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PIXE analysis of ancient Greek copper coins minted in Epirus, Illyria, Macedonia and Thessaly

N. Kallithrakas-Kontos[a,*], A.A. Katsanos[a], C. Potiriadis[b], M. Oeconomidou[c], J. Touratsoglou[c]

[a] *Technical University of Crete, GR-73100 Chania, Greece*
[b] *NRCPS "Demokritos", Aghia Paraskevi, GR-15310 Athens, Greece*
[c] *Numismatic Museum, 1 Tositsa St., GR-10682 Athens, Greece*

Abstract

Ancient copper coins from Greek cities and confederacies such as Amphipolis, Veroia, Dion, Edessa, Magnetes, Stobi, Apollonia, Kerkyra, Pella, Philippoi, Phoenike, and the Macedonian and Thessalian Koina, were analyzed non-destructively by proton induced X-ray emission (PIXE) after removal of the patina. The copper coins were minted during Roman Imperial times (31 B.C.–268 A.D.). Eleven elements were determined quantitatively. The correlation between the composition and the minting time is examined. The results are compared with those of a previous study for coins from the cities of Nikopolis in Epirus and Thessaloniki in Macedonia, in the same period.

1. Introduction

Elemental analysis of ancient coins presents increasing interest in recent years due to their direct relation with the economy and metallurgy of the minting time. The minting time is usually determined with very good accuracy by the archaeologists from the examination of the emperor's portrait on the coin. Gold and silver coins had a higher value than the copper and copper alloy coins: according to the numismatic system of the reign of Augustus, gold coins (aureus) had 25 times higher value than silver ones (denarius), and one silver was equal to 4 brass coins (sestertius); these values were changed later due to alterations in the precious metal values, the content of the coins, etc. [1]. For this reason these types of coins often are preferred for chemical analysis. On the other hand copper coins offer the advantages that are found in larger numbers, include many other metals and their alloys contain different types of higher value metals (zinc, tin, etc.). Copper and copper alloy coins were also affected by the emperor reforms, and metal deterioration (usually increasing content of lead) is also known for this type of coins [2].

In a previous study [3] copper coins from Nikopolis in Epirus and Thessaloniki in Macedonia were examined; this study is extended to the other minor cities of the area of Epirus, Illyria, Macedonia and Thessaly for the period of Roman Imperial times (45 B.C.–260 A.D.). The location of these cities are displayed in Fig. 1 and may be divided in three categories: the first category includes the *civitates liberae* or *stipendiarae* and is composed by the cities Nikopolis, Thessaloniki, Amphipolis, Edessa, Veroia, Apollonia, Kerkyra and Phoenike. In the second one are the

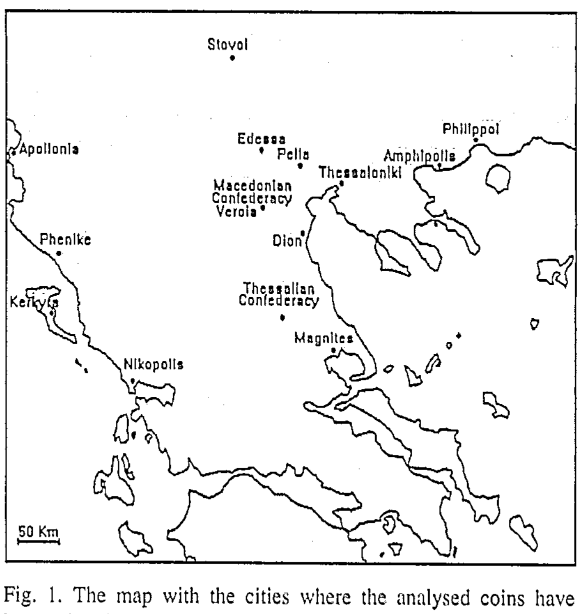

Fig. 1. The map with the cities where the analysed coins have been minted.

* Corresponding author. Fax: +30821 64934, tel. +30821 69455, e-mail: kalli@mred.tuc.gr.

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cities which were Roman colonies: Dion, Pella, Philippoi and Stobi (*municipium*). In the third category coins from confederancies of Macedonia, Magnetes and Thessaly are included; confederancies were religious and political unions among various cities.

PIXE is a powerful method for copper object analysis [4]. In a copper coin many elements (11 in this study) may be analysed simultaneously with an analysis time of about 15 min. Peak overlapping of X-rays from different elements (mainly between S–Pb, As–Pb) can be handled by using experimental X-ray ratio factors. The limited use of the method in this kind of analysis compared with X-ray fluorescence (XRF) may be attributed to the need of a relatively expensive accelerator.

2. Experimental

One of the most serious problems in PIXE analysis of ancient coins is the presence of oxidation products on the coin surfaces (known as patina) with different compositions. A thin metallic depleted layer may also exist under the patina due to diffusion effects. For these reasons the coins were cleaned by the conservation department of the Numismatic Museum of Athens. Before the analysis they were also treated with a glass bristle brush. The results of the PIXE analysis of coins were validated by comparison with other analytical methods and laboratories, analysis of the interior of cut coins, SEM examination, etc. More information about the cleaning process and intercomparison have been previously published [3].

The experiments were performed at the Tandem accelerator laboratory of the NRCPS "Demokritos" by using the PIXE setup. The external beam technique was used with protons of 2.0 MeV in energy on the target. The beam diameter was 3 mm and the current was kept lower than 5 nA (usually about 3 nA) in order to avoid high counting rates at the detectors, that would reduce the detection sensitivity due to the increase of the background noise. Two semiconductor X-ray detectors were used simultaneously, a Si(Li) detector at 45° relative to the proton beam for the low energy X-rays (of sulphur and chlorine) and a Ge(in) detector at 90° for the higher energy X-rays of the other elements. In front of the Ge(in) detector, a 15 mg/cm^2 cobalt foil was placed in order to absorb preferably the characteristic X-rays of copper and avoid interference problems with the neighbouring elements. The total collected proton charge for each analysis was about 2 μC. A computer based system was used for the data collection and analysis. Analysis of two points (from both sides) was found adequate and eleven elements were determined. In case of significant deviations the coins were reexamined and, if necessary, cleaned and analyzed again.

The specimens (coins) were supplied from the basic collection (depot) of the Numismatic Museum of Athens, and were chosen to cover as much as possible the whole minting period, as well as the coin production of as many emperors as possible. Finally, coins on which the cleaning procedure was expected to have insignificant effect, were used.

Table 1
Code names used for the cities

Code	City	Code	City
AMF	Amphipolis	MAG	Magnetes
APO	Apollonia	MAK	Macedonian Confederacy
DIO	Dion	PEL	Pella
EDE	Edessa	STO	Stobi
FIL	Philippoi	THE	Thessalian Confederacy
FOI	Phoenike	VER	Veroia
KER	Kerkyra		

3. Results and discussion

A systematic way of coding the coins was used. According to this, each coin is represented by eight symbols. The first three of these represent the city where the coin has been minted; in Table 1 the code names used for the cities are given. The next three letters represent the emperor and the last two digits our serial number of the

Table 2
Code names used for the emperors. All dates, unless noted, are A.D.

Code	Emperor	Code	Emperor
ANP	Antoninus Pius 138–161	HAD	Hadrianus 117–138
AUG	Augustus 27 B.C.–14 A.D.	JDO	Julia Domna 193–211
CLA	Claudius 41–54	MCR	Macrinus 217–218
COM	Commodus 179–192	MRA	Marcus Aurelius 161–180
CRC	Caracalla 198–217	NER	Nero 54–68
DOM	Domitianus	PLA	Plautilla 198–217
	Domitia 81–96	SPS	Septimius Severus 193–211
GAL	Gallienus 253–268	TIB	Tiberius 14–37
GET	Geta 198–209	TRA	Trajanus 98–117
GOR	Gordianus III 238–244	VAL	Valerianus 253–260

Table 3
The percent compositions (weight) of the analysed coins

Coin	Cu	Sn	Pb	Zn	S	Cl	Fe	Ni	As	Ag	Sb
AMFAUG01	75.6	13.4	6.2	ND	2.7	1.30	0.31	0.13	0.03	0.05	0.12
AMFAUG02	86.3	11.9	0.2	ND	0.6	0.18	0.39	0.20	0.15	0.06	0.13
AMFAUG03	78.1	12.0	5.5	ND	3.6	0.21	0.11	0.04	0.20	0.05	0.14
AMFTIB04	78.8	12.1	5.0	ND	2.5	0.40	0.20	ND	0.05	0.06	0.14
AMFCLA05	84.2	11.7	2.0	ND	1.5	0.18	0.14	0.09	0.02	0.07	0.16
AMFNER06	78.1	11.3	4.5	1.6	2.9	0.19	0.95	ND	0.04	0.08	0.28
AMFDOM07	84.9	7.4	3.6	1.1	2.2	0.20	0.26	0.06	0.02	0.08	0.21
AMFTRA08	85.3	8.3	3.0	0.5	1.4	0.12	0.61	ND	ND	0.07	0.15
AMFTRA09	79.8	13.6	2.4	0.5	3.1	0.17	0.10	ND	0.12	0.10	0.26
AMFANP10	82.5	9.0	3.4	ND	3.8	0.22	0.19	0.09	0.21	0.06	0.39
AMFMRA11	75.8	11.8	5.1	ND	5.8	0.29	0.23	0.10	0.14	0.12	0.54
AMFSPS12	84.3	4.1	4.2	ND	4.2	0.18	0.38	0.79	1.21	0.07	0.42
AMFMKR13	86.9	3.2	5.5	ND	2.9	0.23	0.10	0.13	0.17	0.13	0.65
AMFGO*14	78.3	12.5	4.2	0.6	3.1	0.44	0.21	ND	0.05	0.11	0.32
AMFVAL15	80.3	10.6	3.9	ND	4.3	0.23	0.15	0.06	0.15	0.08	0.27
AMFVAL16	82.5	9.6	4.6	ND	2.7	0.13	0.10	0.06	0.12	0.07	0.13
APOAUG01	77.7	10.5	6.5	0.1	3.8	0.26	0.10	0.23	0.14	0.13	0.29
APOANP02	83.6	7.9	4.6	0.1	2.9	0.24	0.17	0.09	0.06	0.07	0.12
APOGET03	86.1	1.8	5.4	0.1	4.0	0.30	0.13	0.03	0.27	0.17	1.42
DIOTIB01	85.7	9.3	1.4	0.3	2.4	0.13	0.34	0.16	0.16	0.07	0.10
DIOTIB02	77.4	10.0	6.6	0.2	3.0	1.02	0.54	0.12	0.15	0.16	0.22
DIOCLA03	84.0	0.3	5.9	ND	5.5	0.22	0.03	ND	0.20	ND	ND
DIOHAD04	81.8	9.8	3.0	0.4	3.4	0.16	1.01	0.07	0.09	0.06	0.20
DIOGOR05	93.8	0.2	3.1	ND	2.3	0.21	0.09	ND	0.21	ND	0.05
DIOGAL06	82.9	8.8	4.6	ND	2.9	0.21	0.02	0.25	0.12	0.08	0.22
DIOGAL07	78.0	12.6	4.3	ND	4.3	0.37	0.13	0.11	0.08	0.06	0.19
EDETIB01	85.8	9.0	2.1	ND	1.8	0.21	0.21	0.14	0.15	0.09	0.42
EDECRC02	85.3	7.0	2.9	0.3	3.6	0.19	0.15	0.18	0.20	0.12	0.23
EDEGOR03	93.0	0.5	2.7	ND	2.9	0.14	0.46	ND	0.45	0.01	ND
EDEGOR04	84.0	0.3	5.9	ND	9.3	0.22	0.03	ND	0.20	ND	ND
EDEGOR05	89.8	0.2	4.9	0.7	2.6	0.46	0.95	ND	0.43	0.03	0.03
EDEGOR06	83.7	3.4	5.7	ND	3.3	0.18	0.08	ND	0.12	0.30	2.77
FILAUG01	99.4	ND	ND	ND	0.3	0.13	0.05	ND	0.03	0.09	0.08
FILAUG02	98.4	0.9	0.4	ND	0.1	0.10	0.05	0.03	ND	0.07	ND
FOITRA01	84.6	11.1	1.5	0.1	1.2	0.64	0.42	0.10	0.10	0.08	0.16
FOITRA02	82.7	12.0	2.1	0.1	1.7	0.39	0.10	0.15	0.03	0.07	0.10
KERMRA01	88.4	5.1	3.2	ND	2.7	0.33	0.04	ND	0.12	0.05	0.14
KERJDO02	77.2	9.4	6.6	ND	5.9	0.34	0.05	0.05	0.15	0.07	0.25
KERPLA03	87.6	0.4	3.7	ND	3.7	0.52	ND	ND	0.14	0.29	3.82
KERCRC04	74.4	10.2	6.3	ND	8.0	0.46	0.12	ND	0.16	0.09	0.27
KERPS*05	82.9	9.4	3.0	ND	2.7	0.70	0.07	0.11	0.16	0.09	0.22
MAGCRC01	78.4	6.0	9.1	ND	5.2	0.25	0.07	0.08	0.24	0.08	0.57
MAKCLA01	98.7	0.1	ND	ND	0.3	0.21	0.54	ND	0.05	0.09	0.54
MAKCLA02	99.6	ND	0.2	ND	0.1	0.05	0.06	ND	ND	0.02	ND
MAKDOM03	99.4	ND	0.2	ND	0.1	0.05	0.01	ND	0.02	0.05	0.27
MAKANP04	75.7	10.0	8.2	ND	4.9	0.34	0.29	0.10	0.17	0.04	0.17
MAKMRA05	82.4	10.4	3.6	ND	2.5	0.18	0.34	0.11	0.12	0.08	0.33
MAKCOM06	80.0	13.1	3.6	ND	2.4	0.15	0.23	0.12	0.19	0.12	0.21
MAKGOR07	78.8	ND	ND	19.5	0.6	0.28	0.06	0.62	0.13	0.02	ND
MAKPS*08	90.7	2.6	3.1	ND	2.8	0.22	0.18	0.13	0.16	0.07	0.12
MAKPS*09	80.0	7.0	7.4	ND	4.5	0.16	0.21	0.23	0.22	0.11	0.27
PELGOR01	86.2	2.7	6.7	ND	3.4	0.14	0.22	0.10	0.23	ND	0.21
STOAUG01	80.2	0.1	ND	18.5	0.6	0.24	0.08	ND	0.08	0.06	0.15
STOCRC02	84.3	0.2	0.1	13.8	0.4	0.30	0.06	0.36	0.33	0.23	ND
STOCRC03	80.3	0.8	ND	18.0	0.1	0.1	0.08	0.40	0.23	0.07	ND
THEAUG01	85.4	11.3	2.0	ND	1.0	0.10	0.06	ND	0.09	ND	0.04

Table 3 (*continued*)

Coin	Cu	Sn	Pb	Zn	S	Cl	Fe	Ni	As	Ag	Sb
THEAUG02	81.4	12.4	2.6	ND	2.1	0.16	0.19	0.08	0.71	0.11	0.21
THEAUG03	87.6	11.4	0.7	ND	ND	ND	0.16	0.12	0.02	0.03	ND
THEHAD04	91.5	5.6	1.6	ND	0.7	0.14	0.17	0.10	0.07	0.06	0.12
THEHAD05	82.1	9.4	5.1	ND	1.4	0.87	0.29	0.18	0.33	0.15	0.24
THEHAD06	85.7	7.9	4.3	ND	1.6	0.09	0.10	0.07	0.10	0.05	0.07
THEMRA07	84.3	11.6	1.6	ND	0.5	0.75	0.36	0.20	0.41	0.08	0.21
THEMRA08	72.0	18.2	4.6	ND	4.0	0.22	0.22	0.10	0.32	0.11	0.18
THEJDO09	82.1	0.1	0.2	16.4	0.2	0.10	0.05	0.66	0.26	0.07	ND
THEJDO10	81.3	ND	ND	17.4	0.2	0.06	0.04	0.46	0.44	0.07	0.07
THECRC11	74.0	5.7	2.5	14.1	2.5	0.34	0.18	0.24	0.30	0.08	0.10
THEGAL12	83.2	8.0	4.3	ND	3.5	0.18	0.17	0.13	0.33	ND	0.13
VERPS*01	77.5	12.5	5.8	0.5	4.9	0.21	0.14	0.09	0.17	0.12	0.33

ND: not detected.

coin (different numbering for each city). The code names of the emperors are presented in Table 2. The production consisted of copper coins with the portrait of an emperor or member of the royal family on the front side, and pseudoautonomous which metrologically and iconographically proved to belong to the city's production. In the case of the pseudoautonomous coins (coins without the emperor's portrait on the front side) for which the minting date is not always definitely known, the third of the emperor's letters is replaced by an asterisk. The same coding (with asterisk) is also used for coins which have been minted after the emperor's death. It is noted that the first two of the three emperor's letters used, were selected in such a way as to offer distinction between the emperors. Finally, if a pseudoautonomous was not possible to be assigned to an emperor, the symbol PS* was used.

The percent concentrations (weight) of 11 chemical elements in the coins of the examined cities re presented in Table 3. The errors for the determination of copper, tin, lead, silver and antimony were estimated to be 5%, and for the rest of the elements 20% due to interferences from the main components.

In our previous study of copper coins from Nikopolis (Epirus) and Thessaloniki (Macedonia) we have noticed a relatively constant copper to tin concentration (about 10) until 200 A.D. After this year a large decrease was observed for coins from Thessaloniki; in Nikopolis a large deviation of the tin concentration after this year was first observed, then it returned to the initial concentrations. The factor (Cu/Sn) of the present results is plotted in a semilog scale and showed in Fig. 2 vs minting year. A dependence similar to that of the coins minted in Thessaloniki is observed; this is attributed to the fact that most of the coins were minted in the wide area of Thessaly–Macedonia–Illyria (cities in the right part of the map of Fig. 1) and proves an analogous minting practice for all these mints.

Two other elements that in some cases are found in higher quantities are zinc and antimony. According to Carter [5] 1 g of zinc had the same value as 6 g of copper in the coins of Nero, and antimony was used in some cases instead of zinc. The number of minted coins containing more than 5% of zinc and 1% of antimony is displayed as a function of time in Fig. 3. The forms of these histograms are due to the different length of reign time of each

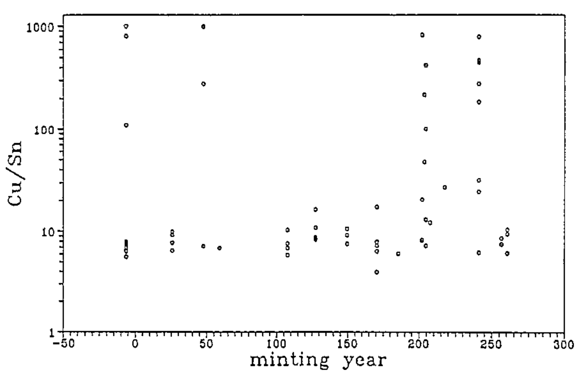

Fig. 2. The concentration ratio of copper to tin (Cu/Sn), as a function of the minting year.

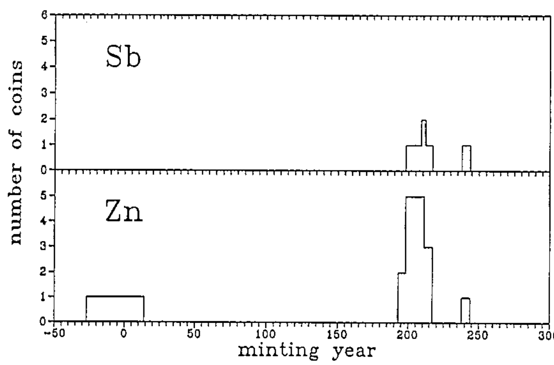

Fig. 3. Histograms of the number of coins with high concentrations of zinc (Zn) or antimony (Sb), as a function of the minting year.

emperor. An increase in the use of these metals is noticed in the same period, around 200 A.D. These conclusions are exactly the same with those for Thessaloniki and Nikopolis. The coins with higher zinc content were minted in the area Thessaly–Macedonia–Illyria, as the coins of Thessaloniki (Macedonia). Two of the three coins with higher antimony content were produced in the area of Epirus (cities in the left part of the map of Fig. 1) as also observed for coins of Nikopolis (Epirus). The smaller number of this type of coins is explained by the smaller number of the analysed coins from this area. In general the results of the present study are in very good agreement with those for the two major cities of the same area (Nikopolis and Thessaloniki) and integrate the research for the Greek copper coins minted during Roman Imperial times.

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