

Preliminary geochemical analysis and mineral micro-inclusions in alluvial gold from the Roman mining area of Pino del Oro (Zamora)

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INTRODUCTION

The Pino del Oro area (Zamora) preserves abundant archaeological remains of mining activity from the Roman period (1st and 2nd centuries AD) (Sánchez-Palencia et al., 2010), where two types of auriferous deposits have been exploited: 1) hydrothermal veins containing quartz and sulphides associated with sinistral secondary structures related to the main semi-ductile dextral strike-slip Villalcampo Shear Zone (González-Clavijo, 1990), dated at 306 ± 3 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$) (Gutiérrez et al., 2015); and 2) Holocene alluvial gold deposits within the current drainage network, mainly in the Fuentelarraya creek (a tributary of the River Duero).

Previous research has focused on geological and archaeological characterization; however, no detailed geochemical study or analysis of mineral micro-inclusions in alluvial gold particles has been carried out. In this study, we have determined the 'geochemical signature' of the alluvial gold, which provides information on the primary deposit and could be used in the traceability of Roman archaeological pieces.

METODOLOGY

Nine sediment sampling points along the Fuentelarraya creek and three soil sampling points from old mining areas were processed using a sluice box and a pan. A total of 455 gold particles were recovered. These were mounted in epoxy resin and polished to study their internal textures under a metallographic microscope. The geochemical composition of alluvial gold was determined using an electron microprobe (EMPA; CAMECA SX100), and the mineral micro-inclusions were analyzed using a scanning electron microscope (SEM-EDS; JEOL 6610LV).

RESULTS

Two types of Au:Ag gold alloys were identified within the studied old particles. The first type corresponds to the core of gold particles (Au₁) 75.32 - 83.44 wt% Au and 24.64 - 16.53 wt% Ag with minor concentrations of Hg (0.01 - 0.04 wt%) and Te (~0.01 wt%). The second type is to the particle borders (Au₂) 99.49 wt% Au and 0.51 wt% Ag resulting of a composition modified by supergene processes. Additionally, 11.80% of the total gold particles contained mineral micro-inclusions. These micro-inclusions comprise both silicate phases (quartz and K-feldspar) and ore mineral phases (Fig.1), predominantly arsenopyrite (Fig. 1A), galena, sphalerite, molybdenite, pyrrhotite, pyrite, chalcopyrite, cobaltite, gersdorffite, ullmanite, berthierite and rutile. Sb, Fe, Cu and Pb sulphides have been found occasionally (Fig. 1B).

DISCUSSION AND CONCLUSIONS

The geochemical composition of the particle cores (Au₁) reflects the characteristics of their primary source (Chapman et al., 2021), consisting of Au:Ag alloys with an Au content ranging from 75.32 to 83.44 wt%, which is properly termed "gold" (Spiridonov and Yanakieva, 2009). Furthermore, their Hg and Te content can be used to define their trace element signature (Liu et al., 2021), also indicating different stages of mineralization paragenesis (Banks et al., 2018).

In contrast, Au₂ are the result of supergene processes, similar to those identified in alluvial gold deposits worldwide. Mineral micro-inclusion species were identified in 11.80 % of the gold particles, providing key constraints on the mineralizing environment. These inclusions are of hypogene origin and are preserved in the placer environment (Chapman and Mortensen, 2016). Arsenopyrite is the dominant inclusion phase in placer populations and is also reported in hypogene gold (e.g., González-Clavijo 1990). Together, these data indicate at least two stages of mineralization, an early stage associated with arsenopyrite formation at homogenization temperatures of 380 – 320 °C, during which arsenopyrite precipitated following quartz formation, and a later stage where gold were precipitated between 250 °C and 320 °C reflecting a complex and polyphase orogenic history.

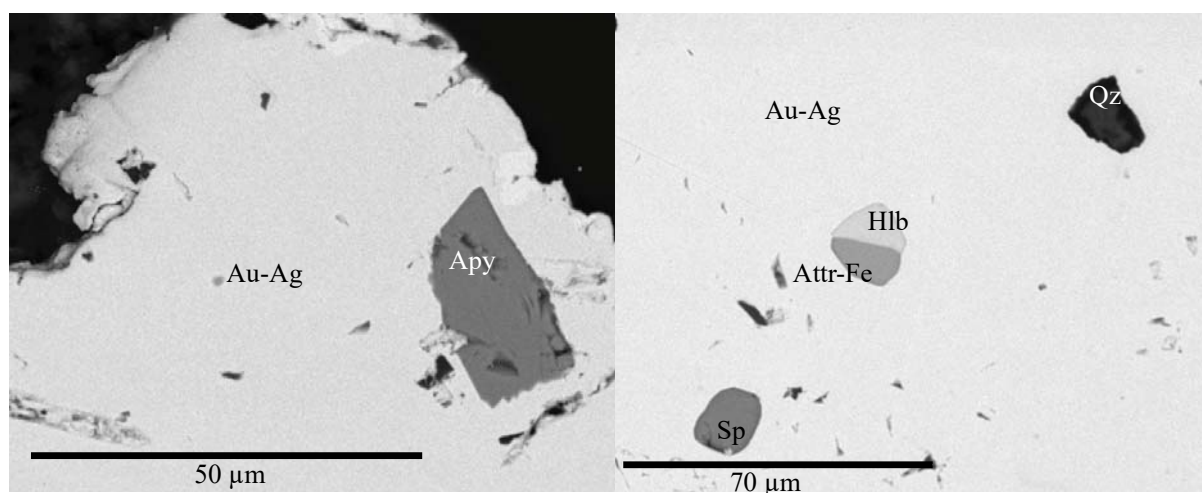


Fig 1. Examples of mineral inclusions observed in gold particles (Au-Ag): A. *Apy* - Arsenopyrite. B. *Qz* - Quartz, *Hlb* - Holubite ($AgPb_9(Sb_8Bi_3)S_{24}$) / *Attr-Fe* - Argentotetrahedrite-(Fe) ($Ag_9(Cu_7Fe_5)Sb_7S_{45}S$) and *Sp* - sphalerite.

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