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Characterization of Kangxi Coins of Tsing Empire by SEM-EDS

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Abstract. The major and minor elements Cu, Zn, Sn, Pb and Fe of coins issued in the Kangxi dynasty of Tsing Empire were analyzed by X-Ray energy dispersive spectrometry using a scanning electron microscope (SEM-EDS). This paper presents the characteristic concentration of elements in the coins, and may act as a criterion for other coins dating back to the Kangxi dynasty. The 73 coins were classified in three groups according to the results. Group 1 with good fineness represents the coins minted in 'Yunnan' province and some coins for special purpose such as the celebration of Kangxi emperor's birthday; groups 2 and 3 represent the coins issued before and after 1684 AD, respectively.

At a concentration range of $0.23\% \sim 6.11\%$, the distribution of lead is not homogeneous in the coins, and the largest diameter of lead inclusion is less than 15 μm. Regional difference is not evident except with coins showing the mintmark 'Yun'. The official degradation of fineness was supported.

Key words: Kangxi coins; dating; archaeometry; SEM-EDS.

Among all the metallic archaeological objects, ancient coins have been extensively studied, yielding fruitful results because of good minting and a large number of documents. Elemental analysis used as a means of characterizing coins is one of the most important approaches in the field of archaeometry. Investigation of the elemental composition and its variation is used to determine fine, debasement, recasting and forge, manufacturing technology and provenance [1]. In the past, many techniques were applied to analyze ancient coins, e.g. proton induced X-Ray emission analysis (PIXE) [2–4], X-Ray fluorescence spectrometry [5, 6] and other unusual techniques [7, 8]. As a kind of fast, nondestructive, multi-elemental analysis method in common use, energy dispersive X-Ray spectrometry for scanning electron microscope (SEM-EDS) will conveniently produce information about the elements contained and their distribution, especially for micro-region enrichment and segregation in a coin.

The Kangxi dynasty (AD1661–1722) was one of the powerful and important periods of the Tsing Empire. At that period the social and economic situation tended towards being stable, the empire was growing strong and prosperous, yet local turbulence still existed. The turbulence most influential on the economy was the Wu San-gui revolt (AD1673–1681). Studying the coin status of that period may to some extent reveal the historical problems.

E. K. Lin et al. [4] reported the results of Kangxi coins using external-beam PIXE methods. However, the number of analyzed coins was small, and the results were not sufficient to represent the coins of that period.

In this paper, we attempt to determine the major and minor elements of coins of the Kangxi dynasty

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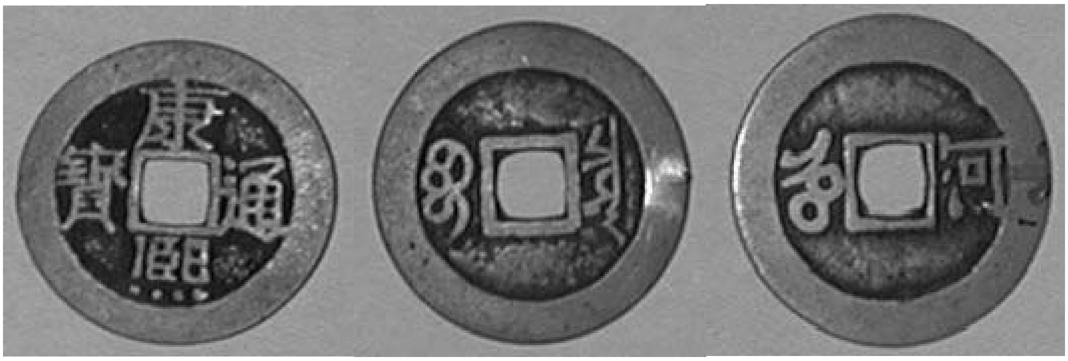


(a) (b) (c)

Fig. 1. Two sides of Kangxi coin. (a) Observed side. (b) Reverse side of a coin minted by the central government in Peking. (c) Reverse side of a coin minted in He-nan province

by SEM-EDS, to produce more detailed results, to classify the coins according to the elements contained and present some problems related to archaeometry.

Experimental

In this study we examined 73 coins. The diameter of all the coins was 2.6 cm, the average weight was 4.2 g, the maximum weight being 5.5 g and the minimum weight 3.6 g, which means there are two standard weights, '1 qian 4 fen' and '1 qian' for the analyzed coins according to the metrology of that period. One 'qian' is about 3.6 g, and one 'qian' is equal to ten fens' [9]. An example of two faces of the copper coins of the Kangxi dynasty is shown in Fig. 1.

Because SEM-EDS is a surface-sensitive analysis technique and the coins are covered with patina, the surfaces of the coins need to be prepared. Three spots of about 2×2 mm at different positions of each coin's surface were polished with 5 metallography sand paper, followed by cleaning with ethanol to remove residues from the polished region. All the analytical procedures were performed on the X-650 SEM and WD-8 EDS [10], and the WD-8 system was upgraded from EDAX9100 (Edax Inc.) to be used online with a modern personal computer. For fast analysis, the semi-quantitative standardless analysis of WD-8 software package with the kernel algorithm adopted the method of DTSA [11]. The work voltage was 20 KV, work distance was 15 mm, tilt angle was 0°, and take-off angle was 38°. Three analytical spots were examined, and the average of their determined values was used as elemental content of the coins. The analytical live time was 120 s in each region. The work beam current was set to ensure that the count rate was about 2000 cps.

For SEM-EDS analysis, a reference sample (national standard GB02104, Zn/Cu alloy) was used to test the quantitative software package.

The analysis of distribution of elemental content was used to investigate the inhomogeneity of the coins. In the polished region, a micro-region was selected for analysis, and the distribution of X-Ray for all elements was obtained except in the case of copper.

Results and Discussion

Kangxi coins can be classified into two main groups according to the mintmark; one was minted in Peking by the central government, the other by local governments. The coins belonging to the central government had two different mintmarks with Manchu characters 'baoquan' and 'baoyuan' only. Those belonging to local governments had 21 mintmarks with Manchu and Chinese characters to identify the coins' different origins [12]. Because some of the Kangxi coins are rare, the analyzed coins included coins minted by the central government and 18 kinds of coins from different local governments; moreover, the amount of each kind was different.

A SEM-EDS spectrum of a coin is shown in Fig. 2, illustrating the results of the measurement. Because the theoretical detection limit of SEM-EDS is about 0.08% [13], only five elements (Cu, Zn, Fe, Sn and Pb) were selected for analysis. The concentration of the elements contained in the coins and the standard

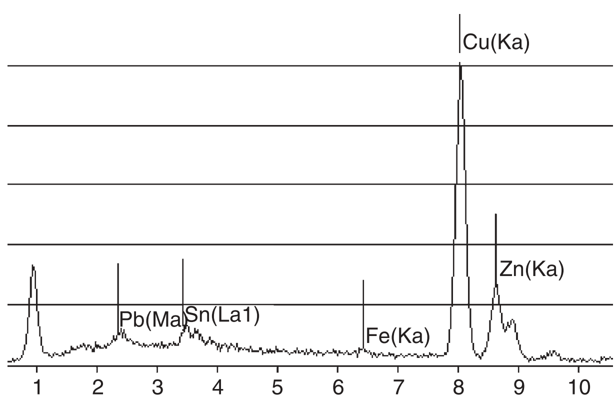
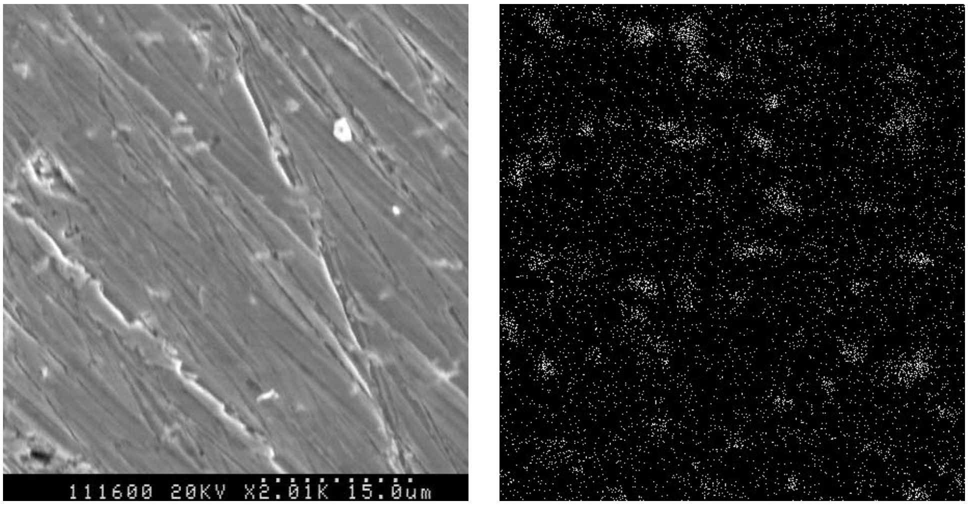


Fig. 2. SEM-EDS spectrum of a 'gongbu' coin sample



a b

Fig. 3. An illustration of the inhomogeneity of lead in the ‘Hubu6’ coin. (a) Electron image of the analyzed region. (b) X-Ray distribution of lead mapping the analyzed region

sample were determined. Throughout the entire procedure, a standard sample is analysed after every six measurements of the coins. Compared with the nominal value of the standard sample, absolute errors of copper and zinc of below 1% were obtained for the determined values and relative errors were lower than 4%. For the minor element Fe (weight percentage $<1\%$) the relative error was up to 25%.

X-Ray area distribution intensity was generated for some coins to investigate the inhomogeneity of the composition of zinc, tin, lead and iron. The amplified ratio was 2000, and the scanning area was about $45 \times 60\,\mu$m. An example of the results is shown in Fig. 3. The distribution of zinc is homogeneous. At a concentration range of $0.23\% \sim 6.11\%$, Pb is not homogeneous in the coins, and the largest diameter of inclusion is less than $15\,\mu$m. For the elements iron and tin, similar results can be observed. Because the concentration of the element is not high, homogeneity hypothesis on the scale of about 2×2 mm can be accepted.

The measured results of the coins are presented in Table 1. The composition of the major elements copper, zinc, tin, lead and the minor element iron ranges from 63.17%, 5.28%, 0.34%, 0.23% and 0.28% to 94.61%, 34.64%, 10.57%, 6.11% and 1.70%, respectively. According to the archaeological documentation, the official ingredients ratio of raw copper and zinc changed from 7:3 to 6:4 in 1684 AD, and the ratio is about 8:2 in Yunnan province [14, 15]. The change in the fineness composition of copper and zinc is substantial and implies the devaluation of the coins. In general, degradation of fineness means that the economic situation deteriorated in that period. But the historical facts are that the Wu San-gui and Taiwan revolts had been suppressed before 1684 AD, the social and economic situation of the Kangxi dynasty was improving and that the most important copper sources in Yunnan province were again controlled by the central government. We can deduce that the economic development after 1684 AD was so fast that the amount of coins could not meet the demands, but also that the degradation of fineness was to prevent the rampancy of private forging. The official degradation of fineness was inevitable.

Following the official list of ingredients, the coins were divided into three logical groups. K-Means cluster analysis was applied to classify them in terms of major element content. The analytical results are shown in Table 2. The central cluster values of the three groups serve as a characteristic centration for dating further Kangxi coins. Group 1 contains ten samples. The concentration of the major elements copper and zinc ranges from 79.88% and 5.28% to 94.61% and 14.88%; group 2 contains 52 samples. The concentration ranges from 66.55% and 14.19% to 76.68% and 26.10%; group 3 contains 11 samples. Concentration ranges from 63.17% and 26.76% to 67.41% and 34.64%. When comparing central values of groups with the official ingredients, the values were evidently higher than the official values. Because the melting point of copper (1356 K) is

Table 1. Elemental concentration (w.t. %) of total of 73 coins

Mint*	Cu	Zn	Fe	Sn	Pb	Mint*	Cu	Zn	Fe	Sn	Pb
Fu1	71.38	21.86	.58	4.25	1.92	He1	69.76	25.52	.83	2.39	1.50
Fu2	71.41	20.12	.69	5.70	2.09	He2	69.52	24.31	.84	3.03	2.30
Fu3	70.91	21.68	.71	4.31	2.40	He3	67.77	24.60	.69	3.54	3.40
Fu4	68.00	23.07	.57	5.64	2.72	He4	71.38	23.37	.63	3.77	.85
Fu5	68.31	21.47	.57	5.70	3.95	Hubu1	63.90	27.31	.83	4.42	3.54
Fu6	69.74	22.19	.62	5.81	1.65	Hubu2	68.09	24.86	1.10	3.82	2.13
Fu7	69.90	20.46	.76	6.73	2.07	Hubu3	72.33	19.49	.68	6.21	1.30
Fu8	71.31	20.64	.88	4.74	2.43	Hubu4	70.39	20.10	.79	4.52	4.29
Fu9	70.79	21.01	.86	5.70	1.65	Hubu5	65.26	28.06	1.01	3.33	2.34
Fu10	84.76	9.58	1.46	1.80	2.40	Hubu6	69.55	23.31	.38	3.83	2.93
Zhang1	68.42	24.90	1.04	1.27	4.37	Hubu7	63.86	27.49	.80	3.66	4.19
Tai1	85.60	8.94	.54	4.45	.48	Gongbu1	69.76	22.88	.74	4.02	2.60
Guang1	63.78	34.64	.96	.39	.23	Gongbu2	73.77	20.12	.63	4.16	1.32
Gui1	63.17	32.37	.99	2.37	1.10	Shan1	73.86	19.86	.68	3.67	2.11
Gui2	68.21	14.19	1.05	10.57	5.98	Shan2	75.62	18.17	.93	4.38	.90
Yun1	79.88	14.88	1.68	1.19	2.37	Shan3	76.68	18.39	.81	2.79	1.32
Yun2	82.41	13.60	1.15	.70	2.14	Shan4	75.66	18.04	.76	3.94	1.61
Yun3	81.99	13.51	1.29	1.27	1.93	Shan5	71.25	20.46	.87	3.96	3.46
Yun4	94.61	5.28	.42	.39	2.31	Shan6	72.80	18.19	1.00	4.56	3.45
Yun5	91.98	5.70	.64	.57	1.12	Xuan1	70.78	23.70	.75	3.75	1.02
Yun6	88.83	8.99	.60	.52	1.05	Xuan2	69.55	21.09	.84	4.13	4.39
Yun7	89.66	8.73	.82	.34	.44	Xuan3	71.74	20.63	.75	5.56	1.32
Yun8	87.08	10.13	.61	.53	1.65	Xuan4	72.57	21.94	.74	2.77	1.97
Zhe1	70.65	25.95	.76	1.84	.79	Xuan5	67.96	21.59	.28	5.26	4.91
Zhe2	67.01	26.77	.83	2.76	2.64	Yuan1	68.70	25.00	.75	3.94	1.61
Zhe3	69.27	24.13	.87	2.65	3.08	Yuan2	66.55	23.87	.67	5.07	3.83
Chang1	63.37	31.84	.68	2.85	1.26	Yuan3	67.41	23.34	.84	4.00	4.42
Chang2	64.78	29.67	1.16	2.25	2.15	Yuan4	69.45	23.15	.82	3.14	3.44
Dong1	66.87	19.59	1.70	4.38	6.11	Yuan5	68.22	25.78	.66	4.19	1.15
Dong2	67.07	24.83	1.02	3.16	3.92	Yuan6	67.41	26.76	.86	4.33	.64
Dong3	67.29	24.22	.66	3.35	4.49	Yuan7	68.50	25.92	.74	3.80	1.04
Su1	64.50	28.44	1.08	4.19	1.79	Yuan8	69.92	21.47	1.02	4.65	2.94
Ning1	68.43	26.10	.55	3.81	1.07	Yuan9	68.61	22.67	.75	4.82	3.14
Lin1	72.50	21.63	.82	2.62	2.44	Yuan10	69.00	19.64	.78	4.60	5.99
Lin2	66.62	24.05	.76	4.73	3.84	Tong1	70.88	21.72	.41	5.89	1.10
Lin3	67.81	24.20	.84	4.16	2.98	Ji1	70.16	24.04	.59	3.32	1.88
Jiang1	65.50	28.97	.69	3.04	1.79						

* The word in the mint column is the Chinese word mintmark representing the province that minted the coins, the following number is the sample number of coins from the same mint.

Table 2. The results of K-Means classification

Group	Cluster center*	Mintmark of coins
1	(86.68%, 9.93%)	Yun1∼8; Fu10; Tai1
2	(70.06%, 22.18%)	Fu1∼9; Zhang1; Gui2; Zhe1, 3; Dong1∼3; Ning1; Lin1∼3; He1∼4; Hubu2∼4, 6; Gongbu1, 2; Shan1∼6; Xuan1∼5; Yuan1∼5, 7∼10; Tong1; Ji1
3	(64.78%, 29.30%)	Yuan6; Hubu1, 5, 7; Jiang1; Su1; Chang1, 2; Zhe2; Gui1; Guang1

* The cluster center is the final central concentration of each group. The first value represents the concentration of copper, the last value shows that of zinc.

higher than the boiling point of zinc (1180 K), and Zn will vaporize, the final content of zinc is less than the ingredient and that of copper is comparatively higher.

All the coins with mintmark 'Yun' belonging to high fineness group 1 are consistent with official ingredients. The coin fu10 differed from the other nine coins with mintmark 'fu' due to its higher degree of fineness and its additional mintmark 'Zi'. In the light of the documentation [16], it is a special coin minted for the celebration of Kangxi emperor's birthday. It is thus understandable why this coin is of superior fineness compared to the other coins of the same mint.

The coin with the mintmark ‘tai’ is rare and difficult to obtain. Having only one example to measure makes it impossible to determine whether it is a forge or not. We can yet conclude that the coins of superior fineness in the Kangxi period had two sources. One was minted in Yunnan province and the other was minted for special purposes such as the birthday of the Kangxi emperor. For group 2 and 3 representing standard coins, regional differences in content of constituents is not evident, and the variation of coins was controlled by the government of different periods, implying that the central government of that period was powerful.

Conclusion

In this study the SEM-EDS method was successfully applied to the preliminary characterization and classification of the coins based on the content of major elements of Kangxi coins. The results of elemental analysis provide more detailed and useful data in archaeometry of Kangxi coins. The change of copper and zink concentration in Kangxi coins is substantial because of the existence of official degradation during this period, which does not imply a deteriorating economic situation. Otherwise, there were no regional differences except in the case of coins with mintmark ‘Yun’.

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