation to a negligible degree that will not influence the result of Pb isotope provenance studies. The key complication of this approach comes from the addition of exogenous Pb, e.g. through alloying and recycling; processes that impact upon all methodologies that address geochemical provenancing. In relation to artefact Au-Cu alloys, the Pb isotope signature will constitute a mix of Cu-derived and Au-derived Pb. At higher Cu contents, such as those established for LBA gold artefacts produced in Britain and Ireland (~3–7 % Cu; see also Chapman et al. 2006), this mixing is likely to limit the application of Pb isotope analysis to the identification of metal pools only, unless unalloyed artefacts can be studied. Whilst artefact alloys with <1% Cu will not be compromised in this way (as discussed in Standish et al. 2015), the practice of Au-Cu alloying does warrant an exploration of alternative isotopic systems, e.g. Ag isotopes, that could be included in the provenance toolkit.

Whilst the strength in Pb isotope analysis is in discriminating between sources on a regional/ore-field scale, and also between different styles of mineralization if their Pb was derived from contrasting geochemical sources, the contrasting controls on Ag isotope ratio variation may provide a useful provenance discriminator at a more local scale. Ag isotope ratios have been shown to discriminate between different mines in the same ore field (Argapadmi et al. 2018), and nuggets in the same placer deposit (Brügmann et al. 2019), suggesting their potential in both linking placer gold with bedrock mineralization and as a discriminator in archaeological provenance studies. Indeed, their application to the latter has already been demonstrated in studies of Ag objects (e.g. Desaulty et al. 2011).

The isotopic approaches outlined above are key components in future studies of archaeological gold. However, that does not preclude the use of compositional data and a robust provenance methodology would combine multiple, independent, geochemical discriminants. With this in mind, it is apparent from our investigation of microfabrics present in both natural and artefactual gold that two important aspects must be considered when planning such studies: 1) the natural gold sampling strategy, and 2) which analytical techniques are most appropriate.

Field sampling of potential gold sources needs to be designed to obtain a representative population of particles to enable accurate characterization of the gold alloy present at the site. It seems clear that for archaeological studies, natural gold ideally requires characterizing using both traditional compositional approaches and through bulk analysis. Chapman et al. (2021b) suggest that around 250 gold particles are typically required to generate an inclusion assemblage dataset that is useful for comparative purposes. The number of particles required to generate a representative melt will vary according to gold particle size, not least because of the size dependence of the rim/core ratio discussed earlier. Presently there are no quantitative studies to provide guidelines in this regard. Field sampling protocols should also include collection of accessory mineral populations that may enter the (s)melt. Mineralogical and chemical analysis of both the heavy mineral fraction and a clay fraction from a placer locality would provide valuable additional information.

When characterizing gold deposits of archaeological interest, the process would ideally start with characterization of the nature and scale of both inter- and intra-particle heterogeneity, e.g. by SEM and/or ToF-MS. This would identify the mineral inclusion suite present in the population, and ascertain where various discriminator elements are located within the gold. However, from an archaeological perspective, the most important factor is to characterize the resulting geochemical signature of the melt, therefore application of the elemental and isotopic signature via bulk techniques, e.g. total acid digestion followed by analysis by solution ICP-MS, are likely to be most appropriate. Laser ablation techniques, or other high-resolution approaches, risk unrepresentative characterization of the gold due to the heterogeneous microfabrics present. For example, the presence of Au-rich rims are likely to be an issue when Ag is used as a key discriminant, particularly when gold particle characterization is based on surface analysis. In addition, heterogeneity of some artefact alloys raises the possibility of unrepresentative sampling of artefact gold, something that could be overcome by prior imaging/mapping of artefact gold by SEM and/or LA-ToF-ICP-MS.

Key points when carrying out archaeological provenance studies of gold

Following the above discussion, it is worth reiterating a number of key points in relation to the nature and composition of gold alloys that should be taken into account when undertaking archaeological provenance studies.

1. Whilst it is acknowledged that, for ease of understanding for the reader, referring to present-day countries or regions has its benefits, it is worth reiterating that compositional controls are not geographical but a consequence of deposit type, i.e. generic geological processes replicated globally in similar tectonic settings (e.g. Chapman et al. 2021b). In an archaeological context, describing a compositional range according to study region may be appropriate, but geographically based terminology cannot be applied to natural gold.
2. The Ag concentration of natural gold alloys are, for the most part, unable to distinguish between different styles of gold mineralisation (Fig. 3). Therefore, the use of Ag as a discriminator in archaeological provenance studies is limited to a simple ‘same or different’ approach, or to rule out potential sources where the Ag content of natural gold is lower than the artefact if deliberate additions of metallic Ag are implausible.
3. Whilst very low or very high Ag values may be suggestive of specific deposit types, there are no distinct properties associated with gold from different geomorphological settings. Placer gold is not a ‘type’ but instead inherits the compositional features of the gold in the hypogene source, which then may or may not be modified in either placer or lateritic environments, e.g. through formation of gold-rich rims. This effect, however, is relative not absolute. Consequently, it is not possible to ascribe a hypogene or placer source of gold exploited in antiquity according to Ag content, as has been suggested in some of archaeological literature (Constantinescu et al. 2012, Nocete et al. 2014).
4. Gold is often regarded as a homogeneous material, but this is demonstrably not the case for both artefact and natural gold (Figs. 2,9). The alloy heterogeneity has implications for the validity of the data sets which characterize material through analysis of a small portion of the target. In the case of natural gold this problem is compounded by the presence of both inter- and intra-particle alloy heterogeneity. The number of gold particles required to generate a robust characterization will vary between localities, and is an unknown at the time of initial characterization. Production of generic guidelines in this regard is considered a research priority.
5. Adoption of LA-ICP-MS has been viewed as advantageous over use of EPMA because the lower detection limits could facilitate generation of a wider range of useful discriminants for ore-artefact comparison. For natural gold, the number of generic elemental discriminants is far lower than might be expected (Chapman et al. 2021b), although the elemental range may be

larger in regionally-specific studies. Interpretation of data sets generated by LA-ICP-MS are best undertaken against a background of understanding the compositional variation within the natural and artefact alloy suites.

6. The mineralogical inventory of the heavy fraction of sediments is a consequence of the geology and mineralization within a river's drainage. Thus, heavy minerals from the host rocks of gold mineralization, such as cassiterite (e.g. in Cornwall, UK: Penhallurick 1986; Jackson et al. 1989), or from separate types of mineralization, such as PGMs (Nixon et al. 1990; Barkov et al. 2018), may be present in a gold placer, and their co-collection is inevitable. Incorporation into a smelting charge may result in either chemical modification of the alloy, e.g. with Sn (Raub 1995), or alteration of its physical characteristics, e.g. with PGM (Meeks and Tite 1980). The presence of PGM inclusions in artefact gold does not infer a gold-PGM source and a Sn-rich Au alloy does not infer natural gold containing measurable Sn. Understanding the permissible compositional range(s) of natural gold from different geological settings provides a basis for informed speculation on both mining and fabrication processes.
7. Counter to the opinion often stated in reviews of provenance approaches to archaeological gold (e.g. Pernicka 2014), it is possible to characterise the Pb isotope signature of gold by MC-ICP-MS, with solution approaches requiring only a few mg of material (Standish et al. 2013; 2014b). Providing the Pb incorporated into artefact gold derives predominantly from the gold source rather than that of any alloying metals (e.g. Cu), the technique can play an important role in archaeological provenance studies (Nocete et al. 2014; Standish et al. 2014a; 2015). Furthermore, other isotopic systems that are yet to be fully investigated may prove to be of use to such studies, such as Ag isotope analysis; there is scope for developing new approaches to provenance archaeological gold.

Conclusions

The development of analytical techniques to characterize natural gold in the context of ore deposit studies has illuminated limitations in simplistic approaches to provenancing that rely only on compositional comparisons of small numbers of natural gold particles and those of artefact alloys. Geological studies have a clear remit to characterize natural gold according to paragenetic criteria, whereas provenance studies require a holistic measure of all materials in the melt charge, along with an appreciation of all the factors that can affect an artefact's composition, including all other materials that enter the charge, mixing, and recycling. Therefore, whilst the former may of use to archaeological provenance studies in constraining the source of metal used for a particular artefact gold alloy, the two datasets are not always comparable.

Analytical protocols developed to characterize the inclusion suite within natural gold are equally informative when applied to artefactual gold. Their value lies not in matching source to artefact but in providing a window to the conditions of goldworking through consideration of the stability fields of the various inclusion species observed. The presence of Cu-rich compounds within artefact gold suggests the deliberate addition of Cu-bearing metal, and this also has implications for matching trace element suites in natural and worked gold. Future studies that take into account both overall

Cu:Sn ratios and the composition of Sn-rich inclusions should help to resolve whether the metal addition was Cu or bronze. The pursuit of an increasing number of elemental discriminants to compare ore and artefact using LA-ICP-MS approaches is compromised firstly by the absence of suitable generic elemental discriminants in natural gold, and secondly by heterogeneity at trace element levels in both natural and artefactual gold, a factor which becomes acute when small sample sets are used. Critically, the heterogeneity of artefactual gold, and the importance of their inclusion suite, only becomes apparent when geological approaches are applied to archaeological samples.

Isotopic characteristics are not as affected by fabrication conditions as much as elemental concentrations. Consequently, isotope analyses may offer a superior basis for provenance studies, although issues of mixing gold from different sources and alloying gold with other metals still remain. Nonetheless, scientifically robust provenance methodology should combine a number of independent analytical techniques, and artefact characterization via both the isotopic and elemental composition of an alloy, together with other included compounds, will yield the most information regarding both metal source and fabrication methods.

Acknowledgements

Dr Barbara Armbruster is thanked for permission to reproduce her photos of gold artefacts shown in Fig. 8, and two anonymous reviewers are thanked for their helpful comments on an earlier version of this manuscript.

Author Contributions

CDS: conceptualization, methodology, writing – original draft, writing – review & editing. RJC: conceptualization, investigating, methodology, writing – original draft, writing – review & editing. NRM: conceptualization, methodology, writing – original draft, writing – review & editing. RDW: investigating. JAS: resources, writing – review & editing.

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Figure Captions

Figure 1: Summary of the pathway from natural gold occurrence to artefact, indicating challenges facing provenance studies. In this scenario, the starting material is a collection of gold particles ('population') from river sediment or other detrital material.

Figure 2: Examples of internal heterogeneity within placer gold particles. A–D BSE images of alloy microfabric. A: variation in Ag contents of gold particles from the same locality (Monaglogh Stream, County Wicklow, Ireland: Moles and Chapman 2019). Numerals indicate wt% Ag. B–D: all samples from County Wexford, Ireland. B: example of gold enriched rim. C: three stages of alloy formation in a single particle. Numerals indicate wt% Ag. D: three stages of gold formation. Numerals indicate wt% Ag. E–G: trace element maps generated by LA-ToF-ICP-MS. Example of heterogeneity at trace level in a gold particle from the Similkameen River, British Columbia, Canada. Concentration is indicated by signal intensity. E: Ag-rich tracks within particles showing slight variation in Au/Ag in particle core. F and G: extreme heterogeneity with respect to Cu and Pt respectively. Note low intensities for Pt. Yellow circle in centre of F indicates diameter of 50µm laser spot size. Choice of position of spot size determines trace element response. Figure adapted from Banks et al. (2018). H–I BSE images of mineral inclusions. H: galena inclusions in gold from St Mary's Loch, Southern Uplands, Scotland. I: swarm of pyrite inclusions in gold from Tyndrum, Scotland.

Figure 3. Mean wt.% Ag values for populations of gold particles from orogenic, magmatic-hydrothermal, and oxidizing chloride-hydrothermal systems (adapted from Chapman et al. 2021b). Figures in parentheses refer to the number of populations in each curve.

Figure 4. Minor element concentrations in gold alloys. A, B: Cu in natural Au alloys. A: cumulative percentile plot of EMP Cu values from 4474 gold particles from the UK and Ireland: Leadhills (818), Mourne Mountains (176), Ochil hills, (1009) South Wales (249), Southern Uplands (212) Sutherland (376) Wexford (277) Wicklow (277). B: cumulative percentile of LA-ICP-MS Cu data (1006 particles total) relating to different gold deposit types in British Columbia. Low sulphidation epithermal mineralization: (53), alkalic porphyry mineralization (329), calc-alkalic porphyry mineralization (121), orogenic mineralization (503). C and D: Sn in natural Au alloys. C: cumulative plot showing Sn contents of natural gold following EMP analysis of 3444 gold particles from British and Irish Localities: central Scotland (485), Mourne Mountains (176), Ochil Hills (1009), South Wales (249), Sutherland (376), Wexford (874), Wicklow (277). D: cumulative percentile of LA-ICP-MS Sn data relating to different types of gold deposit types in British Columbia. Total and deposit breakdown as per Fig. 3B. Cu data for Mourne Mountains from Moles et al. (2013), Cu data for Ochil Hills from Chapman et al. (2005), Chapman and Mortensen (2006). Other datasets unpublished but compiled from other, published, regional studies except Sutherland and South Wales (Chapman, unpublished data). All LA-ICP-MS data from Banks et al. (2018).

Figure 5. A: Pb isotope composition of Irish Au mineralization plotted by geological terrane and sample type (placer gold, lode Au, associated sulphide minerals). B: simplified geological map of Ireland showing geological terranes referred to in Pb isotope plot A. Figure adapted from Standish et al. (2014).

Figure 6. Repeat δ^{109}Ag analyses of gold nuggets from Rio Tipuani, Bolivia, by Brügmann et al. (2019) demonstrating within-nugget homogeneity and therefore potential for tracing placer-lode relationships.

Figure 7. Contaminants of gold particles or gold particle populations which could impact on trace element analysis in provenancing studies. A: gold bearing gossan, Calliachar Burn, Perthshire, Scotland, showing partially weathered sulphide ore. B: example of gold nugget attached to quartz, Yukon, Canada. C: nugget stained with Mn oxide, Loch Tay, Scotland. D: SEM SE image of Mn oxide encrustations on gold nugget, Sutherland, Scotland. E: gold nugget coated with secondary Pb-Fe bearing minerals, Yukon, Canada. F: iron oxide-stained placer gold particles, Tyndrum, Scotland. G: panned concentrate of small gold particles containing other heavy minerals, Sutherland, Scotland.

Figure 8. Photographs of the analysed EBA hilt bands from Collessie, Fife (top left) and Skateraw, East Lothian (top right), and of the LBA 'lock ring' from near Gogarburn House, City of Edinburgh (bottom left). The image at the bottom right shows a 'cuff ring' of the same general type as the analysed example NMS X.FF 3; this one (NMS X.FF 28), like the analysed example, is believed to have been found in Ireland. Photos courtesy of Dr Barbara Armbruster.

Figure 9. Internal characteristics of gold artefacts observed using BSE imaging. Figs A–H: BSE images. A: overview of EBA object NMS X.EQ 53 showing location of $CaSO_4$ inclusion depicted in B. C: overview of LBA artefact NMS X.FE 7 fragment 1 showing zones of Au-rich alloy centre. D: overview of LBA artefact NMS X.FE 7 fragment 2 showing line of analysis traverse. E: part of NMS X.FE 7 fragment 3 showing enlargements with various inclusion types (F,G,H). I: a swarm of Sn-enriched Au areas is clearly visible in the X-ray map for Sn. The Au-rich area in F is accompanied by porosity suggesting Ag removal.

Table Captions

Table 1: Typical compositional characteristics of gold from major gold mineralization styles, summarised from Chapman et al. (2021b). Note that the elemental ranges represent that of individual analysis, rather than mean values for populations of gold particles from different occurrences.

Table 2: Elemental composition and inclusion suite of artefact gold samples from four Bronze Age objects in the collections of the National Museums Scotland, Edinburgh.

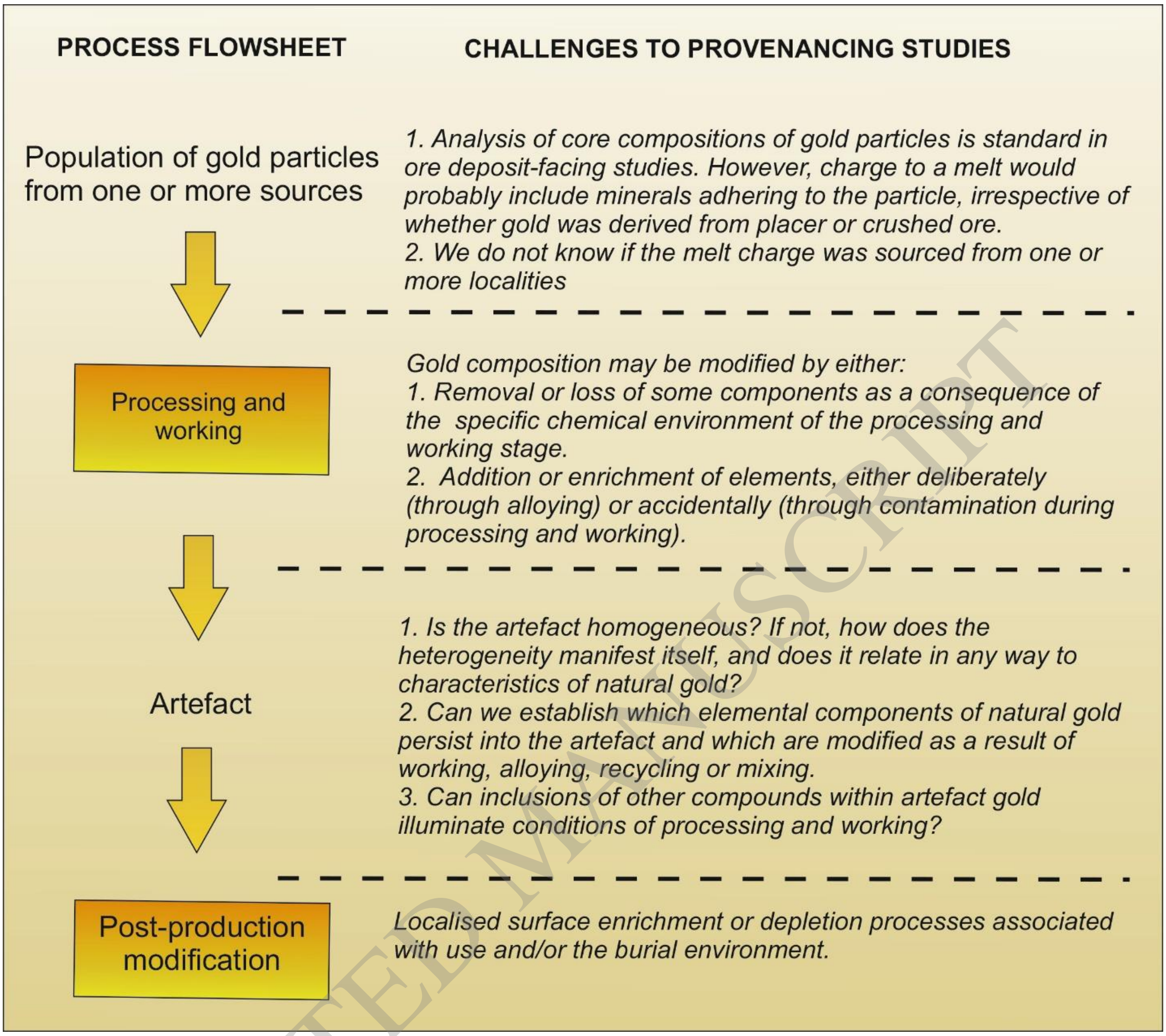
Style of mineralization	**Ag range (wt%)**	**Cu range (wt%)**	**Hg range (wt%)**	**Pd range (wt%)**	**Chemistry of mineral inclusion suite**
Orogenic (Precambrian)	5–50, many <10	to 2	to 3 (occasional)	absent	S±As±(Te+Bi)
Orogenic (Phanerozoic)	4–30	typically <0.02	to 10 (occasional)	absent	i. S ii. S+As iii. S+Te±As±Ag iv. Pb+S+Sb±As
Low-temperature, oxidizing, chloride systems	0–13	to 4 (rare)	to 12	to 12 (occasional)	Se±Te+range of metals
Calk-alkaline porphyries and associated epithermal	0–45	typically 0.02–0.1	typically <0.02	absent	Bi+Pb+Te+S
Alkalic porphyry Cu-Au±Mo mineralization	5–40	to 3	to 11 (occasional)	to 11 (occasional)	Hg+Pd+Pb+Bi+Te+Cu
Low- to intermediate-sulfidation epithermal mineralization	1–50	typically <0.02	to 10 (occasional)	absent	S±As+Te+Ag+Bi
High-sulfidation epithermal mineralization	1–14	to 1	insufficient data	absent	Cu+Pb+Zn+S+As±Te

Table 1

NMS Reg. No. NMS X…	Period	Artefact Type	Find Location	Fragment	Location on sample	No. analyses	Ag wt%		Cu wt%		Sn wt%		Inclusions
							Mean	1SD	Mean	1SD	Mean	1SD	
EQ 53	EBA	Dagger hilt band	Gask Hill, Newton of Collessie, Fife[1]	1	Body	10	8.75	0.07	0.16	0.03	0.19	0.01	$CaSO_4$
EQ 238	EBA	Dagger hilt band	Skateraw, East Lothian[2]	1	Body	13	15.46	0.15	0.21	0.03	0.05	0.01	SiO_2
FF 3	LBA	‘Cuff fastener’	Presumably Ireland[3]	1	Body	13	13.18	0.19	3.75	0.06	0.18	0.06	Sn-Cu-Fe rich blebs
FE 7	LBA	‘Lock ring’	Near Gogarburn House, City of Edinburgh[4]	1	Body	6	13.49	0.08	5.31	0.05	0.21	0.01	
“	“	“	“	2	Body	10	13.59	0.09	5.45	0.1	0.191	0.02	
“	“	“	“	3	Body	n/a	-	-	-	-	-	-	
“	“	“	“	2	Edge	4	2.1	0.27	0.4	0.1	0.07	0.03	-

1. Henshall 1968, 186 and fig. 42.8; Taylor 1980, 19,23,49, 136 (Fi 1), 140, figs 14 and 15, pl. 28
2. Henshall 1968, 183–4 and fig. 42.6; Taylor 1980, 23, 49, 136 (El 2), 140, figs 14 and 15
3. Eogan 1994, 136 (where it is referred to as a ‘sleeve fastener’)
4. Anderson 1886, 143–4, fig. 142

Table 2



1. Analysis of core compositions of gold particles is standard in ore deposit-facing studies. However, charge to a melt would probably include minerals adhering to the particle, irrespective of whether gold was derived from placer or crushed ore.
2. We do not know if the melt charge was sourced from one or more localities

Gold composition may be modified by either:
1. Removal or loss of some components as a consequence of the specific chemical environment of the processing and working stage.
2. Addition or enrichment of elements, either deliberately (through alloying) or accidentally (through contamination during processing and working).

1. Is the artefact homogeneous? If not, how does the heterogeneity manifest itself, and does it relate in any way to characteristics of natural gold?
2. Can we establish which elemental components of natural gold persist into the artefact and which are modified as a result of working, alloying, recycling or mixing.
3. Can inclusions of other compounds within artefact gold illuminate conditions of processing and working?

Localised surface enrichment or depletion processes associated with use and/or the burial environment.

Figure 1

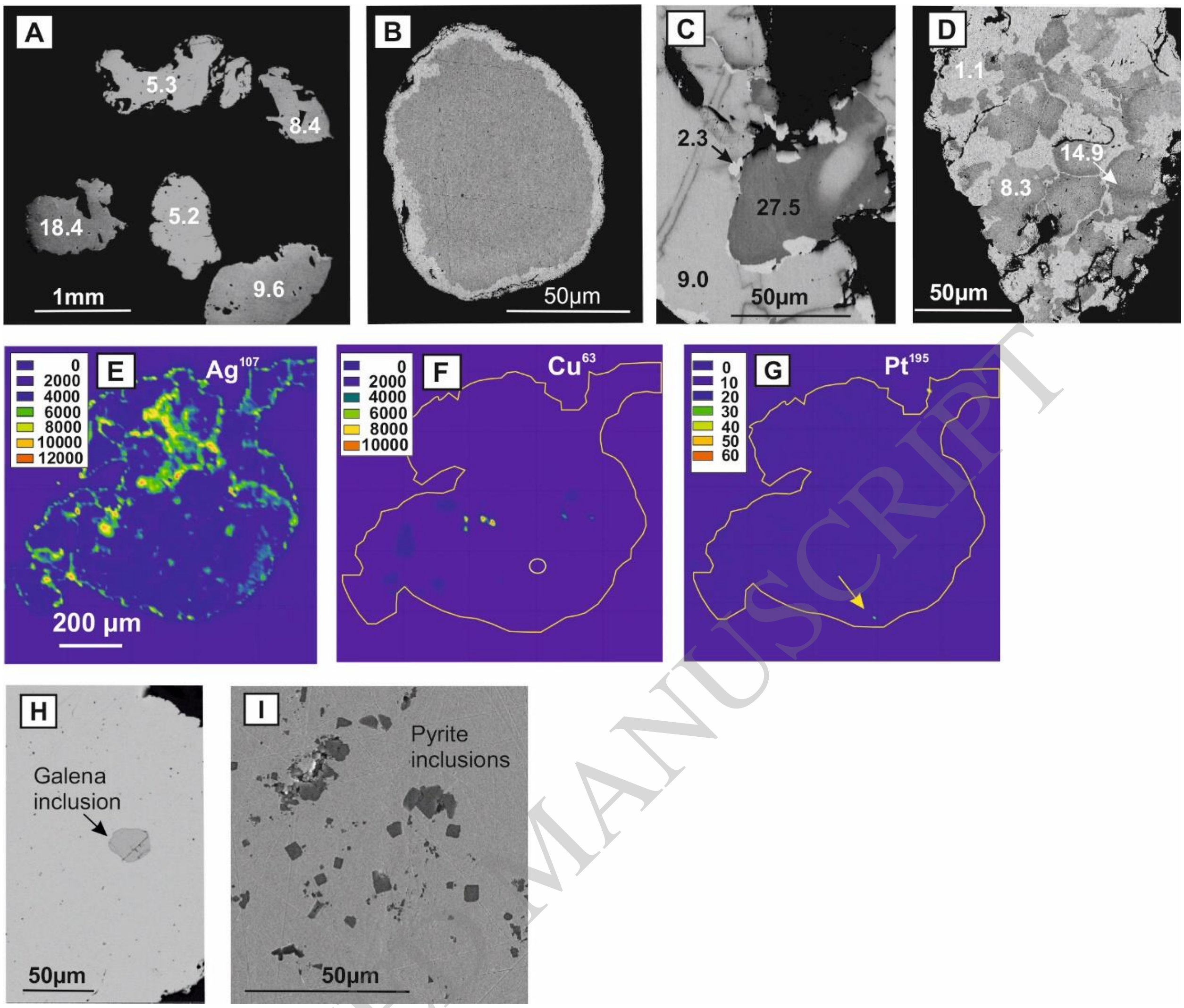

A
5.3
8.4
18.4
5.2
9.6
1mm
B
50µm
C
2.3
27.5
9.0
50µm
D
1.1
14.9
8.3
50µm
E
Ag107
0
2000
4000
6000
8000
10000
12000
200 µm
F
Cu63
0
2000
4000
6000
8000
10000
G
Pt195
0
10
20
30
40
50
60
H
Galena inclusion
50µm
I
Pyrite inclusions
50µm

Figure 2

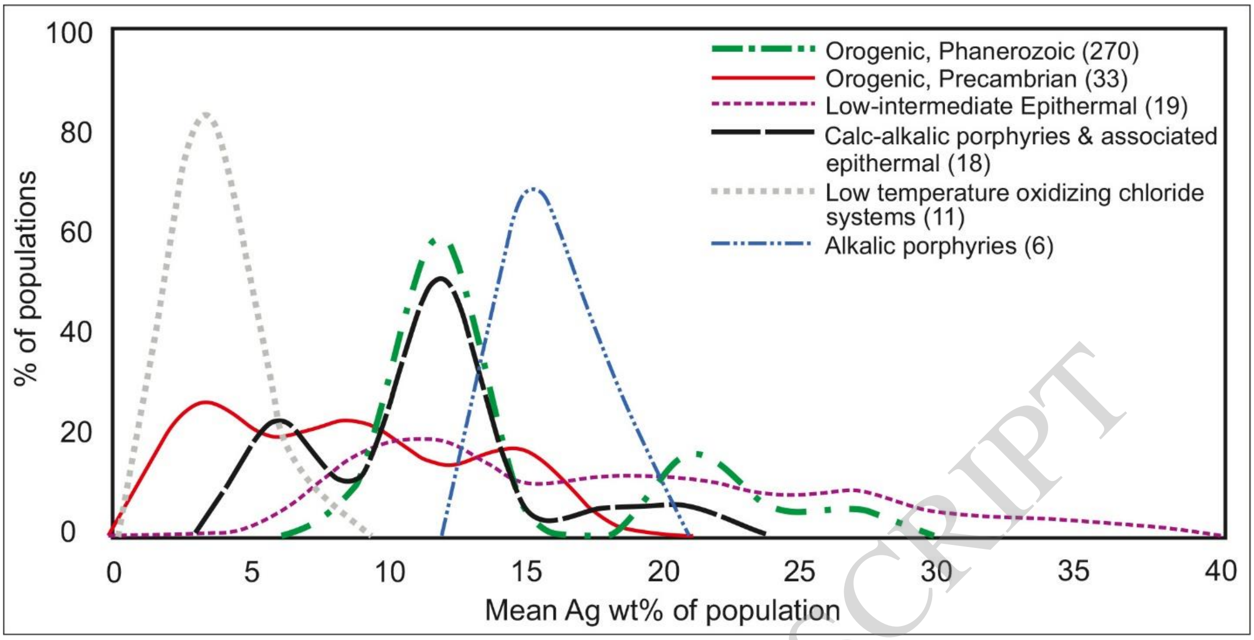

100
80
60
40
20
0
% of populations
0
5
10
15
20
25
30
35
40
Mean Ag wt% of population
Orogenic, Phanerozoic (270)
Orogenic, Precambrian (33)
Low-intermediate Epithermal (19)
Calc-alkalic porphyries & associated epithermal (18)
Low temperature oxidizing chloride systems (11)
Alkalic porphyries (6)

Figure 3

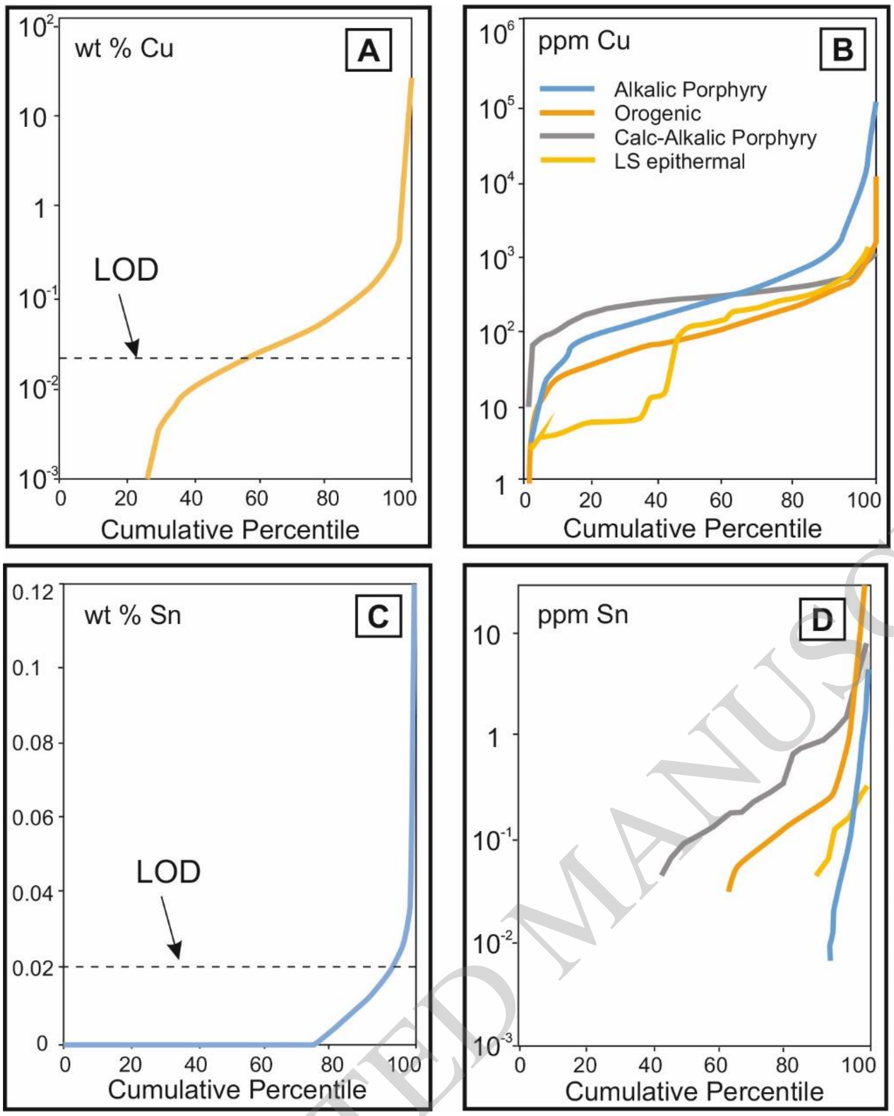

A
wt % Cu
10^2
10
1
10^{-1}
10^{-2}
10^{-3}
LOD
0
20
40
60
80
100
Cumulative Percentile
B
ppm Cu
10^6
10^5
10^4
10^3
10^2
10
1
Alkalic Porphyry
Orogenic
Calc-Alkalic Porphyry
LS epithermal
0
20
40
60
80
100
Cumulative Percentile
C
wt % Sn
0.12
0.1
0.08
0.06
0.04
0.02
0
LOD
0
20
40
60
80
100
Cumulative Percentile
D
ppm Sn
10
1
10^{-1}
10^{-2}
10^{-3}
0
20
40
60
80
100
Cumulative Percentile

Figure 4

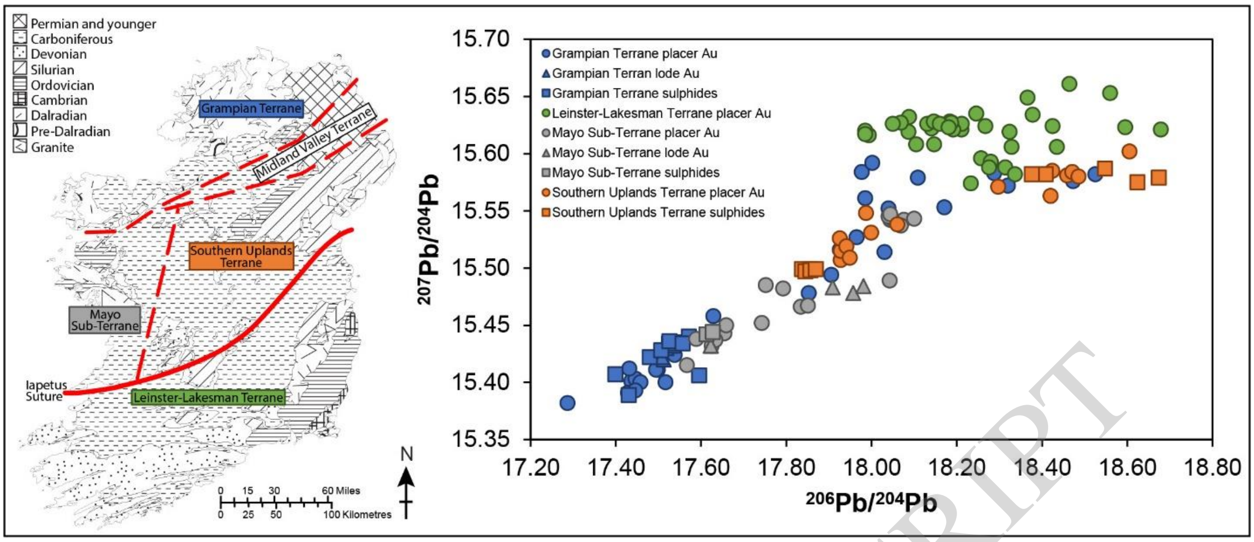

Permian and younger
Carboniferous
Devonian
Silurian
Ordovician
Cambrian
Dalradian
Pre-Dalradian
Granite
Grampian Terrane
Midland Valley Terrane
Southern Uplands Terrane
Mayo Sub-Terrane
Iapetus Suture
Leinster-Lakesman Terrane
0 15 30 60 Miles
0 25 50 100 Kilometres
N
Grampian Terrane placer Au
Grampian Terran lode Au
Grampian Terrane sulphides
Leinster-Lakesman Terrane placer Au
Mayo Sub-Terrane placer Au
Mayo Sub-Terrane lode Au
Mayo Sub-Terrane sulphides
Southern Uplands Terrane placer Au
Southern Uplands Terrane sulphides
15.70
15.65
15.60
15.55
15.50
15.45
15.40
15.35
$^{207}Pb/^{204}Pb$
17.20
17.40
17.60
17.80
18.00
18.20
18.40
18.60
18.80
$^{206}Pb/^{204}Pb$

Figure 5A

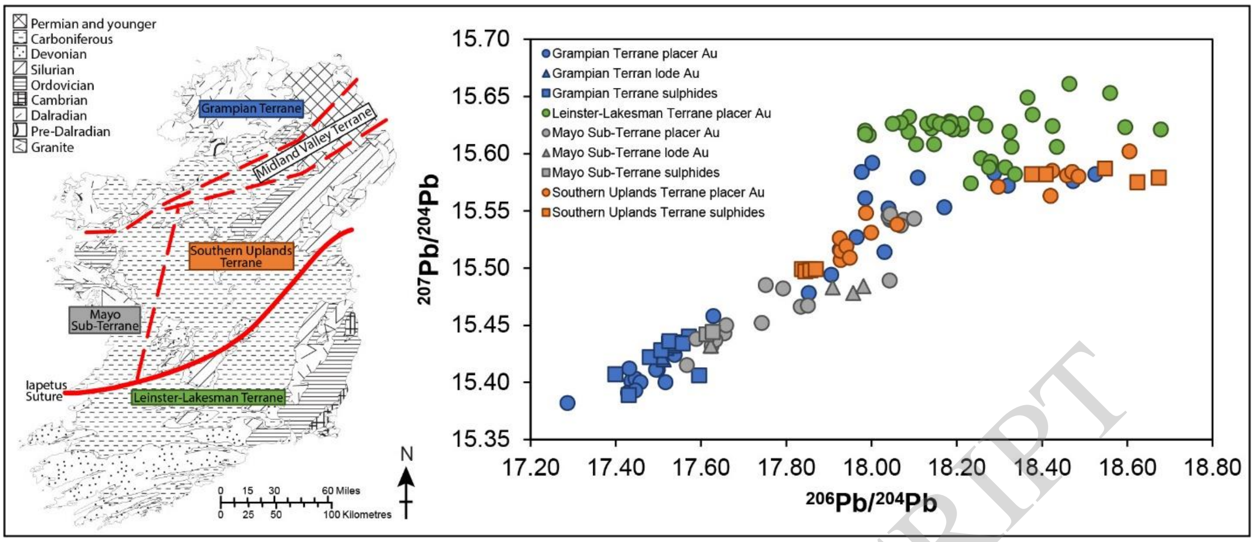

Permian and younger
Carboniferous
Devonian
Silurian
Ordovician
Cambrian
Dalradian
Pre-Dalradian
Granite
Grampian Terrane
Midland Valley Terrane
Southern Uplands Terrane
Mayo Sub-Terrane
Iapetus Suture
Leinster-Lakesman Terrane
N
0 15 30 60 Miles
0 25 50 100 Kilometres
Grampian Terrane placer Au
Grampian Terran lode Au
Grampian Terrane sulphides
Leinster-Lakesman Terrane placer Au
Mayo Sub-Terrane placer Au
Mayo Sub-Terrane lode Au
Mayo Sub-Terrane sulphides
Southern Uplands Terrane placer Au
Southern Uplands Terrane sulphides
15.70
15.65
15.60
15.55
15.50
15.45
15.40
15.35
$^{207}Pb/^{204}Pb$
17.20
17.40
17.60
17.80
18.00
18.20
18.40
18.60
18.80
$^{206}Pb/^{204}Pb$

Figure 5B

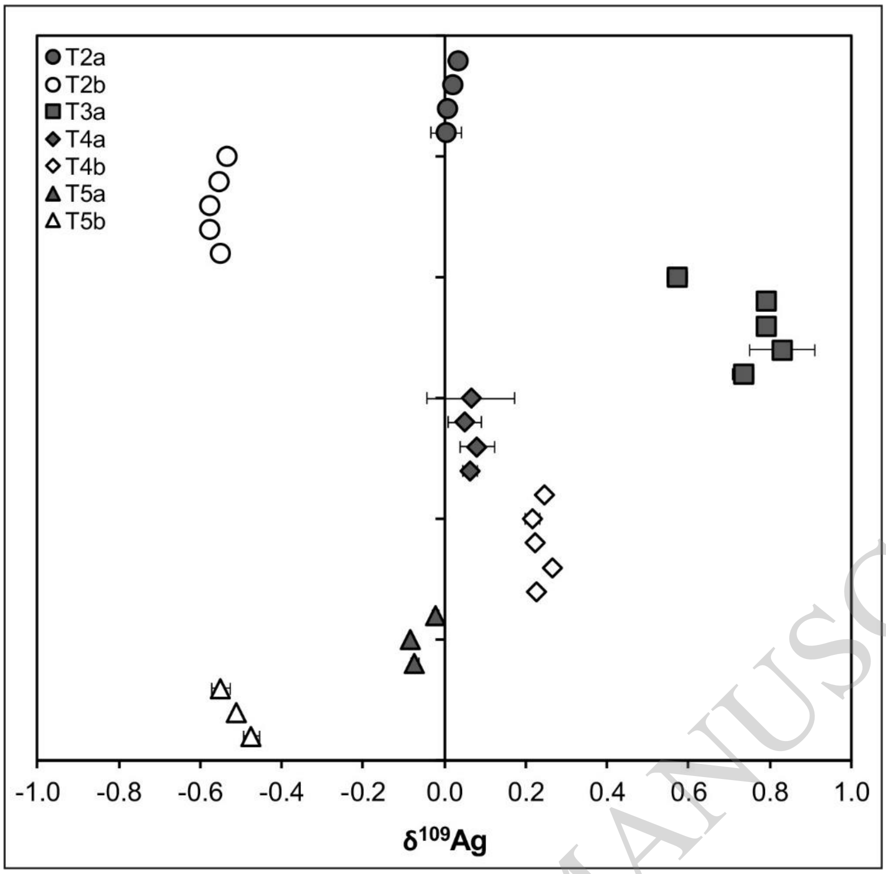


Figure 6

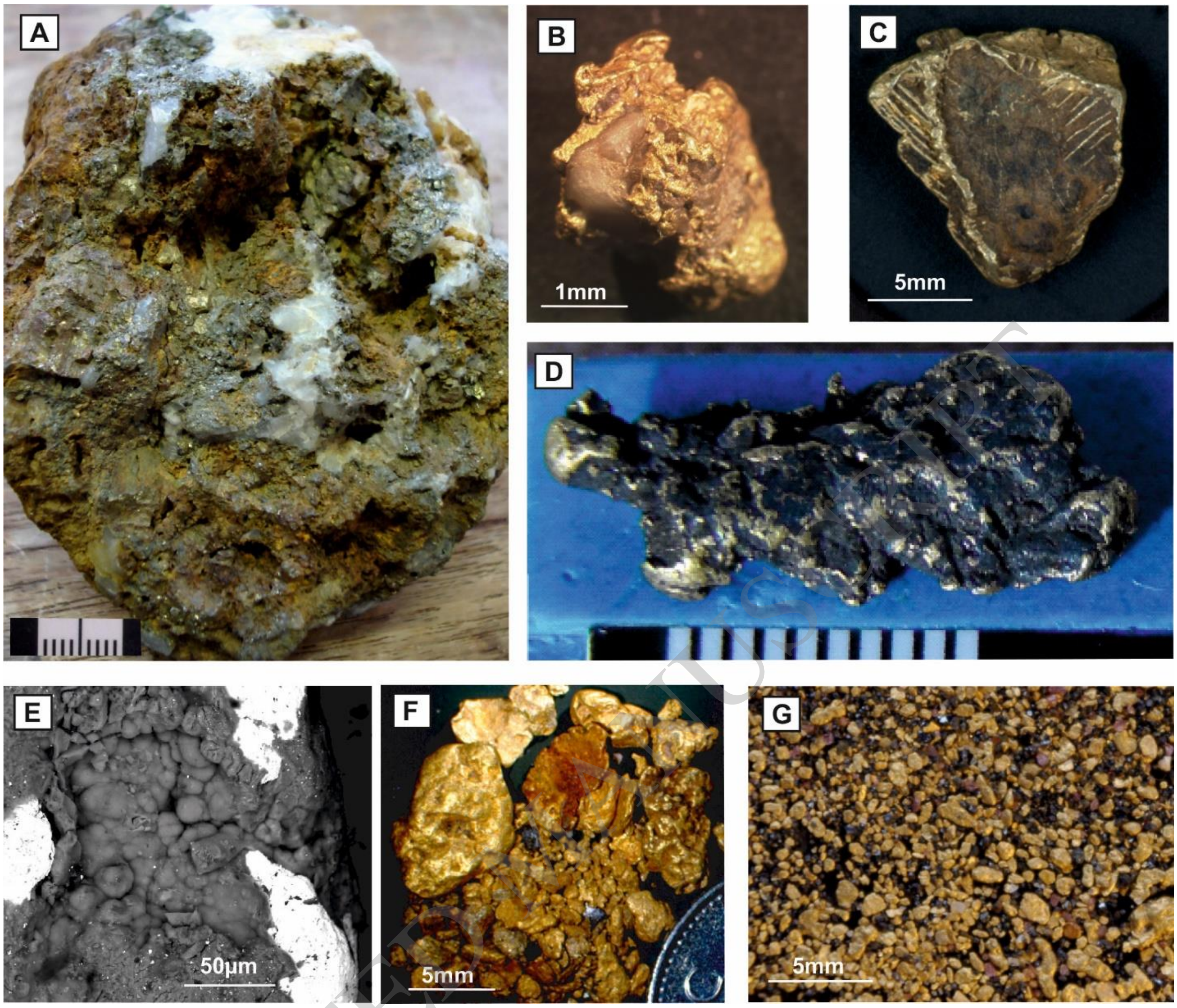


Figure 7

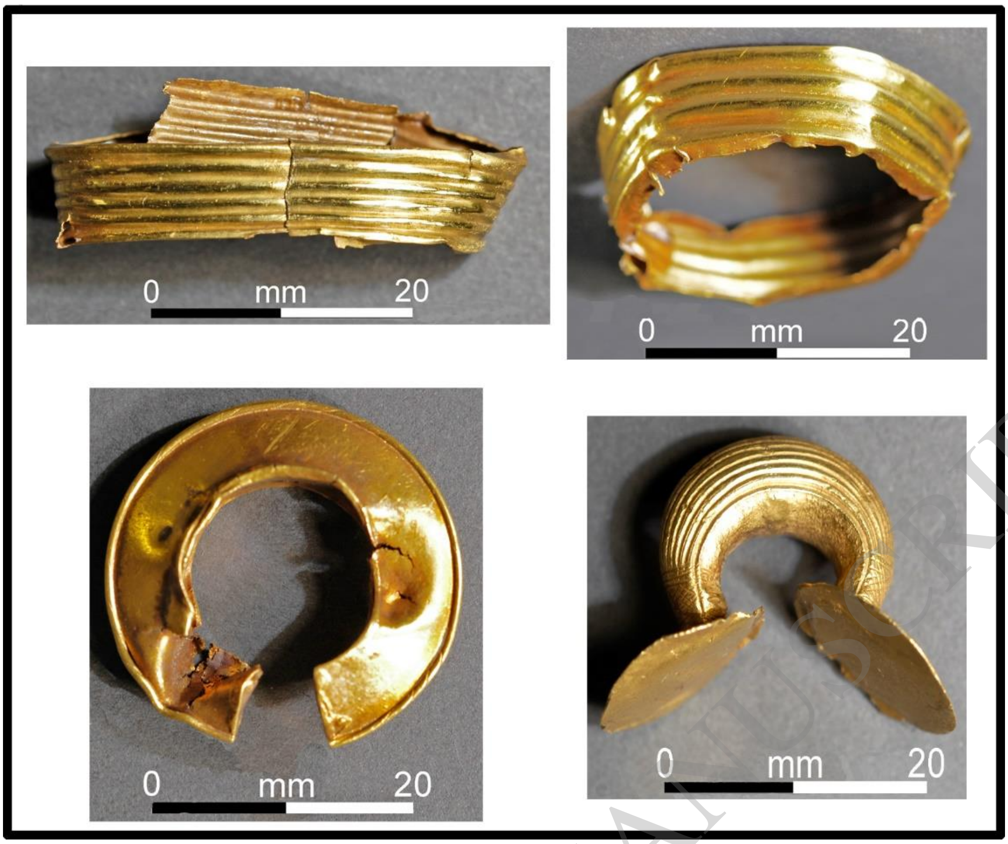


Figure 8

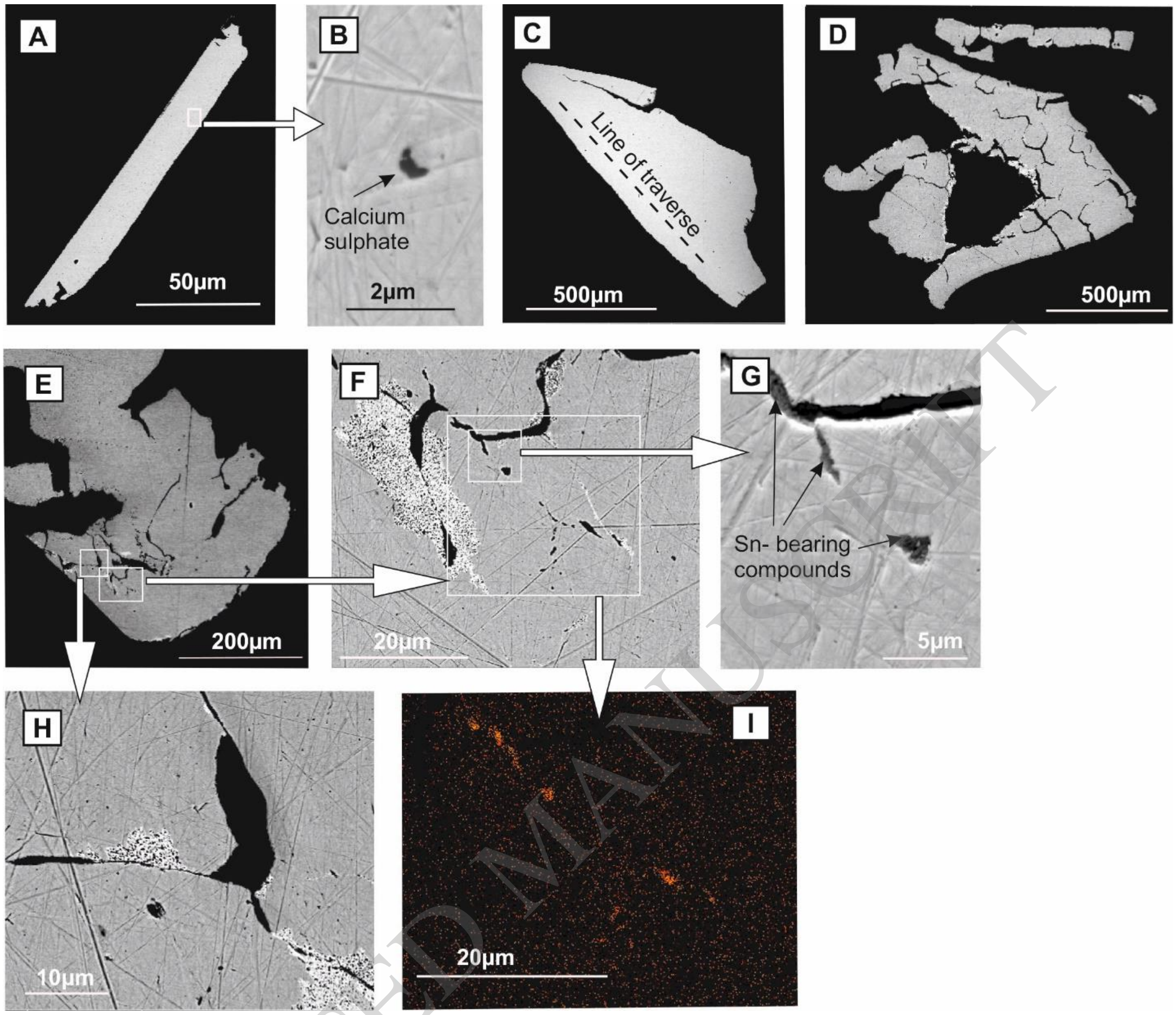

A
50µm
B
Calcium
sulphate
2µm
C
Line of traverse
500µm
D
500µm
E
200µm
F
20µm
G
Sn- bearing
compounds
5µm
H
10µm
I
20µm

Figure 9