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ARCHAEOMETRICAL INVESTIGATION OF ROMAN SILVER COINS FROM BULGARIA

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ABSTRACT

In this study, we provide the results of a micro-XRF archaeometric investigation of 87 Roman silver coins of different types that were discovered in Plovdiv (Central South Bulgaria) as part of coin hoard. 593 Roman coins dating from the middle of the second century AD to the middle of the third century AD comprise the hoard. The primary purpose of this report is to determine the amount of silver in the alloy, as well as the amounts of other elements. A micro-XRF spectrometer was used for the non-destructive analysis. The results indicate that the coins struck from the middle of the second to the middle of the third century AD included varying amounts of the following key elements: silver, copper, lead, and tin. Archaeometric study sheds light on the state's economy during the relevant periods, as well as on coin manufacture and circulation technologies inside the Roman Empire.

On the basis of statistical estimation and correlation analysis, several interesting observations are made about the technologies utilized and the origins of silver ores.

KEYWORDS: Roman silver coins, hoard, chemical composition, alloy, silver ores, micro-XRF, ores, correlation, lead, alloy, copper, non-destructive

1. INTRODUCTION

Silver was a significant currency metal in antiquity, and the value of a coin is a function of the amount of silver contained within the alloy. However, due to the strict standards of the Roman Empire, the amount of silver can vary significantly. For instance, during periods of inflation, the silver content of coins is lower than standard, and thus the amount of silver can be used as a proxy for estimating social, economic, and trade conditions during the relevant historical period.

The elemental analysis of archaeological artifacts is frequently associated with the use of non-destructive methods that provide statistically significant data about the composition of the objects and are quick, unexpensive, and multielement in nature. Although the XRF method is probably the most widely used for the analysis of archaeological samples of various origins, types, and sizes (Bonev et al., 2015; Kousouni et al., 2021; Liritzis et al., 2020, Zlateva et al., 2019), without or almost without sample preparation and treatment, its limitations, particularly for the analysis of ancient alloys, are frequently overlooked (Zlateva, 2017). For example, X-rays have a low penetration and are suitable for surface analyses mainly. However, depending on the geomorphological conditions of the soils in which the items have been stored for many years, the surface of the metal objects changes, forming a so-called "patina".

Historical alloys, such as silver coins, pose several analytical difficulties. When it comes to silver alloys, the patina may contain Ag_2S, Ag_2O, or/and AgCl, which can lead to uncertainties in the analytical data obtained. Another issue is the effect of metal "leakage" and diffusion over time and space, resulting in the surface of the metal object not being representative of the original metal alloy. Ancient alloys are frequently composed of materials or mixtures that are not found in modern alloys. Therefore, the quantification routine must be validated using appropriate certified reference materials.

Although many silver coins from Roman times have been discovered in Bulgaria (Varbanov, 2009, 2014; Prokopov, 1985) and are thus subject to numismatic analysis, visual classification alone is not always sufficient to classify them correctly. As a result, elemental analysis is necessary.

There are a number of archaeometric analyses of Roman silver coins (Bugoi et al, 1999; Butcher and Ponting, 2014; Gitler and Ponting, 2003; Kasztovszky et al., 2005; Ponting, 2009), but no data exist for the territory of modern Bulgaria. Although Ovcharov and Dzanev (2016), as well as our previous investigations (Zlateva, 2019, Zlateva et al., 2021), have been published, the database remains limited.

The purpose of this study is to examine the chemical composition of selected silver coins from the second and third centuries AD to gain a better understanding of the silver supply and economic situation in Roman Philippopolis (Central South Bulgaria) during that period.

2. ARCHAEOLOGICAL BACKGROUND

Seventeen-coin hoards from 2^{nd}-3^{rd} c. AD have been discovered in the city of Plovdiv. While the majority were discovered by chance, seven hoards were discovered in the last 30 years during archaeological excavations on the territory of Roman Philippopolis. Only two of them contain a greater number of coins, while the others contain a small amount of personal money or daily necessities. Nine contain only silver coins; five contain both silver and bronze coins; and three contain only bronze coins.

The peak of treasuring in the provinces of Lower Moesia and Thrace occurred during the Gothic invasions of 248–251 AD. The hoards from the period 238–251 AD account for more than 50% of all known. Two hoards discovered during 2018-2019 excavations in the fortified territory of Philippopolis belong to this period. They are classified as hoards, which are first-rate historical sources due to their complete preservation and well-documented context of discovery (Varbanov, 2020). Their connection to the 250–251 AD invasions is undeniable: at the site at 16 Dr. Valkovich Street, the coins were discovered in the burnt remains of a young man (along with other two skeletons), most likely his personal money, including bronze and silver coins from the period Septimius Severus–Philip the Arab (*terminus post quem* 244–247 AD). As it turned out, the three skeletons of Philippopolis's young citizens who died were never buried but were left in a layer of ruins following the city's destruction. This fact demonstrates the gravity of the destruction, despite that life was not disrupted. The structures below are constructed on an aligned, level surface over the ruins from the middle of the 3^{rd} c. AD. A distant analogy is the situation following the eruption of Vesuvius in Italy, when Pompey and Herculaneum were buried—many of their inhabitants were also discovered with their personal money nearby.

The second hoard, a portion of which is examined here, was discovered in 2019 at the site at 13 Leonardo da Vinci Street. It contains 593 silver coins dating from Antoninus Pius to Philip the Arab (*terminus post quem* 247-249 AD), with a predominance of Gordian

III emissions[1] (44.35%). It is worth noting Antioch's high percentage of emissions (20.7%). The hoard represents a sizable sum for the period and likely belonged to a wealthy individual, possibly a merchant, craftsman, or military man.

3. MATERIALS AND METHOD

The total number of 87 Roman silver coins of different types were analysed as part of two coinages discovered in the city of Plovdiv (see Fig. 1). Table 1 contains detailed information about the coins examined.

Figure 1. Map of Bulgaria and location of Plovdiv

The XRF analysis was carried out using a Bruker M1 MISTRAL Micro-XRF spectrometer (Rh-tube, Peltier cooling, 30 mm^2, Si-drift detector (SDD), Mn-Kα resolution 150 eV, collimator 0.1 mm to 1.5 mm).

For quantitative analysis, we used a software-integrated, standard-supported fundamental parameters method. This method normalizes each element using the spectrum of a pure element, determines the initial concentration using the fundamental parameters method, and achieves an additional increase in accuracy for certain elements by additional standards.

For determination of chemical composition of metal alloys 40W (40 KV/1.0 mA) tube power and 1.5 mm collimator were used with integration time of 30 sec.

A small size spot (about 3 mm^2) of each coin's surface was cleaned with a drill to avoid the effect of patina in the bulk alloy, and the chemical elements were measured for 30 seconds on both sides of the coins.

Table 1. List of the investigated coins.

Emperor	Number of coins	Emperor	Number of coins
145-161, Antoninus Pius	1	218-222, Julia Soaemias	1
189-191, Commodus	2	218-222, Julia Measa	1
193, Didia Clara	1	218-235, Severus Alexander	3
193-210, Septimius Severus	8	229-230, Julia Mamea	1
196-211, Julia Domna	2	235-236, Maximinus "Thrax"	3
196-200, Caracalla	2	238, Pupienus	1
198-211, Plavtilla	1	238-244, Gordian III	36

[1] Monetary emissions means introducing to circulation in economy cash- or non-cash money.

200-210, Geta	2	244-247, Philip I "The Arab"	10
215, Caracalla	2	246-248, Otacilia Severa	1
217-218, Macrinus	2	244-246, Philip II "The Younger"	4
218-222, Elagabalus	4	-	-

4. RESULTS AND DISCUSSION

The analytical data for the coins studied are listed in Table 2, given as a weight percentage. The concentrations of thirteen chemical elements are determined (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ag, Sn, Au, Pb, and Bi).

Total uncertainty was estimated on the basis of analysis of the MBH-33X GM7 and MBH-33X RB1 metal alloy certified reference materials, produced by the MBH Analytical LTD, England and BS SU 936, Brammer Standard Company Inc., USA. The precision of the instrumental analysis using CRMs was better than 8% for the major and microelements. The large data set obtained (comprising of about 6700 elemental-determinations of 13 chemical elements in the 87 silver coins examined) offers considerable statistical potential and gives the possibility to estimate additional information about the production technology of the coins.

All coins examined are made of silver-copper alloy, with an Ag content ranging between 50% and 90%, with an average of 74.77%, and a Cu content ranging between 5% and 42%, with an average of 20.68%. It is established that Ag and Cu have a negative association with a correlation coefficient of 0.95 (see Fig. 2).

Table 2. Elemental concentrations of the investigated coins (in weight %).

Lab. Code	EMPEROR	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Ag	Sn	Au	Pb	Bi
C155.PLD	ANTONINUS PIUS	0.099	<0.001	0.606	<0.001	0.080	5.317	<0.001	<0.001	90.65	0.814	<0.001	1.632	<0.001
C156.PLD	COMMODUS	0.075	0.021	0.536	<0.001	0.083	7.663	<0.001	<0.001	87.59	0.935	<0.001	1.917	0.862
C157.PLD	COMMODUS	0.086	0.032	0.721	<0.001	0.100	8.613	0.091	<0.001	86.9	1.060	0.718	0.956	0.108
C158.PLD	DIDIA CLARA	0.083	<0.001	0.514	<0.001	0.089	8.418	<0.001	<0.001	88.25	<0.001	0.517	1.140	<0.001
C159.PLD	SEPTIMIUS SEVERUS	0.074	<0.001	0.609	<0.001	0.097	5.078	<0.001	<0.001	91.64	<0.001	<0.001	1.146	<0.001
C160.PLD	SEPTIMIUS SEVERUS	0.078	<0.001	0.382	<0.001	0.069	13.8	0.045	<0.001	82.69	0.553	0.647	1.571	<0.001
C161.PLD	SEPTIMIUS SEVERUS	0.072	0.017	0.632	<0.001	0.089	3.525	<0.001	<0.001	90.33	3.261	0.483	1.118	0.454
C162.PLD	SEPTIMIUS SEVERUS	0.058	0.013	0.394	<0.001	0.076	12.72	0.031	<0.001	83.93	<0.001	0.718	1.878	0.073
C163.PLD	SEPTIMIUS SEVERUS	0.075	0.022	0.400	<0.001	0.058	16.109	0.026	<0.001	81.236	<0.001	0.348	1.325	0.170
C164.PLD	SEPTIMIUS SEVERUS	0.044	<0.001	0.252	<0.001	0.089	34.14	0.065	0.264	63.2	0.404	<0.001	1.253	0.096
C165.PLD	SEPTIMIUS SEVERUS	0.050	<0.001	0.338	<0.001	0.107	27.19	0.062	<0.001	70.19	<0.001	0.443	1.142	0.078
C166.PLD	SEPTIMIUS SEVERUS	0.053	<0.001	0.399	<0.001	0.071	11.50	0.054	<0.001	85.9	<0.001	0.507	1.374	0.120
C167.PLD	JULIA DOMNA	0.061	<0.001	0.443	<0.001	0.093	13.26	0.019	<0.001	83.54	<0.001	0.581	1.454	0.063
C168.PLD	JULIA DOMNA	0.064	<0.001	0.335	<0.001	0.082	22.46	0.051	0.157	74.75	<0.001	<0.001	1.705	<0.001
C169.PLD	CARACALLA	0.040	<0.001	0.273	<0.001	0.071	28.72	0.097	<0.001	68.46	0.414	0.544	1.355	<0.001
C170.PLD	CARACALLA	0.055	<0.001	0.441	<0.001	0.069	11.44	<0.001	<0.001	84.03	1.581	0.613	0.622	<0.001
C171.PLD	PLAUTILLA	0.060	<0.001	0.307	<0.001	0.067	24.95	0.074	<0.001	72.32	0.425	0.544	1.245	0.100

C172.PLD	GETA	0.049	<0.001	0.380	<0.001	0.075	15.59	<0.001	0.085	81.70	0.400	0.581	1.122	0.322
C173.PLD	GETA	0.056	<0.001	0.319	<0.001	0.073	25.874	0.061	<0.001	71.111	0.480	0.402	1.268	<0.001
C174.PLD	CARA-CALLA	0.046	<0.001	0.449	<0.001	0.108	15.521	0.070	0.148	82.727	<0.001	<0.001	0.566	0.107
C175.PLD	CARA-CALLA	0.045	<0.001	0.381	<0.001	0.104	13.513	<0.001	<0.001	84.194	<0.001	0.452	1.149	0.058
C176.PLD	MA-CRINUS	0.043	<0.001	0.421	<0.001	0.094	12.29	<0.001	<0.001	85.41	<0.001	0.570	1.116	<0.001
C177.PLD	MA-CRINUS	0.045	<0.001	0.487	<0.001	0.075	9.073	<0.001	0.163	87.81	<0.001	0.644	1.371	<0.001
C178.PLD	ELGABA-LUS	0.029	<0.001	0.423	<0.001	0.077	12.66	0.021	<0.001	85.60	<0.001	0.382	0.562	0.052
C179.PLD	ELGABA-LUS	0.058	<0.001	0.337	<0.001	0.078	25.03	0.171	0.130	69.60	0.668	0.478	2.130	0.090
C180.PLD	ELGABA-LUS	0.057	<0.001	0.301	<0.001	0.046	21.54	0.083	<0.001	75.26	0.705	0.640	1.344	<0.001
C181.PLD	ELGABA-LUS	0.060	<0.001	0.301	<0.001	0.084	25.67	0.081	<0.001	72.14	0.707	<0.001	0.836	0.084
C182.PLD	JULIA SO-SEMIAS	0.071	<0.001	0.409	<0.001	0.071	15.62	0.083	<0.001	78.15	2.081	0.584	2.905	<0.001
C183.PLD	JILIA MAESA	0.050	<0.001	0.290	<0.001	0.062	26.57	0.034	<0.001	70.87	0.833	0.439	0.850	<0.001
C184.PLD	SEVERUS ALEXAN-DER	0.044	<0.001	0.236	<0.001	0.070	36.24	0.063	0.239	60.10	1.033	<0.001	0.944	<0.001
C185.PLD	SEVERUS ALEXAN-DER	0.079	<0.001	0.430	<0.001	0.067	9.580	<0.001	<0.001	88.02	<0.001	0.862	0.880	<0.001
C186.PLD	SEVERUS ALEXAN-DER	0.093	0.013	0.323	<0.001	0.081	24.36	0.034	<0.001	73.05	0.555	0.483	0.941	<0.001
C187.PLD	JULIA MAMAEA	0.064	<0.001	0.258	<0.001	0.085	22.89	<0.001	<0.001	71.69	1.235	0.374	1.325	0.100
C188.PLD	MAXIMI-NUS TRAX	0.068	<0.001	0.275	<0.001	0.075	22.27	0.032	<0.001	76.16	<0.001	0.443	0.517	<0.001
C189.PLD	MAXIMI-NUS TRAX	0.038	<0.001	<0.001	<0.001	0.079	40.35	0.077	0.151	54.87	1.285	<0.001	1.169	<0.001
C190.PLD	MAXI-MUS	0.065	<0.001	0.351	<0.001	0.093	18.92	0.023	<0.001	79.18	<0.001	0.581	0.636	<0.001
C191.PLD	PU-PIENUS	0.044	<0.001	0.405	<0.001	0.093	14.48	0.019	0.080	83.00	0.513	0.467	0.851	0.047
C192.PLD	GOR-DIAN III	0.061	<0.001	0.362	<0.001	0.085	23.53	0.397	<0.001	72.88	<0.001	0.578	1.961	<0.001
C193.PLD	GOR-DIAN III	0.058	<0.001	0.370	<0.001	0.066	19.97	0.048	<0.001	73.72	2.987	<0.001	1.852	<0.001
C194.PLD	GOR-DIAN III	0.056	<0.001	0.368	<0.001	0.050	17.22	0.025	<0.001	79.75	0.727	0.529	1.174	<0.001
C195.PLD	GOR-DIAN III	0.045	0.015	0.284	<0.001	0.062	28.82	0.058	<0.001	69.01	0.489	0.549	0.631	<0.001
C196.PLD	GOR-DIAN III	0.068	0.014	0.484	<0.001	0.077	11.11	0.030	<0.001	80.79	3.255	0.362	3.549	<0.001
C197.PLD	GOR-DIAN III	0.066	<0.001	0.371	<0.001	0.058	25.12	<0.001	<0.001	67.41	3.372	<0.001	3.594	<0.001
C198.PLD	GOR-DIAN III	0.058	0.017	0.410	<0.001	0.062	17.73	0.052	<0.001	76.01	2.871	<0.001	2.746	<0.001
C199.PLD	GOR-DIAN III	0.047	<0.001	0.266	<0.001	0.084	31.47	0.068	<0.001	60.85	4.599	<0.001	2.245	<0.001
C200.PLD	GOR-DIAN III	0.060	<0.001	0.316	<0.001	0.058	24.09	0.062	<0.001	69.12	4.408	<0.001	1.722	0.138
C201.PLD	GOR-DIAN III	0.050	<0.001	0.366	<0.001	0.068	19.53	0.034	<0.001	76.69	1.242	<0.001	1.862	0.131
C202.PLD	GOR-DIAN III	0.063	0.017	0.541	<0.001	0.067	5.419	<0.001	<0.001	90.68	0.821	0.418	1.874	0.088
C203.PLD	GOR-DIAN III	0.160	0.034	0.845	<0.001	0.125	17.83	0.066	<0.001	76.52	2.641	<0.001	0.550	<0.001
C204.PLD	GOR-DIAN III	0.069	0.023	0.330	<0.001	0.051	23.34	0.042	<0.001	74.54	<0.001	0.401	0.706	<0.001

C205.PLD	GOR-DIAN III	0.040	<0.001	0.379	<0.001	0.076	22.35	0.050	<0.001	74.60	0.793	0.420	1.278	<0.001
C206.PLD	GOR-DIAN III	0.066	0.011	0.326	<0.001	0.066	22.92	0.044	<0.001	68.48	2.713	<0.001	5.216	<0.001
C207.PLD	GOR-DIAN III	0.057	<0.001	0.438	<0.001	0.079	13.98	0.044	<0.001	82.79	0.899	0.392	1.152	0.098
C208.PLD	GOR-DIAN III	0.071	<0.001	0.503	<0.001	0.074	15.18	0.131	<0.001	73.34	6.058	0.360	3.781	<0.001
C209.PLD	GOR-DIAN III	0.075	<0.001	0.291	<0.001	0.072	24.29	0.067	0.170	69.95	2.789	<0.001	1.222	<0.001
C210.PLD	GOR-DIAN III	0.068	<0.001	0.377	<0.001	0.084	31.02	0.125	0.230	64.22	2.454	<0.001	0.429	<0.001
C211.PLD	GOR-DIAN III	0.069	0.017	0.233	<0.001	0.073	31.48	0.228	0.170	65.45	1.198	<0.001	1.008	0.061
C212.PLD	GOR-DIAN III	0.081	<0.001	0.361	<0.001	0.097	40.55	0.179	<0.001	55.95	1.113	<0.001	0.746	<0.001
C213.PLD	GOR-DIAN III	0.080	<0.001	0.384	<0.001	0.085	23.88	0.143	<0.001	71.39	1.981	0.490	1.149	<0.001
C214.PLD	GOR-DIAN III	0.080	<0.001	0.384	<0.001	0.067	22.47	0.279	<0.001	74.56	0.788	0.449	0.729	0.102
C215.PLD	GOR-DIAN III	0.057	<0.001	0.559	<0.001	0.064	6.317	<0.001	<0.001	90.11	0.560	0.437	1.838	<0.001
C216.PLD	GOR-DIAN III	0.069	<0.001	0.320	<0.001	0.065	30.55	0.356	<0.001	66.37	1.279	<0.001	0.919	<0.001
C217.PLD	GOR-DIAN III	0.063	<0.001	0.290	<0.001	0.083	30.60	0.235	0.137	66.46	1.465	<0.001	0.574	0.052
C218.PLD	GOR-DIAN III	0.066	<0.001	0.490	<0.001	0.074	15.56	0.049	0.300	76.29	3.205	<0.001	3.947	<0.001
C219.PLD	GOR-DIAN III	0.074	<0.001	0.499	<0.001	0.066	22.96	0.201	<0.001	68.89	4.458	0.497	2.284	<0.001
C220.PLD	GOR-DIAN III	0.039	<0.001	0.270	<0.001	0.077	35.75	0.770	<0.001	54.51	4.322	<0.001	3.781	<0.001
C221.PLD	GOR-DIAN III	0.058	<0.001	0.441	<0.001	0.057	12.41	0.211	<0.001	81.27	1.868	<0.001	3.573	<0.001
C222.PLD	GOR-DIAN III	0.056	<0.001	0.544	<0.001	0.079	13.53	0.292	0.179	75.64	4.076	<0.001	5.168	<0.001
C223.PLD	GOR-DIAN III	0.060	<0.001	0.531	<0.001	0.075	14.78	0.029	<0.001	81.12	2.052	0.366	0.969	<0.001
C224.PLD	GOR-DIAN III	0.072	<0.001	0.501	<0.001	0.047	15.17	0.058	<0.001	80.91	1.173	0.432	1.567	<0.001
C225.PLD	GOR-DIAN III	0.058	0.019	<0.001	<0.001	0.076	36.58	0.137	0.195	55.13	3.484	<0.001	4.235	0.070
C226.PLD	GOR-DIAN III	0.053	<0.001	<0.001	<0.001	0.145	42.09	0.318	0.102	50.97	1.346	<0.001	2.726	0.071
C227.PLD	GOR-DIAN III	0.073	<0.001	0.364	<0.001	0.085	23.92	0.115	<0.001	72.06	1.906	0.402	0.652	<0.001
C228.PLD	PHILIP THE ARAB	0.071	<0.001	0.237	<0.001	0.082	30.98	0.102	<0.001	64.83	1.276	<0.001	1.892	<0.001
C229.PLD	PHILIP THE ARAB	0.070	<0.001	0.330	<0.001	0.080	28.73	0.132	<0.001	65.43	1.980	0.478	2.316	<0.001
C230.PLD	PHILIP THE ARAB	0.071	<0.001	0.383	<0.001	0.055	21.18	0.080	<0.001	72.46	2.666	<0.001	3.099	<0.001
C231.PLD	PHILIP THE ARAB	0.045	<0.001	0.418	<0.001	0.071	25.64	0.113	<0.001	70.47	1.565	0.343	0.984	<0.001
C232.PLD	PHILIP THE ARAB	0.057	<0.001	0.434	<0.001	0.058	15.12	0.050	<0.001	80.64	1.249	0.342	1.947	<0.001
C233.PLD	PHILIP THE ARAB	0.037	<0.001	0.636	<0.001	0.060	9.236	<0.001	<0.001	85.88	1.928	<0.001	2.210	<0.001
C234.PLD	PHILIP THE ARAB	0.096	0.036	0.750	<0.001	0.137	23.86	0.346	<0.001	70.12	2.425	<0.001	0.672	<0.001
C235.PLD	PHILIP THE ARAB	0.063	<0.001	0.323	<0.001	0.063	22.65	0.120	<0.001	73.18	0.947	0.358	2.098	<0.001

C236.PLD	PHILIP THE ARAB	0.057	<0.001	0.298	<0.001	0.062	21.69	0.122	<0.001	74.77	<0.001	0.327	2.247	<0.001
C237.PLD	PHILIP THE ARAB	0.045	<0.001	0.248	<0.001	0.074	27.58	0.176	<0.001	68.40	1.341	0.376	1.674	<0.001
C238.PLD	OTA-CILIA SEVERA	0.063	<0.001	0.234	<0.001	0.077	39.90	0.380	<0.001	54.35	1.955	<0.001	2.566	<0.001
C239.PLD	PHILIP SON	0.086	<0.001	0.252	<0.001	0.080	38.69	0.099	0.198	58.24	1.570	<0.001	0.745	<0.001
C240.PLD	PHILIP SON	0.059	0.019	0.414	<0.001	0.060	17.47	0.081	<0.001	76.08	1.796	0.415	1.532	<0.001
C241.PLD	PHILIP SON	0.070	<0.001	0.438	<0.001	0.069	21.83	0.041	0.175	71.34	3.061	<0.001	2.948	<0.001
C242.PLD	PHILIP SON	0.060	<0.001	0.373	<0.001	0.060	15.05	0.037	0.084	79.44	2.301	0.420	2.139	<0.001

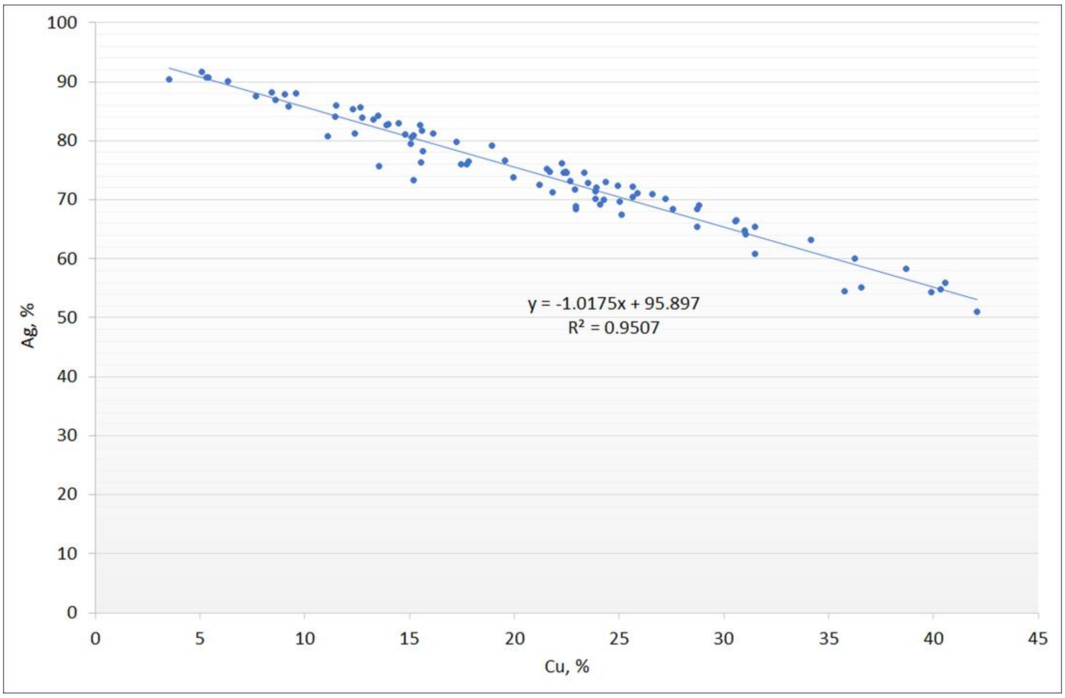

Figure 2. Bi-dimensional plot of Ag vs Cu.

Copper and silver concentrations in the samples followed a normal distribution, as illustrated by the histograms in Fig. 3. The most common examples are those in which the silver content ranges be-tween 70% and 90% and the copper content ranges between 30% and 10%. However, the majority of coins are manufactured of an alloy with a silver-to-copper ratio of 3:1. (Fig. 1). Copper's significant presence in the silver coins under examination implies that it was intentionally added to the alloy. While it is well documented that integrating copper into silver strengthens the alloy and lowers coin wear caused by circulation (Bugoi et al. 1999, Masjedi et al., 2013), a higher copper concentration can be seen as an attempt to rein in inflationary processes. Historically, only three types of silver sources were employed: natural silver, chlorargyrite (AgCl), and galenite (PbS), with the latter being the most frequently used. The most well-known of the ancient mines was the Laurium silver-lead deposit, which was exploited continuously from 500 BC until 100 AD (Conophagos, 1980, Rosenthal et al., 2012). Spanish miners (Rio Tinto) also contributed significantly (Graddock, 2015). These mine crafts had to apply a sophisticated procedure to obtain silver. Silver's native metal content is limited, while mineral ores such as sulphide, argentite, and chloride are also present in nature in trace amounts. Silver occurs as a trace element in a variety of other mineral ores, including copper and gold, but primarily lead ores. Lead ores include sulphide (galenite, PbS) or carbonate (cerussite, $PbCO_3$) with associated sphalerite (ZnS), and copper minerals (Masjedi et al., 2013; Uzonyi et al., 2000). All of these silver sources, however, require the cupellation process (oxidative removal of lead as PbO at a temperature of about 950 °C) and therefore are difficult to proceed.

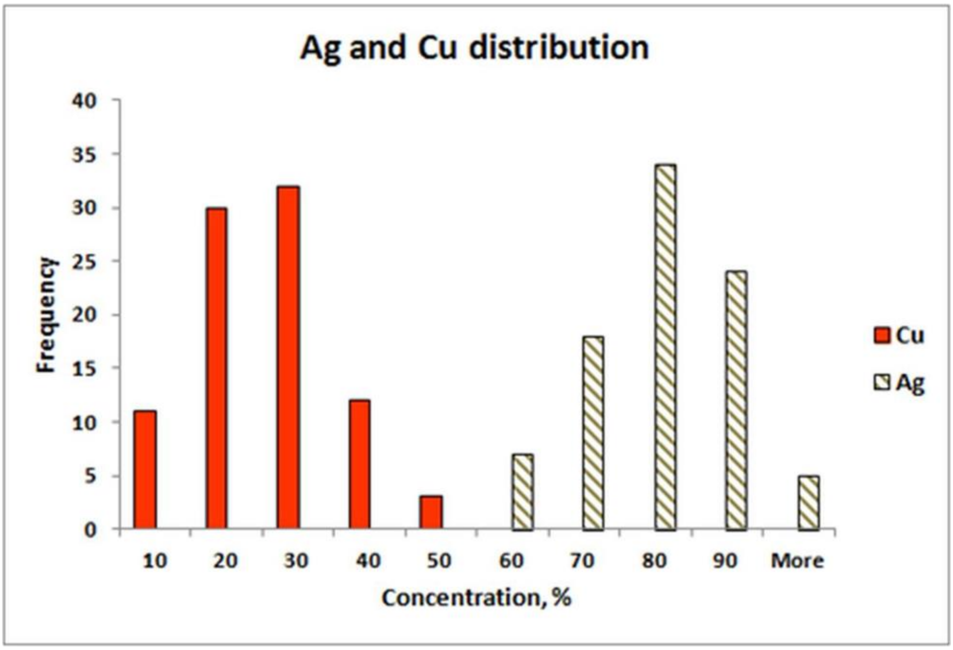

Figure 3. Histogram of the distribution of Ag and Cu.

The elements of interest among detectable ones despite silver include Cu, Au, Pb, Bi and the most useful of them are Au, Bi and Pb (see e.g. Bugoi et al., 1999; Davis 2014; Flament and Marchetti, 2004).

The analysed coins contain roughly 0.5% iron, which is a result of natural impurities in the ores utilized in the pyrometallurgical process (up to 4% of the iron is soluble in the copper). The Fe can be also attributed to external pollution with dust incrusted at the surface of the coins, as stated by Masjedi et al., (2013).

Au and Bi are the most important trace elements for determining the source of silver. These are derived from argentiferous ores, which were initially used to extract silver. The concentration of gold in the majority of the coins analyzed is approximately 0.5%, indicating that the raw materials were cupellated (in which the gold is not separated from the silver in silver ores, Kuleff, 2015). Ag and Au are solid solutions, whereas Ag and Cu have a considerable miscibility difference.

Bi and Sn, in general, behave similarly to Ag when silver-bearing galenite (PbS) is used as a source of Ag, and so larger concentrations of Bi and Sn can be considered as markers of galenite use. On the other hand, some authors state that a high bismuth content suggests the utilization of Bi-rich ores. (Gale, 1980).

After cupellation, Bi and Pb persisted in insulating silver at quantities of 0.5–1.0% of the original composition, but a lengthy process reduced their concentrations. Simultaneously, Sn is removed from the silver, and the level of Sn in silver is often less than 0.1%. Cu is reduced to 0.2%, whereas Zn is reduced to less than 0.1%. The studied coins exhibit the same tendency.

Co, Ni, and As, are all common tracers in copper ores, but they are only related with silver ores if the silver is recovered from cerargyrite (AgCl) or argentite (Ag_2S). There are just a few samples with traces of As and none with concentrations of Co exceeding the method's limit of detection, while the level of Ni fluctuates between 0.05 and 0.10%.

The presence of both Bi and Pb implies that galenite (PbS) was used as an ore source, whereas the presence of Pb but not Bi indicates the usage of chlorargyrite (AgCl).

Additional information is available in the table (see Table 3), which includes a statistically significant value (up to 0.6) for the correlation between chemical element concentration levels. Correlation study reveals a positive correlation between Cr-Mn, Mn-Fe, Fe-Ag, and As-Au, but a negative correlation between Cu-Ag and Fe-Cu. The positive correlations between Cr-Mn and Mn-Fe, Fe-Ag, and As-Au, as well as the negative correlations between Cu-Ag and Fe-Cu, could be explained by the fact that various sources of Cu- and Ag-mineral ores were used to produce silver. We observed similar correlations in our previous investigations (Zlateva, 2019), which examined a portion of the Roman hoard of coins dating from the same period (1st-3rd c. AC) and discovered in the Panagyurishcte district (and also in South Central Bulgaria), but the primary difference is the Fe-Cu correlation (positive there and negative in this study). As previously stated, approximately 0.5% Fe is the normal value, which is attributable to the natural impurities present in the ores utilized in pyrometallurgical methods (till 4% of the iron is solubility in the cooper).

Table 3. Correlation matrix between the elements.

Corrl	Cr	Mn	Fe	Ni	Cu	Zn	As	Ag	Sn	Au	Pb	Bi
Cr	1.00											
Mn	0.66	1.00										
Fe	0.46	0.78	1.00									
Ni	0.26	0.73	0.36	1.00								
Cu	-0.12	-0.05	-0.70	0.12	1.00							
Zn	0.00	0.51	-0.05	0.22	0.42	1.00						
As	0.21	1.00	-0.08	-0.22	0.23	-0.19	1.00					
Ag	0.08	0.05	0.63	-0.11	-0.98	-0.49	-0.27	1.00				
Sn	0.12	0.05	0.20	0.01	-0.01	0.23	0.33	-0.19	1.00			
Au	0.16	0.21	0.15	0.14	-0.26	0.04	0.61	0.32	-0.27	1.00		
Pb	-0.09	-0.49	0.04	-0.21	-0.01	0.24	0.18	-0.17	0.59	-0.20	1.00	
Bi	0.33	0.06	0.41	-0.07	-0.40	-0.25	-0.28	0.34	0.07	0.06	0.07	1.00

It's interesting to see the correlation between the degree of Ag distribution and the time of coinage, i.e., from the ruled Emperors. We illustrate the time-dependent variation in silver content in Fig. 3. During the Antonines (The Five Good Emperors: Nerva (96-98 AD), Trajan (98-117 AD), Hadrian (117-138 AD), Antoninus Pius (138-161 AD), and Marcus Aurelius (161-180 AD)), Roman denarii were known for their extremely high silver content – up to 90% – owing to the Roman Empire's unprecedented prosperity and economic stability. The coin by Antoninus Pius studied contains the highest concentration of silver and is consistent with historical sources. The coins with a greater Ag content in our study are those of Commodus (86-87%), who succeeded Marcus Aurelius as the last Emperor of the Antonines. This result matches our prior investigations (Zlateva, 2019).

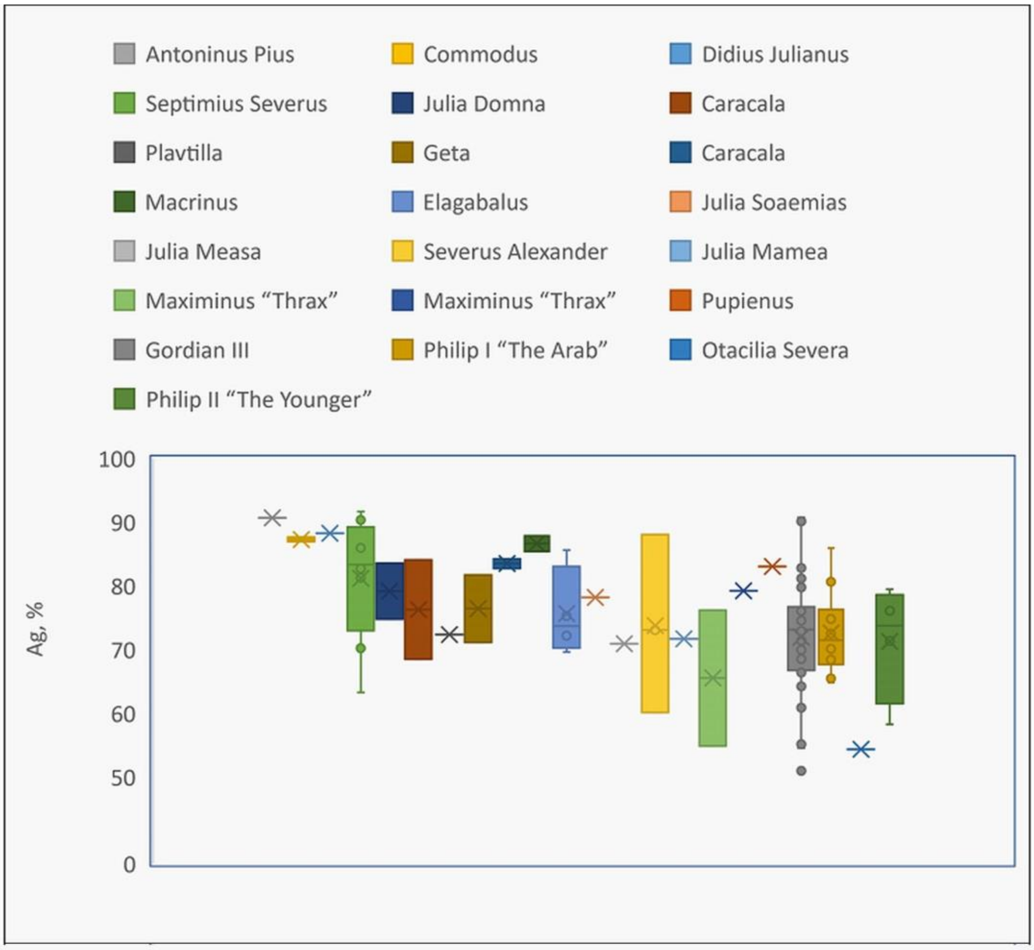

Figure 3. Distribution of silver content and the time of coinage.

During the reign of Septimius Severus, coins of varying silver contents were issued. Silver content ranged between 80% and 90% in the era 193-202 AC (six studied coins), but substantially declined in the period 202–210 AC (two coins with silver of 63 and 70%). As noted by Butcher et al., 1997, the earlier coins of Septimius Severus were issued by separate mint – the so called "Eastern" (Laodicea and Emesa) which struck of coins between 193-164 and 202 AC in addition to the mint of Rome. The same is true of Julia Domna's (wife of Septimius Severus) silver content: the studied coins (lab indexes C-167.PLD and C-168.PLD) contain 83 and 75% Ag, respectively. One likely cause is that the army has grown in size, resulting in an increase in maintenance expenditures.

Caracalla minted a new coin type known as Antonianii (double denarii) with a silver content of approximately 69% (specimen C-169.PLD, issued 200 AC), but older denarii with a higher silver content remained in circulation (C-170.PLD, issued 196-197 AC, 84% Ag). The coin of Plavtilla (wife of Caracalla, C-171.PLD) contains 73% silver, which may be attributed to the reuse and remelting of older silver denarii.

Throughout the third century AD, the Roman Empire was subjected to several raids by Germans and Persians, as well as numerous civil wars, which resulted in the loss of ore supply. During the reign of Elgaballus, the silver content declined again (to an average of 72%), although the coins of Julia Soemia and Julia Maesa (the Emperor Elgabalus's mother and grandmother, respectively) have a silver content of 78 and 71%, respectively.

Severus Alexander governed from 222 to 235 AC, but he was deposed by a rebellious army, and Maximinus "Thrax" became Emperor. There are coins from this period with varying silver content, ranging from 54 to 88%. The small number of studied coins (3 from Severus Alexander and 3 from Maximinus "Thrax") precludes statistical analysis, yet silver content is still low in general. Julia Mamea's coin comprises 72% silver (she was Severus Alexander's mother and co-regent).

The total of 36 coins from Gordian III are investigated here, and as previously stated, they represent 44.36% of the currency hoard. The silver content of coins from this period can be classified into three groups: the first group contains coins with a very low silver content (specimens C-212, C-220, C-225, and C-226.PLD) – approximately 54% Ag; the second group contains coins with a silver content of 90% Ag (C-202.PLD, C-215.PLD); and the third group contains coins with a silver content ranging from 61% to 83% with an average value of 73%. The currency of Gordian III's successor, Philip I "The Arab," bears the same value, while the coin of his wife, Otacilia Severa, contains just 54% silver. The coins of Philip II "The Younger," the son of Philip I "The Arab" and his wife Otacilia Severa, have an average silver content of 72%, with the exception of specimen C-239.PLD, which has a silver content of 58%. It is well known that Philip I "The Arab" used six Roman mines; four of them produced coins for himself with a higher content of silver than the other two, which had been used to produce coins for his wife and son, and the present results confirm this.

All these reported variations in the silver content of coins from the same time period could be explained by various issues of them or by used ores. In general, Pb isotopes may help identify potential ore locations, and this analysis should reduce the range of possible ore sources. Of course, Pb-isotopes analysis requires destructive methods of sample preparation; it is more expensive, time-consuming, and requires a high-resolution ICP-MS instrument.

5. CONCLUSION

Chemical analysis of silver Roman coins found in the 2-3 century treasure shows copper as a major impurity in the silver alloy. Copper content varies between 10% and 30%, which corresponds well to the historical and economic conditions of the time period under examination. During a period of upheaval in Roman society, coin sponsors decided to increase the copper content of the precious metal alloy. It can be assumed that the coinages are an important and reliable historical source, when they are supported and synchronized with other sources - written and archaeological, as is the case with Philippopolis.

In conclusion, XRF spectrometry analysis enables rapid, cost-effective, and non-destructive examination on-site at a wide scale. The scale enables statistical analysis that reveals broad groups within the data, which may then be examined numismatically. Gold, lead, bismuth, and copper are all critical elements for triaging. Copper was added to the metal following cupellation (as copper, not bronze). While assumptions about the place of production or the source of the ore can be formed based on the elemental composition alone, confirmation requires study of the lead isotopes, which limits the number of putative ore sources to a number.

The current examination is merely a portion of a larger project to research Roman currency riches discovered on Bulgarian soil, which will culminate in the publication of a catalogue listing all analyzed samples. This enables broader generalizations to be formed regarding the evolution of Roman coins.

AUTHOR CONTRIBUTIONS

Conceptualization, B.Z. and D.L.; methodology, B.Z.; software, I.I.; validation, B.Z., and D.L.; resources, V. V.; data curation, V.V.; writing—original draft preparation, B.Z., D.L. and V.V.; project administration, V.B.

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