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Application of PIXE for elemental analysis of ancient Chinese artifacts

E.K. Lin *, C.W. Wang, Y.C. Yu, W.C. Cheng, C.H. Chang, Y.C. Yang, C.Y. Chang

Institute of Physics, Academia Sinica, Taipei, Taiwan

Abstract

Proton induced X-ray emission (PIXE) is a well-known method for elemental analysis in many different specimens for various applied studies. In this paper, we report an application of PIXE analysis for a series of ancient Chinese coins from the Tang Dynasty to the Ming Dynasty (AD 618–1679). Ninety-six PIXE spectra were obtained from forty-eight samples of the ancient coins with the use of a Ge(Li) X-ray detector. On each sample two spots at different positions on the flat surface were irradiated per run by 3 MeV protons from a NEC 9SDH-2 pelletron tandem accelerator. The principal component elements (Cu, Pb, Sn and Zn) and others (Fe, Sb, Ni and As) were determined for the analyzed coins. Variations in composition with a time span of about one thousand years for the examined coins were observed. The results are presented and aspects of the evolution of Chinese metallurgy in casting coins are discussed.

1. Introduction

In the course of China's long history, copper coins (named as "tong-bao" or "yuan-bao") have been most widely used in ancient China and circulated as an exchange medium on the market for more than two thousand years. Traditionally, new coins were issued as the change of a reign of emperor. Among these ancient coins, many are rare and precious at present. It is known that since the Tang dynasty (AD 618–906) bronze coins were produced and existed for a very long period until brass coins appeared sometime in the Ming Dynasty (AD 1368–1679) [1]. At what age of the reign such a change of technique in casting of ancient Chinese coins took place is worth investigating. The aim of the present work is to explore this question from a detailed PIXE analysis.

Proton induced X-ray emission spectroscopy using a high-resolution HpGe detector is known as a very useful technique in applied physics research and has been widely applied to quantitatively determining the major and trace elemental composition of ancient artifacts. In this paper, we report elemental data of ancient Chinese copper coins covering three dynasties of Tang, Soong (AD 960–1126) and Ming including several individual reigns, and to examine their composition variations throughout a time period of about one thousand years.

* Corresponding author. Tel. +886 2 7323075, fax +886 2 7834187.

2. Experiment

Experiments were performed on the 9SDH-2 pelletron tandem accelerator using a 3 MeV proton beam. The X-ray measurements were carried out with an external-beam milliprobe [2] using a Canberra 30 $mm^2 \times 5$ mm Ge(Li) detector, placed at 135° relative to the incident beam. The experimental setup, milliprobe arrangement and detection geometry are similar to the one described in previous works [2,3]. Briefly, the milliprobe was installed at the end of our 30° beamline at the accelerator. A 10 μm thick kapton foil was used as an exit window through which the beam passes into the air, and a cobalt foil (8.9 mg/cm^2) which was inserted in front of the detector was used as an absorber to attenuate the intense flux of the Cu K_α and K_β X-rays, one of the most abundant element in all analyzed coins. On each sample, two different impact spots on the flat surface were irradiated per run with about 5–10 nA proton bombardment. The beam spot on the sample was less than 2-mm diameter for the X-ray measurements. All spectra were recorded with conventional electronics followed by a Canberra series-95 MCA.

Samples examined in this work consisted of 48 ancient Chinese coins, belonging chronologically to 25 reigns of the dynasties of Tang, Soong and Ming. These coins all have a diameter of about 2.4 cm. In the course of measurements, continuous runs were made over several days, and each day the run was begun with a measurement of reference materials. For the present PIXE analysis, we used the reference materials NIST SRM 1118 aluminum brass and USSR CRM 871 leaded bronze as standards for

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the determination of elemental concentrations in the analyzed coins. The certified values of mass content of element in the reference materials are known to be of 1% accuracy for Cu, Pb, Sn and Zn in CRM 871, and for Cu and Zn in SRM 1118 as well. The main elements of interest in this analysis are Cu, Pb, Sn and Zn which have characteristic X-rays in the energy range 8.0–29.2 keV.

3. Results and discussion

To illustrate the results of the measurements of 96 PIXE spectra, we show in Fig. 1 a typical PIXE spectrum obtained by 3 MeV proton beam bombardment on sample 39, a Wan-lih coin (1576). Using the GUPIX software program [4,5], we carried out an analysis of all PIXE spectra to determine the concentration of elements in the samples. A consistency of better than 1% was found for the data obtained for the standards at several different runs. Values of contents of main elements in the standards obtained from the analysis are in good agreement with the certified values to within 1%. Tables 1–3 summarize the results of the determined contents of Cu, Pb, Sn, Zn, Fe, Ni, Sb and As. The values shown are the mean concentration obtained from two runs for beam impact at two different positions on the surface of the samples. Variation of the obtained values at two different positions was found to be generally less than 5% for Cu and 10% for Pb and Sn.

For coins minted in the Tang Dynasty of ancient China, we obtained in this analysis eleven samples for three different coins, known as Kai-yuan, Chian-yuan, and Huey-chuan Kai-yuan; others not analyzed are rare and difficult to collect. The sample 1 for the Kai-yuan coins was found to have the lowest Sn content among the 11 examined Tang coins. Table 1 shows measured contents of the major elements Cu, Pb and Sn with an average ratio of Cu to (Pb + Sn) = 1.7 : 1, 1.8 : 1, and 1.9 : 1 for Kai-yuan, Chian-yuan and Huey-chuan Kai-yuan coins, respectively. It is noted that most of the samples for the Kai-yuan coin and Chian-yuan coin were found to contain higher Pb than Sn, while the case is reversed for the Huey-chuan Kai-yuan coin. The minor elements Zn, Fe, Ni, Sb and As were observed; they appear usually in ancient Chinese coins [6–8].

From the results of 19 samples for Soong coins shown in Table 2, it appears that there are no significant variations in the Cu content from reign to reign of the Soong Dynasty. The average Cu content is 63%, which is slightly higher as compared to the analysis of coins minted earlier in the Tang dynasty. The compositions of the major elements for the analyzed Soong coins are in the ratio Cu : Pb : Sn = 63 : 24 : 11. In most cases, our data show higher Pb and lower Sn contents, and the contents of minor elements Zn, Ni, Sb and As appear to be smaller, as compared to the Tang coins.

Our data obtained for both Tang and Soong coins indicate that they were all made primarily of bronze. A distinctive feature is that the Zn content is at low levels with an amount of less than 0.5%. An earlier analysis of some Tang and Soong coins has been made by Sano et al. [7]. Comparatively our data and theirs, as given in Tables 1 and 2, are seen to be in fairly good agreement except for Sn for some samples. The difference in Sn values between this work and that of Sano et al. [7] may arise from the different source of samples used for the analysis and geographic origin of casting coins in ancient China. We noted that a mean standard deviation of about 45% was given for Sn data in the work by Sano et al. [7]. Considering uncertainties of theirs and ours (about 15%), the appeared difference in Sn content seems not to be prominent.

For a period of 166 years after the Soong dynasty the coining technique was expected to have considerable ad-

Table 1
Result of PIXE analysis of ancient Chinese coins in the Tang dynasty: elemental composition in percent by weight. Numbers in the parentheses are the results of measurement by Sano et al [7]. Estimated uncertainty: ~ 5% for Cu, ~ 10% for Pb and < 15% for Sn

Reign	Sample	Cu	Pb	Sn	Zn	Fe	Ni	Sb	As
Kai-yuan	1	61.6	32.2	2.93	0.94	1.02	< 0.07	0.23	0.22
(AD 621)		(63.0)	(30.9)	(0.1)	(0.37)	(1.0)	(0.04)	(0.93)	(2.8)
	2	50.8	26.9	20.1	0.61	1.40	< 0.08	< 0.1	
	3	53.9	25.4	20.0	0.43	0.18	< 0.08	0.24	
	4	69.8	17.6	11.9	0.26	< 0.08	< 0.07	0.44	
	5	64.7	19.9	14.5	0.65	< 0.22	< 0.1	0.20	
	6	64.4	25.1	10.0	0.67	< 0.08	< 0.08	< 0.1	
Chian-yuan	7	63.4	17.8	16.2	0.36	0.48	0.14	0.55	0.34
(758)	8	60.7	15.9	21.7	0.28	0.43	< 0.03	0.17	
	9	62.7	19.1	15.1	0.71	1.56	0.16	0.59	
Huey-chuan	10	61.1	11.5	25.2	0.30	0.17	0.10	0.55	0.29
Kai-yuan (845)	11	64.2	12.1	20.4	0.47	1.51	< 0.1	0.43	< 0.1

vancement. We analyzed 18 samples for the Ming coins minted in the different reigns. The results as listed in Table 3 indicate that the Cu content for the analyzed Ming coins increases toward a high value of about 80%, while the Sn content becomes considerably lower. The Hung-wuu coin (samples 31 and 32) were found to have an average ratio of Cu : Pb : Sn = 66 : 25 : 8. Next to the Hung-wuu, the Yang-lo coin (samples 33 and 34) and fourteen others (samples 35–48) were selected for analysis. A remarkably high Zn content was observed for the sample 36 and this distinctive feature continued to be present for samples 37–48 of coins minted in the later periods. Evidently, all samples 36–48 for the Ming coins (Jia-jing period and later) were found to be made of brass with a Zn content in the range 11–28%. The observed presence of Zn and the decrease of Pb and Sn contents indicate a significant change of materials used for coining.

We have selected three samples (samples 35, 36 and 37) of the Jia-jing coin for the present analysis. They were probably produced in the different years during the Jia-jing period (1522–1567). The Zn content was found to be very low for sample 35, however, it is remarkably high for both the samples 36 and 37. With a hypothesis that the sample 35 of the Jia-jing coin was produced earlier than the other two, our results indicate that in the earlier Jia-jing period the coins were still made of bronze, while the change to

Table 2
Result of PIXE analysis of ancient Chinese coins in the Soong dynasty: elemental composition in percent by weight. Number in the parentheses are the results of measurement by Sano et al. [7]. Estimated uncertainty: ~ 5% for Cu, ~ 10% for Pb and < 15% for Sn

Reign	Sample	Cu	Pb	Sn	Zn	Fe	Ni	Sb	As
Chwen-huah (AD 990)	12	63.7	16.4	19.0	0.39	< 0.03	< 0.03	0.47	< 0.01
Jyh-tao (995)	13	72.7	17.1	8.81	0.32	< 0.03	< 0.08		
		(73.9)	(17.8)	(7.3)	(0.09)	(0.03)			
	14	60.6	27.4	10.1	0.27	0.19	< 0.04		
		(66.1)	(23.9)	(9.6)	(0.08)	(0.04)			
	15	58.8	23.7	16.7	0.49	0.19	< 0.04		
Jing-der (1004)	16	63.6	24.8	10.2	< 0.1	< 0.03	< 0.02		
		(64.6)	(26.8)	(8.1)	(0.07)	(0.01)			
Tien-shi (1017)	17	67.2	22.7	8.65	0.26	< 0.02	< 0.04		
		(67.2)	(21.6)	(10.0)	(0.09)	(0.77)			
Tien-sheng (1023)	18	62.0	26.2	10.3	< 0.1	0.17	< 0.05		
		(65.7)	(24.0)	(9.7)	(0.09)	0.02			
Huang-soon	19	65.2	22.3	11.3	< 0.1	< 0.01	< 0.02		
		(65.7)	(28.9)	(5.0)	(0.08)	0.01			
	20	62.2	21.1	15.5	0.28	< 0.11	< 0.03		
		(65.0)	(23.8)	(9.8)	(0.08)	0.12			
Shi-ning (1068)	21	62.4	28.6	7.96	< 0.1	0.40	< 0.02	< 0.1)	< 0.02
		(68.7)	(20.2)	(10.7)	(0.08)	(< 0.01)		(0.06)	(0.02)
	22	59.7	21.9	17.1	0.21	< 0.07	< 0.04	0.11	0.13
Yuan-feng (1078)	23	62.8	26.9	7.96	0.31	< 0.08	< 0.04	0.12	
		(61.5)	(36.0)	(1.5)	(0.08)	(0.03)		(0.10)	
	24	67.5	19.6	11.9	< 0.2	0.22	< 0.04		
		(67.4)	(24.4)	(0.4)	(0.10)	(1.9)		(2.5)	
Yuan-youh (1086)	25	55.3	32.0	11.1	< 0.1	< 0.05	< 0.03	< 0.09	< 0.03
		(64.8)	(26.0)	(8.9)	(0.08)	(0.02)		(0.01)	(0.02)
	26	63.5	25.1	9.0	0.30	0.71	< 0.03	< 0.1	0.20
Sheng-soon (1101)	27	60.3	25.8	10.1	0.24	1.50	< 0.04	< 0.1	0.16
		(69.5)	(24.5)	(5.3)	(0.10)	(0.08)		(0.13)	(0.16)
	28	61.6	24.4	12.8	0.35	0.13	< 0.05	0.11	< 0.03
Jeng-her (1111)	29	62.3	30.6	6.11	0.26	0.54	< 0.04	< 0.04	< 0.1
		(61.1)	(33.2)	(3.9)	(0.08)	(1.2)		(0.1)	(0.21)
	30	65.7	18.0	13.9	0.36	0.24	< 0.05	0.15	< 0.34
		(66.4)	(27.6)	(4.5)	(0.13)	(0.3)		(0.19)	(0.43)

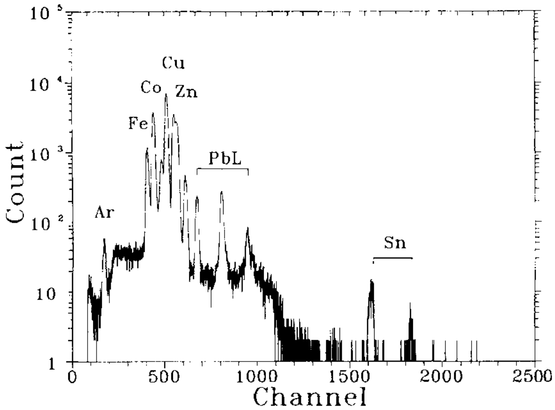

Fig. 1. PIXE spectrum of the Wan-lih coin (sample 39) obtained by 3 MeV proton beam bombardment on the surface of the coin at one irradiation. The observed Co peak is induced by the fluorescence in the absorber inserted between the target and the detector.

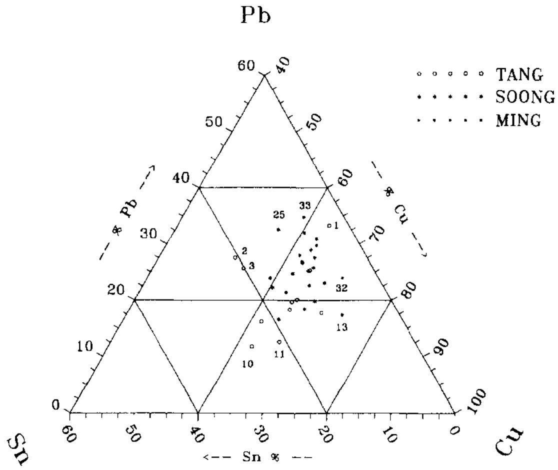

Fig. 2. Ternary diagram of Cu, Pb and Sn concentraions for the 35 bronze coins (samples 1 to 35) of various periods. Data points are plotted as the percent by weight of each element with the normalization Cu + Pb + Sn = 1.

brass coin appears to take place sometime in the later Jia-jing period. It is noted that the zinc content obtained in the analyzed Ming brass coins varies in a range 11–29% and is somewhat lower as compared to those found in the Ching brass coins (1644–1911) [8]. To get an accurate knowledge of the beginning of the age of brass coins in ancient China, it is necessary to analyze a larger set of representative Ming coins.

Table 3
Result of PIXE analysis of ancient Chinese coins in the Ming dynasty: elemental composition in percent by weight. Estimated uncertainty: ~ 5% for Cu, ~ 10% for Pb and Zn, and ~ 15% for Sn

Reign	Sample	Cu	Pb	Sn	Zn	Fe	Ni	Sb	As
Hung-wuu (1368)	31	62.2	26.6	10.5	< 0.1	< 0.06	< 0.06	0.22	
	32	69.8	23.7	5.5	< 0.3	< 0.2	0.06	< 0.06	
Yang-lo (1403)	33	58.2	34.4	6.18	0.13	0.03	0.07	0.11	
	34	59.9	21.7	7.45	0.25	0.2	< 0.06	< 0.06	
Jia-jing (1528)	35	61.8	28.9	6.57	1.30	0.18	< 0.1	0.25	0.11
	36	67.5	16.0	1.79	14.5	0.07	< 0.07	< 0.03	< 0.03
	37	63.1	18.4	2.99	14.3	0.26	< 0.03		
Lung-ching (1567)	38	70.4	2.82	4.51	21.1	0.17	< 0.1		
Wan-lih (1576)	39	67.9	9.76	0.80	19.4	0.34	0.10		
	40	74.9	5.9	6.4	12.3	0.35	0.17		
Tien-chii (1621)	41	60.9	4.71	3.97	28.4	0.77	0.05	0.22	
Chung-jen (1628)	42	81.1	2.64	< 0.1	16.1	0.05	0.12		< 0.1
	43	68.0	3.98	0.61	24.0	0.44	0.21		0.11
Hung-kuang (1645)	44	71.2	5.60	< 0.1	18.9	0.11	0.18	0.59	0.20
Yang-lih (1647)	45	75.3	3.57	0.24	20.2	0.55	0.09	1.03	0.06
Lih-yung (1658)	46	78.2	4.29	1.81	10.7	3.71	0.04	< 0.02	0.20
	47	69.6	11.4	0.53	16.3	2.12	0.02	< 0.02	< 0.02
Jau-wuu (1678)	48	75.7	5.49	1.66	13.4	2.47	0.06	< 0.02	0.26

As discussed above, we identified samples 1–35 for coins of Tang, Soong and Ming to be made of bronze. Fig. 2 shows a ternary diagram of Cu, Pb and Sn concentrations in these bronze coins of various periods. The black points for Ming coins and star points for Soong coins are seen to cluster in the region of Cu (60 to 73%), Pb (16 to 34%) and Sn (5 to 20%) and appear to be in one classification, while the open-circle points for Tang coins are rather scattered and seem to be in the other classification. It gives us a clear view that Soong and Ming coins are relatively concentrated in one region, while concentrations for Tang coins, produced in an earlier period, vary in a rather large range. Apparently the ancient Chinese coining technique in the Tang Dynasty was still in a premature stage of development.

4. Conclusion

We have made a detailed PIXE analysis and obtained elemental information on 48 ancient Chinese bronze and brass coins (7th to 17th AD), and show the distribution of Cu, Pb and Sn concentrations for the Tang, Soong and Ming bronze coins (samples 1–35). For these bronze coins, the zinc content was found at trace level, and was likely introduced from the ore and casting stone vessel. A new age of casting coins involving a change of the coining technique in China appeared in the middle of the Ming Dynasty. Our data obtained for the Ming coins (samples 36–48) provide evidence that the beginning of the ancient Chinese brass coins appeared in the reign of Jia-jing Emperor (1522–1567). The obtained variations of elemental composition may contribute to the investigation of the archaeological significance of the ancient Chinese coins and give a useful information for studying effects of elemental contents on the physical property of coins minted in ancient China.

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