Journal of Archaeological Science 68 (2016) 12–23

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Platinum group placer minerals in ancient gold artifacts – Geochemistry and osmium isotopes of inclusions in Early Bronze Age gold from Ur/Mesopotamia

Moritz Jansen [a, d, *], Sonja Aulbach [b], Andreas Hauptmann [a], Heidi E. Höfer [b], Sabine Klein [b], Michael Krüger [c], Richard L. Zettler [d]

[a] *Forschungsstelle Archäologie und Materialwissenschaften, Deutsches Bergbau-Museum, Herner Straße 45, D-44791 Bochum, Germany*
[b] *Institut für Geowissenschaften, Goethe-Universität Frankfurt, Altenhöferallee 1, D-60438 Frankfurt am Main, Germany*
[c] *Institut für Anorganische Chemie, Leibniz Universität Hannover, Callinstraße 1, D-30167 Hannover, Germany*
[d] *University of Pennsylvania Museum of Archaeology and Anthropology, 3260 South Street, Philadelphia, PA 19104, USA*

ARTICLE INFO

Article history:
Received 12 April 2015
Received in revised form
18 February 2016
Accepted 26 February 2016

Keywords:
Gold
Inclusions
Platinum group elements (PGE)
Osmium isotopes
Ophiolite complexes
Provenance studies
LA-MC-ICP-MS
EPMA

ABSTRACT

One of the most significant characteristics of the gold artifacts from the Early Dynastic Royal Tombs of Ur, Mesopotamia are numerous inclusions consisting of the platinum group elements (PGE) osmium–iridium–ruthenium. In nature, minerals of PGE (PGM) are enriched along with gold and other heavy minerals in placer deposits. During metallurgical gold extraction from placer material and subsequent production of artifacts, PGMs were incorporated in the gold artifacts due to their refractoriness almost unmodified. In order to evaluate their potential for provenance studies of gold, the PGE inclusions were analyzed for their chemical and Os-isotope compositions. They contain highly variable concentrations of Os (26–70 wt.%), Ir (14–62 wt.%) and Ru (0.4–45 wt.%). $^{187}Os/^{188}Os$ isotope ratios vary between 0.118 und 0.178. Due to the high Ru content of the alloys, the chemical composition point to a geological context of ophiolite complexes. Os isotope ratios are a powerful tool to narrow down the potential ore sources for the gold. However, the interpretation of calculated model ages is difficult due to the unknown genesis of the parental magma. Calculated ages (290–610 Ma) for measured $^{187}Os/^{188}Os$ of 0.125 using different reference values could indicate placers close to Paleozoic ophiolites like Samti (Takhar) in Northern Afghanistan and Zarshouran (Western Azerbaijan) in Iran, but need to be confirmed by additional measurements of their Os isotope signature in the future. Other archaeological relevant sources of PGM and gold could be excluded by direct comparison of their Os isotope data: 1.) old Neoproterozoic ophiolites from the Eastern Desert type (750–800 Ma), Egypt, 2.) young Mesozoic ophiolites from the Samail complex (96 Ma) in Oman. Thus, in combination with other tracers the Os isotope ratio is a valuable source for provenance studies.

1. Introduction

Provenance studies of archaeological gold artifacts to trace their geological origin through chemical analyses are a heavily debated topic in archaeometallurgy (Guerra and Calligaro, 2003; Watling et al., 1994; Tamas et al., 2009; Pernicka, 2014). Famous investigations at the beginnings are the large series of analyses (ca. 5000 analyses) of prehistoric gold artifacts by Hartmann (1970, 1982). He classified different types of gold according to five major and minor elements (Ag, Cu, Sn, Ni, Pt). But as these analyses were solely focused on artifacts themselves and excluded a characterization of natural gold occurrences, no direct links between the gold types and a provenance of the gold artifacts could be established. For provenance studies based on the chemical composition, very sensitive methods are needed to detect the small amounts of additional tracers (for a comparison of methods see Guerra and Calligaro, 2004). In recent years gold artifacts have been increasingly investigated with trace element measurements by mass spectrometry coupled with laser ablation and compared with

---

* Corresponding author.
E-mail address: moritz.jansen@bergbaumuseum.de (M. Jansen).

http://dx.doi.org/10.1016/j.jas.2016.02.004

potential natural gold resources chemically (Kovacs et al., 2009; Hauptmann and Klein, 2009; Schlosser et al., 2009). One of these results, e.g., is that the gold of the famous Sky Disc of Nebra could have originated from deposits in Cornwall, England (Ehser et al., 2011).

Already in the 1970s, platinum group element (PGE) inclusions in gold artifacts were considered a potential indicator for the geological origin of gold (Young, 1972). First described by Petrie and Quibell (1896) in ancient artifacts from Egypt, and often mistakenly referred to as “platinum inclusions” (i.e., to Pt itself), these inclusions consist of alloys dominated by osmium (Os), iridium (Ir), and ruthenium (Ru) and only subordinated by platinum (Ogden, 1976; Zwicker, 1998; Miniaci et al., 2013; Troalen et al., 2014; Lemasson et al., 2015). However, the large variability in the chemical composition of PGE inclusions does not allow a distinction between artifacts from different archaeological sites and periods including artifacts from the Royal Tombs of Ur and does not seem to be useful for provenance studies (Meeks and Tite, 1980).

Another approach to trace the origin of gold is the Os-isotopic characterization of the PGE inclusions. Radiogenic ^{187}Os is produced by the decay of ^{187}Re. Platinum group minerals typically occur in chromitites of ophiolite complexes and adopt the Os isotopic composition of the convecting mantle during their formation, while Re is excluded from the mineral (Gonzalez-Jimenez et al., 2014). The potential of the Os isotope method applied to PGM (PGE minerals) is based on the fact that the Os isotope evolution stops in absence of the parent element Re and can therefore provide model ages for their geological formation if the source from which they formed is correctly identified (e.g. depleted mantle, primitive mantle). First measurements of the Os isotopic compositions of PGE inclusions in ancient gold artifacts were performed on Celtic and Lydian coins (Junk, 2001; Junk and Pernicka, 2003). Although similarities between Celtic and Lydian coins were determined on the one hand, a wide variation within the Os isotope signatures of individual coins was found, precluding isotopic fingerprinting.

The Royal Tombs of Ur with hundreds of gold artifacts manufactured in a broad range of goldsmith techniques are one of the most impressive and largest finds of Early Bronze Age gold work. These artifacts have high potential as a case study for determining their metal provenance, in particular because no gold deposits are known in the alluvial plains of Mesopotamia; therefore, either the gold metal or the artifacts necessarily needed to be imported. Cuneiform tablets from the 3rd and early 2nd millennium BC provide references for the origin of gold found in Mesopotamia, although the evidence is scare. It has to be considered that the site names mentioned there do not necessarily designate deposits but most likely trading posts. Some names, however, can be assigned to geographical locations (after Maxwell-Hyslop, 1977; Potts, 1994, 1997; Moorey, 1999): Egypt cannot be identified in the cuneiform texts; hence, trade between Egypt and Mesopotamia can likely be excluded. The ancient *Hah(h)um* und *(Mar)daman* could indicate South-Eastern Anatolia as a source for gold, and *(H)arali/u* and *Su*land may lie in the hinterland of Western Iran. Frequently, gold from *Meluhha* is mentioned, which is interpreted as the present-day North-West India. Here, just as in Mesopotamia, gold deposits do not occur on the expansive alluvial plains. The sources of *Meluhha* must be sought most likely in Afghanistan or other neighbors (Maxwell-Hyslop, 1977).

For the first time PGE inclusions in gold from the Royal Tombs of Ur time were identified by Young (1972). He stated that the gold had to derive from the Pactolus River in Western Anatolia, since alluvial gold from this region was the only source he knew in the Middle East containing PGE minerals. Maxwell-Hyslop (1977) then discussed additional occurrences of alluvial gold with PGM in Eastern Turkey as sources of gold from Ur. She suggested further research on gold occurrences in Iran, Afghanistan, and Central Asia since gold was likely traded over long-distance routes together with lapis lazuli.

Cultural contact between Ur and Afghanistan is evident through the presence of numerous artifacts of lapis lazuli found in the Royal Tombs of Ur. As a mineralogical rarity it occurs in the Middle East only in Badakhshan, Afghanistan. In immediate vicinity to the lapis lazuli deposits, rich gold placers can be found at the Amu Darya River. There are also occurrences of tin placers in Western Badakhshan, which in combination with the above-mentioned materials presents strong evidence for the supply of various raw materials from Afghanistan to Mesopotamia (Stech and Pigott, 1986).

The site Shortugai is located in close proximity to the placer deposits of Badakhshan. It was a settlement of the Harappan culture hundreds of kilometers from the Indus Valley (Francfort, 1989). In contact with the Bactria-Margiana Archaeological Complex, this trading post likely provided access to the lapis lazuli deposit in Sar-i Sang as well as alluvial gold deposits along the Panj/Amu Darya River at Samti and the lower Kokcha River (Kenoyer and Miller, 1999). Although the dating of Shortugai is somewhat later than that of the Royal Tombs of Ur, gold trade networks linked to the Indus valley (*Meluhha*) are certainly plausible. From there, gold could have been transported with other items such as lapis lazuli to Mesopotamia.

The present study based on gold artifacts is part of a joint project on the scientific investigation of metal artifacts and mineral materials of the cemetery from Ur. In this study, the goal was to determine whether PGE inclusions are suitable as a tracer to obtain information on the origin of gold. However, our results indicate that successful provenance studies must include a combination of tracers as lead isotope ratios, trace element patterns, and supporting archaeological data. The artifacts analyzed in this study belong to the Near Eastern collection of the Penn Museum (Philadelphia, USA). More than 70 samples from mostly fragmented gold artifacts were obtained by cutting gold sheets with a diameter of about 5 mm. In half of these samples PGE inclusions were observed (37 of 72). The archaeological context of the artifacts is compiled in Table 1. Most of these objects came from the intact so-called 16 Royal Tombs of the Early Dynastic Period, e. g. the King's Grave (PG 789) and the Great Death Pit (PG 1237); in addition a few artifacts from later times could be analyzed. It should be emphasized that the archaeological relevance of the artifacts, the composition of the gold itself, and the production and processing techniques to form the artifacts will not be discussed in this manuscript. These topics are investigated in our project, but will be published elsewhere.

2. Methods

PGE inclusions in ancient gold artifacts are in some cases macroscopically visible, they can reach sizes up to 200 microns and more. As PGE inclusions have a more or less two-dimensional exposure in the gold artifacts, their real dimensions below the surrounding gold matrix are unknown and we are not able to present more details on their size in this study. The digital microscope (type Keyence VHX-2000 and type Olympus DSX100) has proved appropriate for the identification and documentation of PGE inclusions (Fig. 1a).

Smaller inclusions in samples of the gold artifacts were identified by scanning electron microscopy combined with semi-quantitative energy dispersive measurements (SEM-EDX, type Zeiss Supra VP with SDD detector Noran System 7, standard-free quantification using fundamental parameter method) at the