NANOSCALE (2024)

SUPPLEMENTARY INFORMATION

Nano-micro crystals revealed on tang dynasty gilded bronzes using advanced TEM-SEM and synchrotron methods.

Ioannis Liritzis ^{*a,b} Sophie Cazottes ^c, Thierry Douillard ^c, Muriel Véron ^d, Josep Roqué-Rosell ^e, Carlo Marini ^e, Partha Pratim Das ^f, Alejandro Gomez-Perez ^f, Athanassios S. Galanis ^f, Stavros Nicolopoulos ^f, Panagiota Manti ^g, Junchang Yang ^h and Xiangyu Zhang ⁱ

- a. Laboratory of Yellow River Cultural Heritage, Key Research Institute of Yellow River Civilization and Sustainable Development & Collaborative Innovation Center on Yellow River Civilization, Henan University, Kaifeng 475001, Minglun Road 85, China. E-mail: <u>liritzis@henu.edu.cn</u>
- b. Alma Mater Europaea (AMEU) ECM, Slovenska Ulica 17, 2000, Maribor, Slovenia
- c.Univ Lyon, INSA Lyon, CNRS, MATEIS, UMR 5510, 69621, 20 Avenue Albert Einstein, Villeurbanne Cedex 69621, France
- d. SIMAP Laboratory, CNRS-Grenoble INP, BP 46 101 rue de la Physique, 38402 Saint Martin d'Hères, France
- e. ALBA Synchrotron Light source & Univ. of Barcelona, Spain
- f. NanoMEGAS SPRL, Rue Émile Claus 49 bte 9, 1050 Brussels, Belgium
- g. Department of Environment, Ionian University, Zakynthos, Greece
- h. Research Centre of Material Science and Archaeology, Institute of Culture and Heritage, Northwestern Polytechnical University, Xi'an, China
- i.Xi'an Institute of Conservation and Archaeology, 710068, Xi'an, China. E-mail: yangjunchang@nwpu.edu.cn

*Corresponding authors.

E-mail address: liritzis@henu.edu.cn (Ioannis Liritzis) & Junchang Yang (yangjunchang@nwpu.edu.cn)

S1: Au alloy thin layer subjected to TEM-EDS

TEM-EDS was collected with FEI T20 (200 KV) microscope at Nanomegas laboratory

(Brussels) from the FIB cut which is from the interface between the corrosion and the bronze

material. In the thin "gold layer" main presence of Hg and Au is confirmed (Fig. S1)

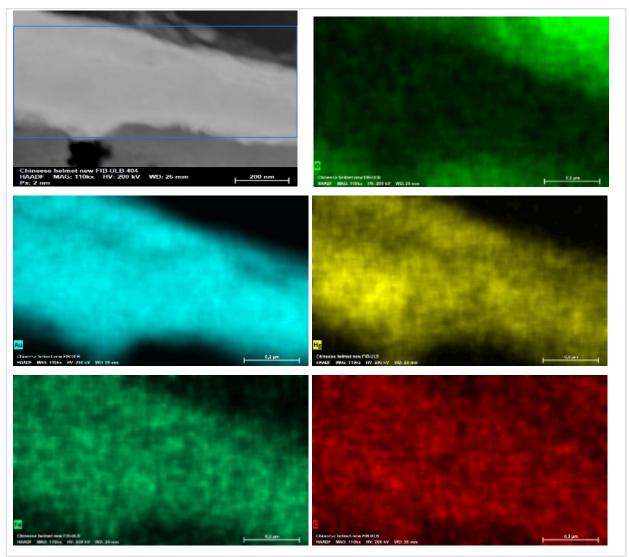
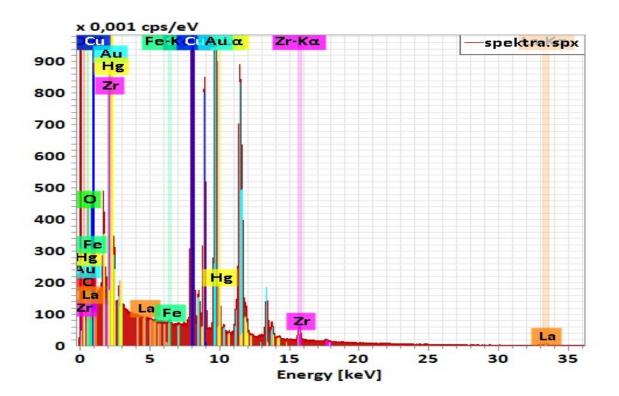
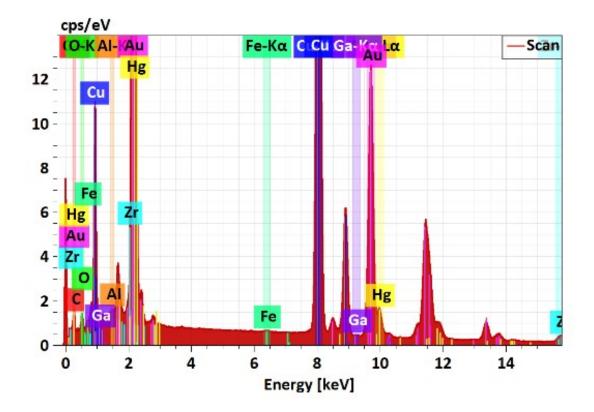


Fig. S1: TEM –EDS of 0-38 keV of the FIB cut shows the presence of Au in the thin gilding layer. Mapping of Fe, C, O, Au, is shown and Hg (yellow) is also detected, at 200nm scale. Upper (left) black and white photo is the High-angle annular dark-field imaging (HAADF) made by Scanning Transmission Electron Microscopy (STEM).





	Element	At. No.	Line s.	Netto	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
	С	6	K-Serie	0	0,00	0,00	0,00	0,00
State States	0	8	K-Serie	21921	0,19	2,14	0,03	16,54
	Cu	29	K-Serie	11498239	0,00	0,00	0,00	0,00
	Zr	40	K-Serie	110669	3,10	6,26	0,12	3,82
	Au	79	L-Serie	6007550	86,32	80,66	8,66	10,03
	Hg	80	L-Serie	681947	10,08	9,25	1,03	10,25
	Al	13	K-Serie	40410	0,19	1,31	0,03	16,11
	Fe	26	K-Serie	18792	0,12	0,39	0,03	24,32
all and a second	Ga	31	K-Serie	0	0,00	0,00	0,00	0,00
432 HAADF MAG: 56,0kx HV: 120 kV WD: 26 mm 400 nm Px: 4 nm 400 nm				Sum	100,00	100,00		

Fig. S2 TEM –EDS spectra of 0-14 keV of the FIB cut shows chemical elements and the presence of Au and Hg in the thin layer film. Table gives the EDS chemical elements present. Data show that the layer is not homogeneous, it is probably of $Cu_7Au_3Hg_{0.2}$ composition.

S2: EBSD-SEM

Although EBSD measurements allowed to identify metallic copper and gold at the core metal, also tenorite, cuprite, malachite, azurite, nantokite, atacamite, brochantite, chalcocite and covellite were checked their presence at the core metal corrosion layer. Both EDS and EBSD mappings confirmed that core metal had been oxidized from inside into cuprite and developed a corrosion layer of malachite (Table S1). The data is from the Crystallography Open Database [49].

Phase name	Space group	a(Å)	b (Å)	c (Å)	Mean Z
Cu	Fm3m	3.58	-	-	29
Au	Fm3m	4.07	-	-	79
CuO Tenorite	C12/c1	4.65	3.41	5.11	18.5
Cu ₂ O Cuprite	Pn3m	4.25	-	-	22
Cu ₂ CO ₃ (OH) ₂	P2 ₁ /c	9.502	11.974	3.240	
Malachite					
Cu ₃ (CO ₃) ₂ (OH) ₂	P2 ₁ /c	5.008	5.844	10.336	
Azurite					
Cu ₂ S	P6 ₃ /mmc	3.89	-	6.88	
Chalcocite					

Table S1: Candidate phases used during this study.