Chemical Tracers in Archaeological and Natural Gold: Aliseda Tartessos Treasure and New Discovered Nuggets (SW Spain)

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Abstract

The gold outcrops employed by the ancient kingdom of Tartessos, settled in the SW of the Iberian Peninsula from ca. 10th to the 6th century BC, for the Aliseda treasure manufacture, has been discovered. This paper reports on the finding of collected gold nuggets, more than 80 units up to 218 g, in an ancient mining area located in Casas de Pedro (Extremadura, SW of Spain). The comparative physical-chemical analyses between these gold nuggets picked at present and the archaeological gold collected in 1920, have been performed by microscopy, X-ray diffraction (XRD), thermo-luminescence (TL), X-ray photoelectron spectrometry (XPS) and electron microprobe analyses (EMPA). Pieces of Aliseda treasure and the picked gold nuggets show a highly homogeneous chemical composition of trace elements namely: As 0.01%, S 0.02%, Bi 0.35%, Fe 0.016%, Ag 0.8%, Sb 0.05% and Te 0.04%. The small difference between both gold samples is only of 0.2% extra copper in Aliseda due to an anthropogenic addition of a silver-copper mixture during a second firing of the jewel to weld ornamental spheres.

Key Words. – Tartessos, Geochemistry, XPS, EMPA, TL, XRD, TG-TG-DTA, Gold Nuggets, Archaeology.

Introduction

Tartessos was a civilisation located on the southwest of Iberia, at the mouth of Guadalquivir river in Cadiz-Huelva (Spain) dated back from about 1000 B.C. up to 600 B.C. [1-3]. During the Greek colonisation of the Mediterranean Sea, both Tartessian with Phoenicians and Greeks competed to dominate the Mediterranean trading. The Tartessos kingdom covered an extensive area of the Iberian south-west including several mining areas of gold, silver and copper such as Rio Tinto, Tharsis, Sierra Morena, Tejada la Vieja, Aznalcollar, Sotiel, Lomero Poyatos, La Zarza, etc., as far as the south of Extremadura [4-5]. The trade association to Phoenicians involved incorporating the oriental culture to the indigenous material culture, the pottery, architecture, technology and even religious and burial customs was strong defining the Orientalizing period [6]. In the 6th century B.C., Tartessos disappears suddenly from history destroyed by the Carthaginians. Greeks, Phoenicians, Minoans and ancient Hebrews were fascinated by the Tartessians' rich emporium of valuable and precious metals (gold, silver, copper, etc.), produced by the mines of Rio Tinto [7]. In 1920 and following years, several treasures and items from Tartessos were discovered, e.g., the Aliseda treasure (Badajoz) composed by necklaces, bracelets, combs and some other unidentifiable things made of gold and silver.

The examination of several gold nuggets sets collected by the local miners (Fig. 1a) of Casas de Don Pedro, a small village of Badajoz at 120 km from the Aliseda treasure discovery (Fig. 2), allows to confirm that all nuggets display the same characteristics, as follows: (i) flat shapes, (ii) quartz and iron oxide inclusions, (iii) minor abrasion and polished surfaces by alluvial attrition resembling melted gold cooled onto a flat surface, (iv) milky quartz with little gold veins and (v) clay soil. The nugget sizes range from 1 g up to 218 grams. The minimum gold nuggets weight, circa 1 g, is explained for the metal detector threshold, under which it does not beep. Finally, we have had a set of 86 nuggets loaned to be analysed, weighing 375 g in total (Fig 1a and b).

An important area dug out by illegal metal detectorists surrounds two possible ancient Tartessos mine pits under true risk to be destroyed by the present legal gold prospecting excavation works. The initial target of the study was to clarify the natural versus artificial origin of these large gold nuggets, weighing up to 218 g, recently found in Casas de Don Pedro (Badajoz, Spain) (Figures 1a, 1b, and 2). The second part of the study was elucidating the geological origin of the nuggets and their geochemical linkages with the

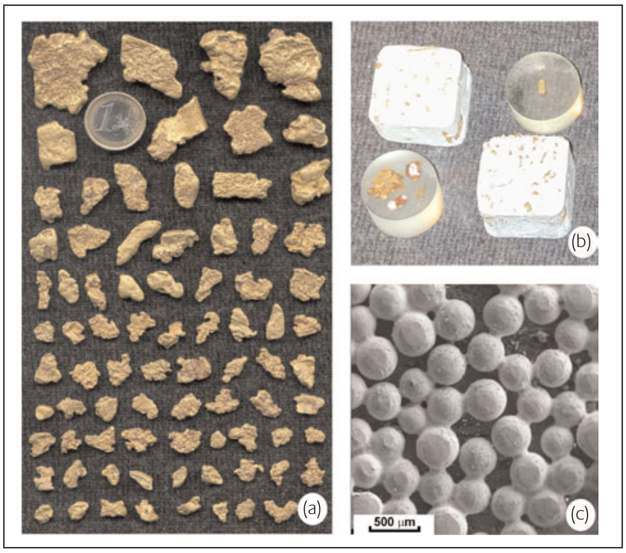

Figure 1

(a) Set of gold nuggets from Casas de Don Pedro collected with metal detector. (b) Gold nuggets bounded with gypsum for non-destructive analyses by Electron Microprobe Analysis, (c) Ornamental gold micro-spheres from the Tartessos Aliseda treasure welded by granulation techniques with a copper-silver mixture

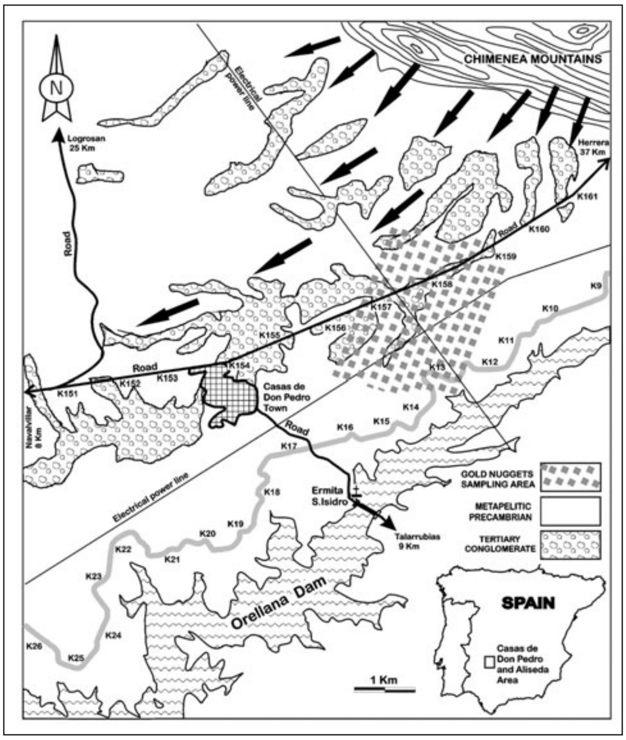

Figure 2

Geological sketch of the gold nuggets sampling area of Casas de Don Pedro (Badajoz)

Aliseda treasure to ensure the discovery of one of the ancient gold mines of the Iberian Tartessos Civilization. The presence of goethite (α-FeOOH), the inclusions of natural quartz crystals and the existence of fragments of milky quartz with gold veins, as well as the outer silver loss and all chemical analysis demonstrate the natural gold nuggets origin. Here is revealed close chemical relationships between the archaeological Tartessos gold of Aliseda (Badajoz) and the large gold nuggets of Casas de Don Pedro (Badajoz) providing two reasons to protect both, gold nuggets and outcrops since they are: (i) the best mineralogical samples of native gold in Spain, (ii) the ancient mining source of the Tartessos treasure gold of Aliseda (Figure 1c).

Experimental

From the analytical point of view, the selection of sample sets was focused on four different targets: (i) Origin study of the native gold nuggets by in-situ field geology together with a short selection of paragenetic minerals and host-rocks; (ii) Gold nuggets identification of the natural versus artificial origin, analysing their inclusions, e.g., iron oxides and quartz, by Microscopy to examine textural details, X-ray diffraction (XRD) to determine phases, Thermoluminescence (TL) to detected possible archaeological sample pre-heating, X-ray photo-electron spectroscopy (XPS) and Electron Microprobe Analysis (EMPA) to perform chemical analyses using different excitation sources, i.e., X-rays in the XPS case and electrons in the EMPA case, with different analytical penetration depth; (iii) Non-destructive chemical analyses of forty gold nuggets by EMPA providing information about their geochemistry, homogeneity and the hydrothermal genetic process; (iv) The EMPA comparative analyses of both, gold nuggets and four gold pieces of the Tartessos Aliseda treasure to perform the chemical correlation. Mineral phases were determined by X-ray powder diffraction using a Phillips PW1710 powder diffractometer with CuKα radiation. X-ray photoelectron spectroscopy (XPS) data were acquired with a VG ESCALAB 200R spectrometer equipped with a hemispherical electron analyser and a MgKα X-ray exciting source. The samples were mounted on a sample rod placed in a pre-treatment chamber and heated at 423 K under vacuum for 1 h prior to being moved into the analysis chamber. Energy regions (20 eV) of the photoelectrons of interest were scanned at 20 eV spectrometer pass energy, chosen as a compromise enabling acceptable resolution to be obtained within reasonable data acquisition time. Fe 2p, N 1s, O 1s, Si 2p, Si 2s, Cu2p and Au4f emissions were recorded. Intensities were estimated calculating the integral of each peak after subtraction of Shirley shaped background and fitting the experimental curve to a mixture of Lorentzian and Gaussian lines of variable proportion. All binding energies (BE) were referenced to the adventitious C 1s line at 284.9 eV. This reference gave BE values accurate to within ±0.1 eV. Thermoluminescence (TL) measurements were performed using an automated Risø TL system model TL DA-12 [4], this TL-reader is provided with an EMI 9635 QA photomultiplier and the emission was observed through a blue filter (a FIB002 of the Melles-Griot Company) where the wavelength is peaked at 320-480 nm; FWHM is 80 ± 16 nm and peak transmittance (minimum) is 60%. It is also provided with a $^{90}Sr/^{90}Y$ source with a dose rate of 0.021 Gy s^{-1} calibrated against a ^{60}Co photon source in a secondary standards laboratory [9]. All TL measurements were carried out using a linear heating rate of 5 K/s from room temperature up to 773 K under N_2 atmosphere. Four aliquots of 5.0±0.1 mg each of quartz inclusions from nuggets gold were used for each measurement. The sample was carefully powdered with an agate pestle and mortar to avoid triboluminescence [10]. The incandescent background was subtracted from the TL data. The gold mineral inclusions, e.g., quartz and hematite, were coated with a thick (ca. 10 nm) graphite layer, in a Bio-Rad SC515 sputter coating unit, prior to being introduced in the chamber of the EMPA. Obviously, the isolated gold pieces, e.g., Aliseda rings or single nuggets, were not necessary to be coated since gold has an excellent conductivity under the electron beam. To perform the non-destructive analyses of native gold samples (Figure 1a), groups of nuggets were bound together with gypsum and softly polished offering a flat surface to the EMPA beam; the gypsum binder allows a further easy desegregation (Figure 1b). The crystal-chemical characteristics of gold were determined on data series of electron microprobe analyses (Jeol Superprobe JXA-8900M), bulk and channel-selected (TAP, PETJ, LIF, PETH) X-ray spectra search and by identification routines. The used standards were natural and synthetic crystals from the collection of the “Servicio de Microscopía Electrónica Lluis Bru”, Complutense University, Madrid.

Results and Discussion

From a geological point of view, the gold nuggets are settled in the boundaries of the pediment conglomerate fans in contact, or very close, to the Low Precambrian meta-pelitic rocks (Figure 2). Making a SW-NE section, from this gold nuggets area towards the Chimenea Mountains, as the catchment area of the auriferous fans, we found the Low Ordovician Arenig (quartzite), the Medium Ordovician Llanvirn (meta-pelite) and the Low Silurian (black slate and sandstone). All the Chimenea Range is strongly sheared with NS and EW faults and fissures filled with subvertical milky quartz veins having carbonates and iron oxide masses as well as pockets without visible gold. This shear-zone deformation of late Precambrian-Paleozoic basement has been well studied [11-12] and it has a comparable geology to be a gold-bearing deposit classified as deep setting of chlorite-carbonate-type, similar to Yellowknife in Canada [13-14], Xallas in Spain [15] or in the Hercynian in France [16]. The presence of hydrothermal $CaCO_3$ in the quartzite veins suggests an epithermal gold deposition by boiling water with CO_2 and poor in sulphur [17]. The second part of the gold nuggets formation was a short transport as pediment and colluvium’s of 4-6 km producing sedimentary quartz pebbles, milky quartz boulders with native gold veins and illitic claystone.

The XRD results of the nugget brown inclusions displays semi-quantitative mineralogical analyses with approximately 70% quartz and 15% hematite and 15% goethite (Figure 3a).

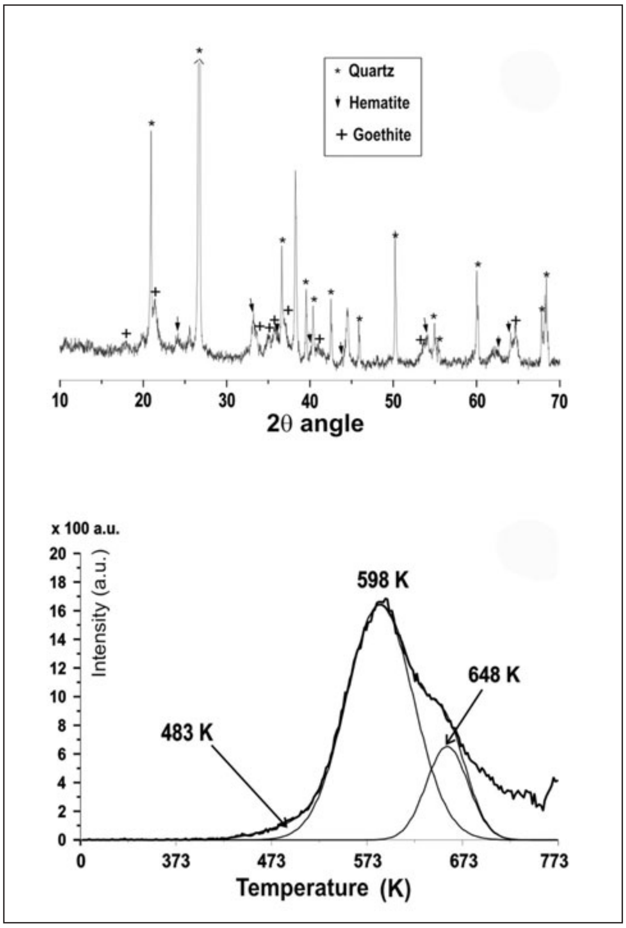

Figure 3
(a) X-ray diffraction of gold inclusions, (b) Thermoluminescence of natural inclusions of quartz from the gold nuggets

Thermoluminescence glow curves of quartz from the golden nuggets were deconvoluted using Gaussians, despite this type of fitting does not make physical sense; it is very useful to ascertain the position of maxima temperatures (Figure 3b). Three dominant overlapping Gaussian-shaped curves appear peaked at 483 K, 598 K and 648 K. The small one, at lower temperature, has the lowest lifetime (ca. 800 years) that is the reason because the ratios of the intensities of peaks 1, 2 and 3 are approximately 1:19:8. The lifetime of the 598 K and 648 K peaks are $1{\cdot}10^8$ years and $>1{\cdot}10^8$ years respectively [18]. The appearance of the 598 K peak as the more intense one indicates that no heating (or clock resetting) was applied to this material. The origin of this emission is due to the effect on the quartz of long exposure to natural alpha, beta and gamma emitters (such as U, Th and K) and cosmic rays.

The Fe 2p core-level spectrum recorded by XPS shows two components: a minor one at a BE of 710.3 eV (33 %at) attributed to a small amount of Fe_2O_3, and a major one at a BE of 711.5 eV (67 %at) due to FeOOH species (Figure 4). Apart from gold, other emissions coming from nitrogen, silicon and copper were also examined. (i), The most intense Au $4f_{7/2}$ peak of gold displays two components at BEs of 84.0 eV (86 %at) and at 85.5 eV (14 %at) associated to Au metal and Au-O bonds, respectively (Figure 4a); (ii), N 1s peak

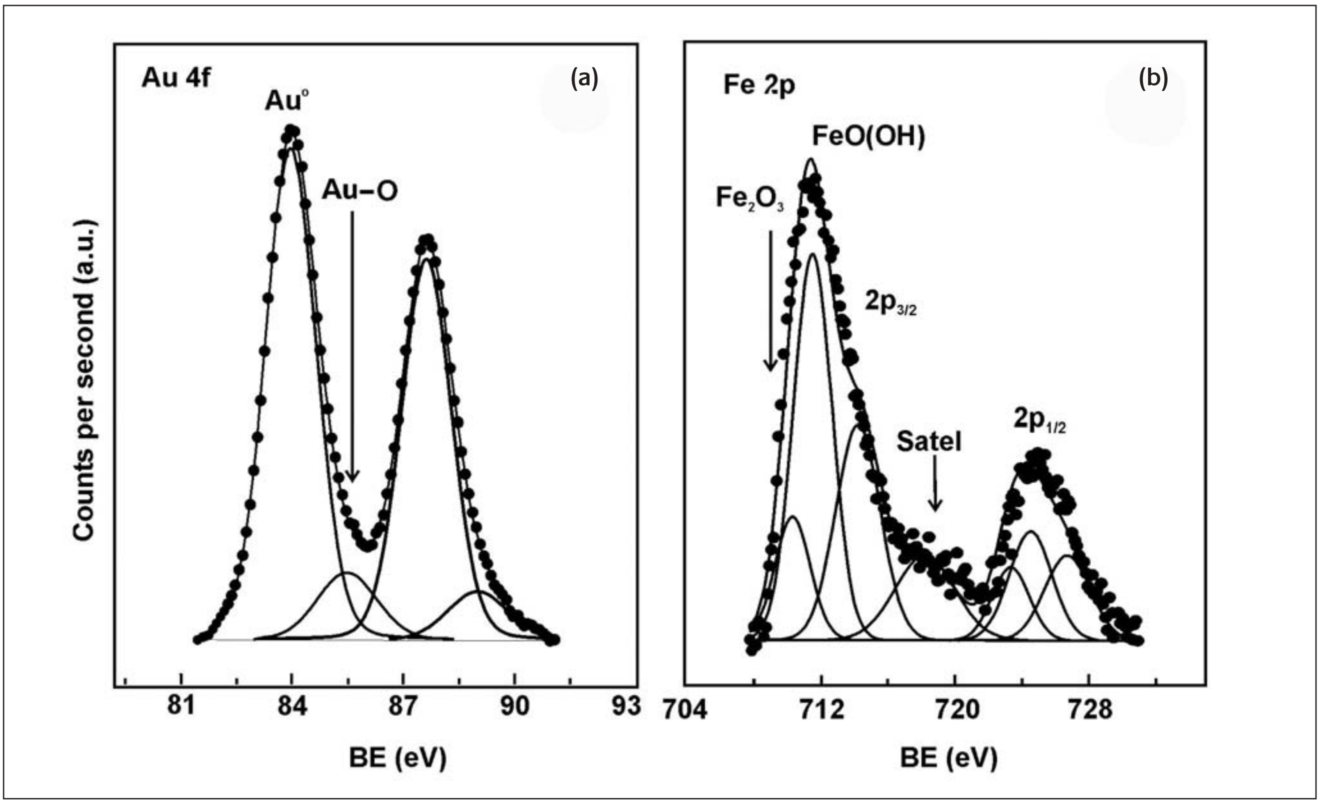

Figure 4

X-ray Photoelectron Spectroscopy of gold nugget inclusions: (a) Au 4f and (b) Fe 2p core-level spectra of inclusions from the gold nuggets. The main amount of a FeOOH component shows a non-fired hydrous phase

displays three components at 398.6 eV (30 %at), 399.6 eV (44 %at) and 400.8 eV (26 %at) attributed to organic pollution from the soil humus; (iii), Si 2s peak at 153.3 eV comes from the host quartz vein; and (iv), Cu $2p_{3/2}$ peak with components at 931.9 eV (69 %at) and 933.4 eV (31 %at) which looks as alloyed Cu-Au and as a copper oxide species, respectively. This set of analytical data together with perfect textures of mineral inclusions observed under the binocular lens point unequivocally to natural samples and not to anthropogenic melted phases. In addition, the presence of several zones of milked quartz and different iron oxides is in good agreement with the mentioned epithermal gold deposition.

The EMPA analyses of both types of gold, i.e., archaeological Aliseda treasure and the large native nuggets, display the most profitable results. The 60 analyses by EMPA were performed in 40 gold nuggets; here (Figure 5a) only 30 are included with a total sum above 96%. The other half was rejected since, by the non-destructive used method, it is difficult to focus these bad polished surfaces, as follows: (i) The triangle plot Ag vs Sb vs Bi (Figure 5a) display a very coherent population in the region “b”. This homogeneous population of the most abundant elements (Ag-Sb-Bi) stem from a narrowly linked geological origin. (ii) The three isolated samples in the region “a” have no silver. These analyses were performed in the narrow external outer, that shows darker by backscattering, and they report on silver losses carried out probably during the alluvial transport. (iii) Figure 5b shows the Te/S ratios of the nuggets gold set telling about approximately twice tellurium than sulphur in good agreement with the proposed epithermal gold deposition by boiling water with CO_2 and poor in sulphur such as this case. (iv) Figure 6a is a comparative plot of the minor elements between the outer and the inner nugget in a well polished-analysed sample mounted in polyester (Figure 1b). It is interesting to observe silver lost from the outer area however other elements such as Bi, Sb or Te are not removed. (v) Figure 6b displays three analyses of Tartessos rings from the Aliseda treasure and a representative nugget-12 offering the following comparisons: (1) The chemical analyses of trace elements of Aliseda samples are very similar between them as well as to Casas de Don Pedro nuggets, (2) All Aliseda samples show a very little amount of copper that has also been detected in nuggets by XPS but not by EMPA, in any case, more than 0.2% of copper could be added in the archaeological smelting by contamination or to dump the metal melting point. (3) The total amount of silver, which circa 0.5% has been observed in all gold artefacts and nuggets. (4) Minor variations are also detected in the archaeological jewellery such as the sample Aliseda-1 with more tin and less antimony, in this case, clearly attributed to the anthropogenic contamination in the artisan procedure. (vi) Figure 6c put side by side chemical analyses taken on the top of the Aliseda micro-spheres and analyses performed in the melted joint between these spheres. The resultant observation is the same anthropogenic addition of a minor amount of silver-copper mixture to dump the eutectic point in the welding process during a further re-baking of the

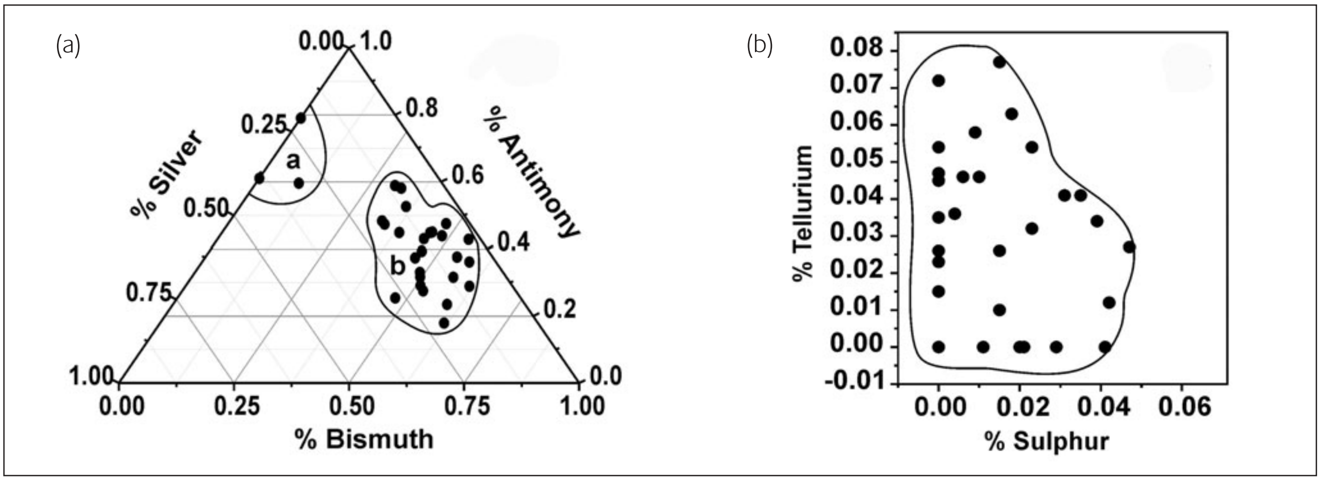

Figure 5

(a) The region "b" of the main trace elements of Sb-Ag-Bi in gold nuggets display an homogenous population having the same geological origin. The region "a" is gold nugget analyses without silver performed in the external nugget outer. (b) The approximately more abundance of tellurium element than sulphur inform about an epithermal gold formation

jewel. This later addition of Cu-Ag explain the little difference between gold from Aliseda and Casas de Don Pedro in an unambiguous overall coincidence. (vii) Figure 6d shows as our experimental melted sphere using gold from Casas de Don Pedro nuggets has no different trace elements in respect to both, natural and archaeological gold (Figure 1b). The Aliseda-1 and Nugget-core display representative analyses of gold-source and gold-product plus the minor additional copper. The conclusion is that our experimental melting operation does not leak out trace elements.

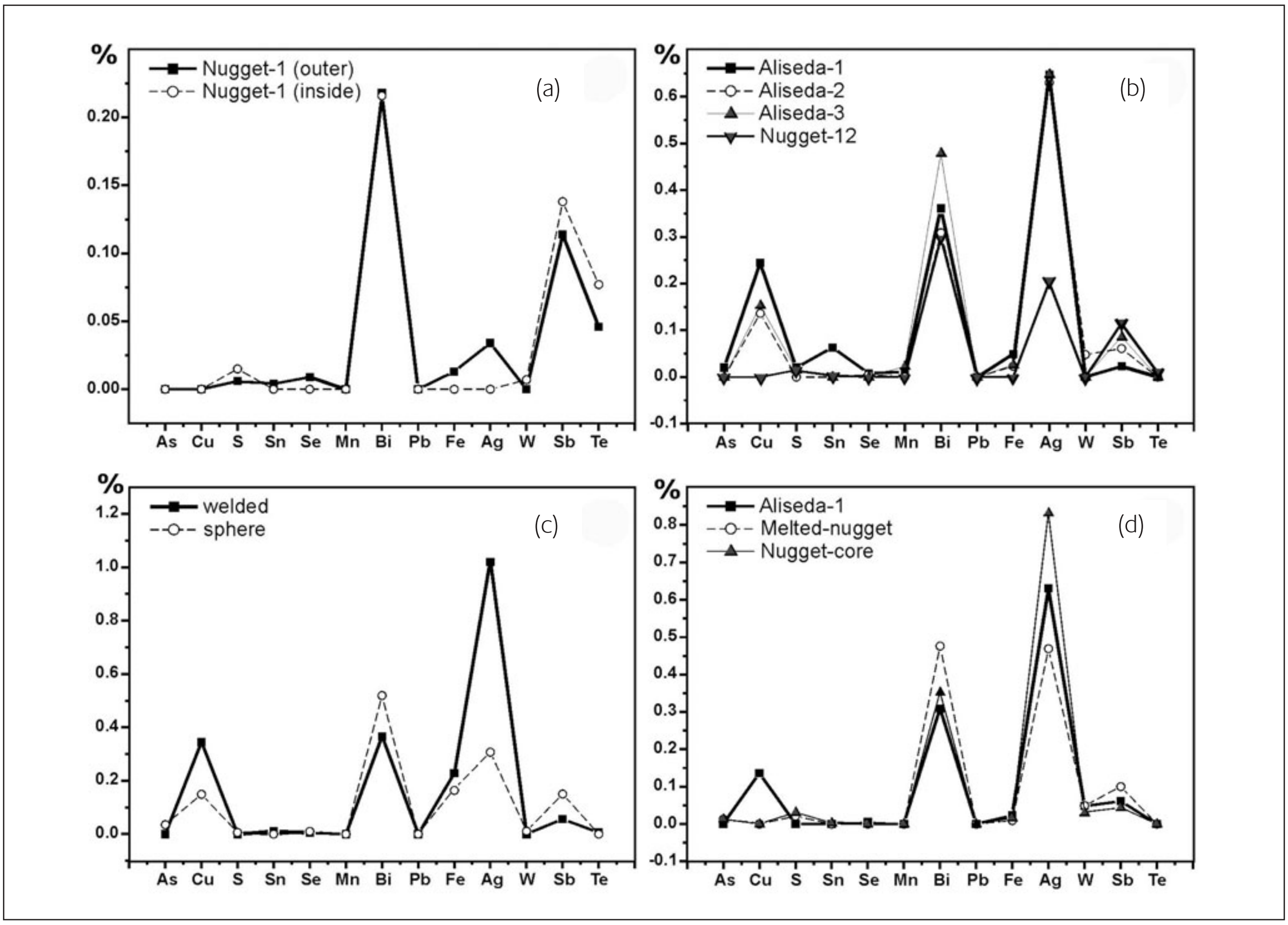

Figure 6

Comparative plots of the Electron Microprobe Analyses, as follows: (a) The outer and core of gold nuggets, (b) The Aliseda Tartessos gold with a representative gold nugget, (c) Different parts of the Aliseda manufacture, Welded-joint and sphere, (d) A driven laboratory nugget melting which does not introduce significant chemical changes

Conclusions

(1) New gold nuggets of Casas de Don Pedro (Badajoz) are in the low part of Tertiary conglomerates very close to the bottom boundary with the Precambrian basement. The primary origin can be found in the quartzite veins of the catchments area, which circa 5 km away. These veins with chlorite, calcite and iron oxides are hosted in the Ordovician metapelite rocks of the Chimenea Range which is strongly sheared. This geological setting points to an epithermal gold deposition by boiling water with CO_2 and poor in sulphur coming from deep through faults.

(2) The gold nuggets area of Casas de Don Pedro was probably picked by the ancient Tartessos Aliseda jewellers by simple recollection outside. Nowadays, the gold nuggets are being recollected using metal detectors at 40-50 cm deep by many local illegal archaeological prospectors. Two possible ancient Tartessos mine pits may be under true risk to be destroyed with legal permission by the mining gold prospecting excavation works.

(3) Nuggets are natural native gold, and not anthropogenic melted metals, since the XRD, and XPS analyses of iron oxides detect goethite inclusions in the gold nuggets and the TL measurements of quartz inclusions shows maximum peaks around 1600 a.u. characteristic of natural not-heated samples. The micro-textures of mineral inclusions in the gold cavities also display fresh natural parageneses.

(4) The gold nuggets population show a highly homogeneous chemical composition of trace elements with the following standard composition in cores: As 0.01%, S 0.02%, Bi 0.35%, Fe 0.016%, Ag 0.8%, Sb 0.05% and Te 0.04%. In the external outer only is appreciated a whole loss of silver attributed to fluvial erosion. The Te/S ratio is 2 in good agreement with an epithermal gold deposition by boiling water with CO_2 poor in sulphur.

(5) The trace elements of Aliseda rings are very similar among them and with the Casas de Don Pedro nuggets. Aliseda samples have a little amount of copper that has also been detected in nuggets by XPS but not by EMPA. The approximately 0.2% additional copper in Aliseda Samples could be added in the archaeological smelting. Furthermore, the comparative analyses of Aliseda micro-spheres and Aliseda welded-joints show anthropogenic addition of a silver-copper mixture during granulation techniques of the jewel which also explains the little difference between the gold from Aliseda and Casas de Don Pedro. This hypothesis is also supported in a driven laboratory melting Casas De Don Pedro gold nuggets which has generated a sphere with no different chemical composition of trace elements.

(6) The final whole conclusion is the discovering of the ancient mining area in which the ancient Tartessos collected gold nuggets to manufacture the spectacular treasure of Aliseda.

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