Study of the silvering process of ancient Roman coins using nuclear-physical methods and complementary techniques

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Motivation

Monetary system in ancient time was a challenging task, influenced by economic crisis, availability of metal sources and monetary reforms. In particular, the Ag content of the currency minted for about sixty years by the Antoninii emperors reflected the economic health or crisis of the Roman Empire. At the beginning, the Antoninianus denomination was a silver-rich coin (up to 80% of Ag), but gradually was devalued becoming a bronze coin with a very low content of silver (about 2-3% of Ag).

Materials and Methods

Two of ancient Roman silver coins (one of them was mint as barbarian imitations of roman coin), dating back between III-IV Century AD have been characterized. We used a set of modern micro- and non-invasive analytical techniques: Focused Ion Beam - Field Emission Scanning Electron Microscopy - Energy Dispersive X-ray Microanalysis (FIB-FESEM-EDXM), Scanning Electron Microscopy (SEM-EDX), Micro X-Ray Fluorescent analysis (μXRF), Synchrotron and Neutron -based Computer Tomography (CT), Synchrotron - based X-Ray Diffraction (XRD), Neutron Radiation Analysis (NRA) and other complementary methods.

Results

The results revealed that a complex Ag-Cu and Ag-Cu-Pb-Sn alloys was used. The use of alloys was common in the flourishing years of the Roman Empire. In the prosperous periods, Romans produced Ag-Cu alloys with relatively high silver content for the manufacture of both the external layers and inner nucleus of coins. This study also revealed that, although surface silvering processes were applied in different periods of crisis under the reign of Antoninii, even during crisis, Romans produced Antoninianus of high quality. **It possible, moreover, a first attempt to improve the silvering procedure using Hg-Ag amalgam has been identified, because Hg was detected in the upper silver layer of coins.**

Acknowledgement

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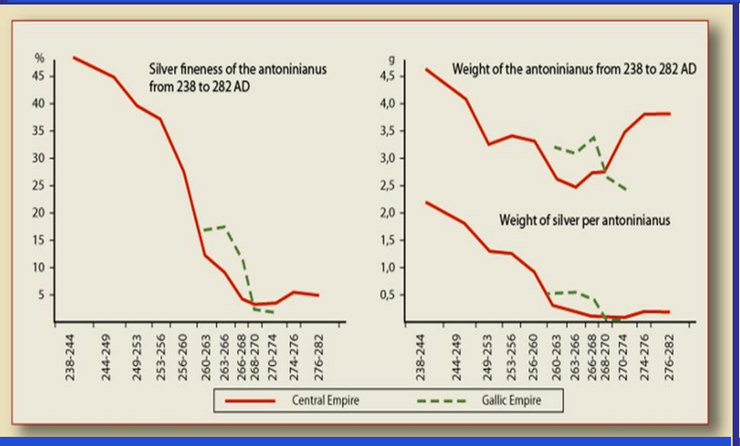
Coin 1

Coin 2



http://www.ric.mom.fr/en/info/sysmon#haut

Mass percent (%)

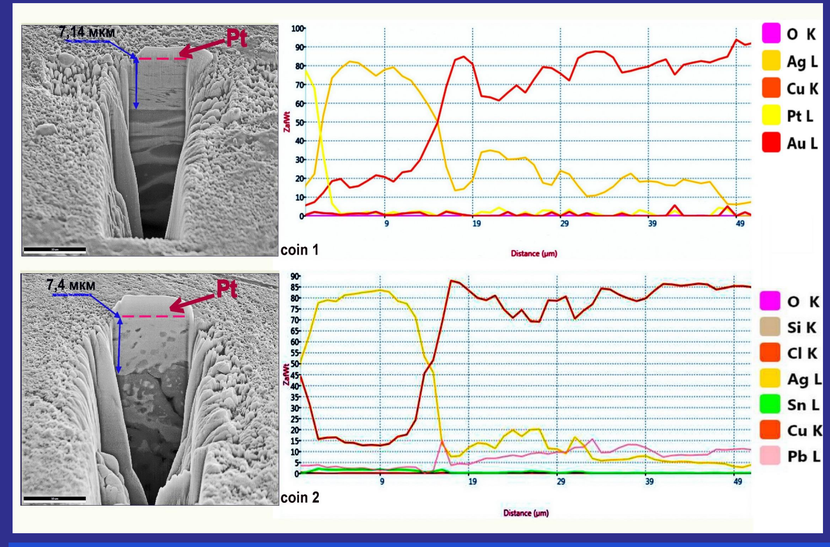
Spectrum	Na	Al	Si	Cl	Ag	K	Sn	Ca	Fe	Ni	Cu	Zn	Au	Pb
Coin1A#1	0.80	0.15	0.57		29.49	0.94		0.27	0.88	0.51	62.97		0.49	1.81
Coin1A#2	0.00	0.17	0.32	0.38	35.44	0.94		0.44	1.06	0.43	57.74			3.03
Coin1A#3	0.00	0.08	0.24	0.65	64.37	1.61		0.14	2.65	0.34	26.46			2.54
Coin1A#4a	0.89	0.07	0.16	2.16	48.73	1.79		0.60	1.96	0.33	34.74			2.70
Coin1R#4v	0.14	0.13	0.08	0.00	71.08	2.20		0.39	3.25	0.26	18.05			2.42
Coin2A#4g	0.37	0.23	0.25	1.65	69.55	2.50		0.88	3.27	0.22	11.93			3.39
Coin2A#3	2.51	0.03	0.33	0.36	4.20		1.47	0.09	0.26		86.72		1.84	0.91
Coin2R#1		0.24	0.38	0.05	2.38	0.07	0.66	0.01	0.13		93.26		0.68	1.30
Coin2R#2	0.00	0.05	0.31	0.94	8.38	0.33	5.07	0.30	0.42	0.22	76.22	2.47	1.05	2.67

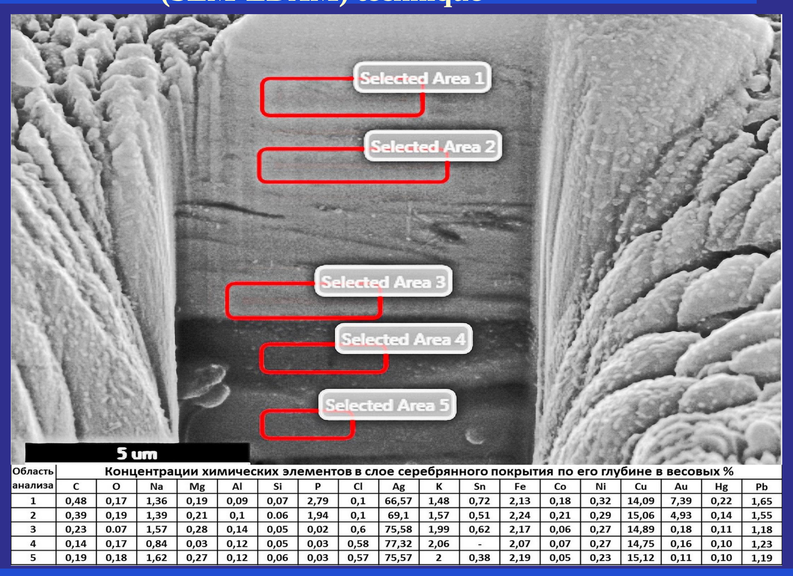
Coin-1 (core)

Coin-1,2 (Surface Avers/Revers)

Coin-2 (core)

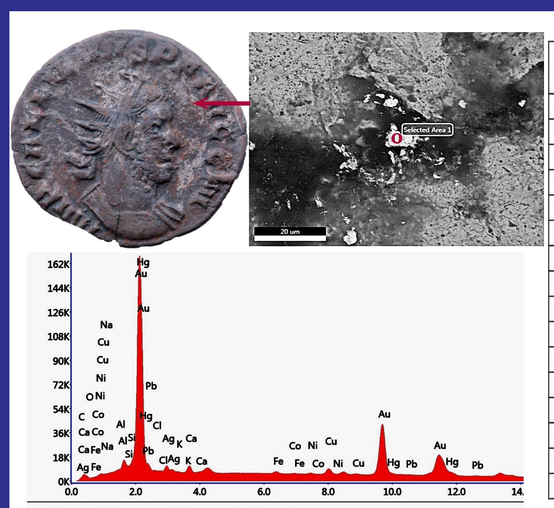
Chemical element composition of Coin-1 and Coin-2 (SEM-EDXM) technique



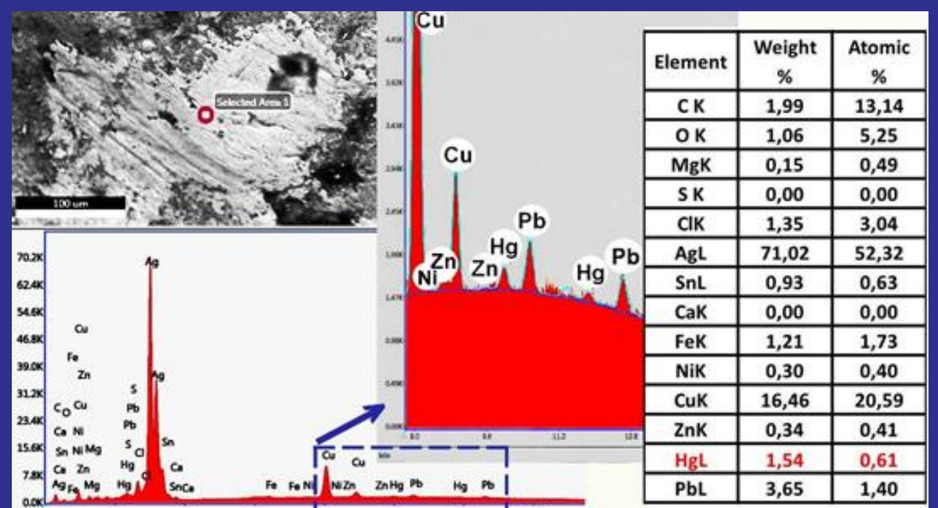


Область анализа	Концентрации химических элементов в слое серебряного покрытия по его глубине в весовых %																
	C	O	Na	Mg	Al	Si	P	Cl	Ag	K	Sn	Fe	Co	Ni	Cu	Au	Hg	Pb
1	0,48	0,17	1,36	0,19	0,09	0,07	2,79	0,1	66,57	1,48	0,72	2,13	0,18	0,32	14,09	7,39	0,22	1,65
2	0,39	0,19	1,39	0,21	0,1	0,06	1,94	0,1	69,1	1,57	0,51	2,24	0,21	0,29	15,06	4,93	0,14	1,55
3	0,23	0,07	1,57	0,28	0,14	0,05	0,02	0,6	75,58	1,99	0,62	2,17	0,06	0,27	14,89	0,18	0,11	1,18
4	0,14	0,17	0,84	0,03	0,12	0,05	0,03	0,58	77,32	2,06	-	2,07	0,07	0,27	14,75	0,16	0,10	1,23
5	0,19	0,18	1,62	0,27	0,12	0,06	0,03	0,57	75,57	2	0,38	2,19	0,05	0,23	15,12	0,11	0,10	1,19

Focused Ion Beam - Field Emission Scanning Electron Microscopy – Energy Dispersive X-ray Microanalysis (FIB-FESEM-EDXM) technique: chemical element profiling

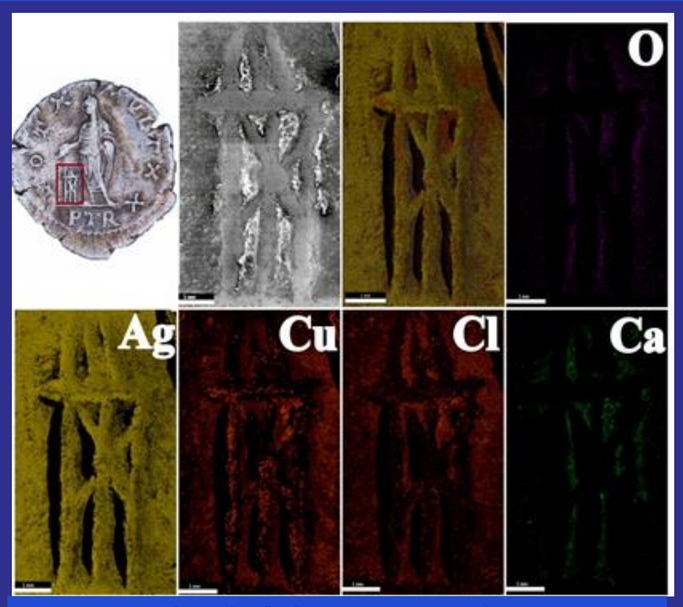


Element	Weight %
C K	0,00
O K	1,32
NaK	0,00
AlK	0,05
SiK	0,00
ClK	0,23
AgL	2,98
K K	0,00
CaK	2,01
FeK	0,93
CoK	0,15
NiK	0,36
CuK	2,37
AuL	83,58
HgL	4,92
PbL	1,09



Element	Weight %	Atomic %
C K	1,99	13,14
O K	1,06	5,25
MgK	0,15	0,49
S K	0,00	0,00
ClK	1,35	3,04
AgL	71,02	52,32
SnL	0,93	0,63
CaK	0,00	0,00
FeK	1,21	1,73
NiK	0,30	0,40
CuK	16,46	20,59
ZnK	0,34	0,41
HgL	1,54	0,61
PbL	3,65	1,40

Scanning Electron Microscopy – Energy Dispersive X-ray Microanalysis (SEM-EDXM) technique: chemical element Hg was detected in the upper silver layer of coins, the silvering procedure using Hg-Ag amalgam has been identified



Chemical elements mapping

Neutron Radiation Analysis (NRA) (Ref. AgCu)

Элем.	Eg, кэВ	Coin 1 Мас. сод.	Coin 2 Мас. сод.
Cu	962.0	53.8(11)	79.4(16)
Ag	550.6	44.6(14)	11.2(4)
Si	1778.8	0.25(6)	3.45(14)
P	1266.1	≤ 0.05	≤ 0.06
S	2230.2	≤ 0.08	≤ 0.06
Cl	1219.5	≤ 0.15	0.6(3)
Fe	846.8	0.10(5)	0.09(4)
Zn	1039.2	≤ 0.09	≤ 0.17
As	264.6	0.21(7)	≤ 0.05
Cd	558.0	1.00(10)	≤ 0.07
In	933.8	≤ 0.23	≤ 0.10
Sn	1171.3	≤ 0.12	2.80(22)
Sb	909.8	≤ 0.29	≤ 0.3
W	903.2	≤ 0.45	≤ 0.5
Ir	129.4 m	≤ 0.09	≤ 0.10
Au	547.6	≤ 0.44	≤ 0.5
Hg	368.0	≤ 0.13	≤ 0.14
Pb	569.6	≤ 0.44	0.8(5)
Bi	1609.0	≤ 0.21	≤ 0.21

Neutron Radiation Analysis (NRA)