

## Nondestructive analysis of an ancient Chinese copper coin

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### ABSTRACT

Raman microspectroscopy, X-ray photoelectron spectroscopy (XPS) and X-ray energy dispersive spectroscopy (EDS) were used to identify the matrix elements near the surface and components of the verdigris of an ancient Chinese copper coin *Sui wuzhu* which was excavated in *Shanxi* province of China. The main components of surface corrosion products included  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  with small amounts of  $\text{Cu}_2\text{O}$ ,  $\text{CuPbSO}_4(\text{OH})_2$ ,  $\text{PbCO}_3$  and  $\text{PbO}$ . The matrix elements included copper, lead and carbon with small amounts of iron, oxygen and sulfur. The amount of copper is higher than that of lead, although the total amount of the two is less than forty percent. The results are of great importance not only to the identification of Chinese ancient copper coins, but also to the ancient Chinese casting technology and chemical refining. Moreover, the study offers significant fundamental information to the research on the influence of heavy metal on the health of ancient coin users.

**KEYWORDS:** Chinese ancient coin *Sui wuzhu*, nondestructive analysis, verdigris, Cu-Pb alloy, archaeology, preservation of cultural relics

### 1. INTRODUCTION

In ancient China, all kinds of *wuzhu* coins have been in circulation for more than 800 years until the *Sui* dynasty (AD 581-618) which was established by Jian Yany, the first emperor of *Sui* dynasty, which replaced the *Northern Zhou*

dynasty in 581. The *Sui wuzhu* coins were then cast in *Kaihuang Yuannian* (the first year of the *Sui* dynasty), and so they are also called as the *Kaihuang Wu Zhu* coins. They were cast delicately and in a tidy manner in different sizes and weights. The standard coins generally are about 2.5 cm in diameter, and 3.0 to 3.4 g in weight, while smaller ones are about 2.3 cm in diameter and 2.25 to 2.3 g in weight. The symbol characters "*Wu Zhu*" on one side were written in seal script, and should be read transversely from right to left. The two strokes of the character '*Wu*' connect usually in streamline curves, while some in crossed straight lines. There is a vertical line near the right side of the centre square threading hole, and a wide edge around the coin on the back [1]. The *Sui* was the last dynasty when *wuzhu* coins were circulated in the ancient China and has a history of about 1400 years.

The composition, appearance, features and the circulation properties of the ancient coins not only reveal the social superstructures, economic conditions and levels of productive force at that time, but also reflect the casting level and the art philosophy at that time. In addition, in terms of the archaeology, the results of quantitative composition of ancient coins provide a wealth of information for the identification of the age of the coin. Moreover, it can also provide information to the research on the influence of heavy metals on the health of ancient coin users.

Raman microspectroscopy, X-ray photoelectron spectroscopy and X-ray energy dispersive spectroscopy are important nondestructive analysis tools in quantitative archaeology, for identification and protection of historical relics.

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The components, the features of corrosion environment, and the influence of the casting ways on modification process of some ancient bronze artifacts such as ancient bronze tripod, Chinese bronze money-tree, broken bronze sword, bronze mirror, etc. have been studied in the past [2]. For example, the analysis of the head and body parts of copper spears showed the differences in elemental components and it can be judged that the spears were cast using vertical molds [3]. The corrosion process of Chinese bronze money tree was clearly confirmed by using the high spatial resolution capacity of the Raman microspectroscopy [4]. Raman analysis has been used in the study of the surface fragments of a copper Buddha cast of *Tang* dynasty (618-907), which indicated that the addition of lead into the copper matrix which remains as an independent phase in the casting process could keep the material from rusting [5]. There is also a study using different nondestructive analyzing tools, on the effect of soil environment around the burial site on the corrosion of bronze sword cast during the *Xizhou* dynasty, indicating that leach-out of copper from the matrix in the corrosion process leaves tin as the major corrosion product [6]. However, to date few reports exist on analyzing the components and corroded surface of ancient *Sui wuzhu* coins by non-destructive evaluation methods. Hence we use Raman microspectroscopy, EDS and XPS to analyze the matrix elements near the surface and the corroded products on the surface of an ancient Chinese copper coin, *Sui wuzhu*, excavated in *Shanxi* province of China.

## 2. EXPERIMENTAL

### 2.1. Samples and materials

The *Sui wuzhu* coin weighs 3.3876 g, has a diameter of 25.8 mm and thickness of 1.0 mm. The size of the centered thread-line hole is 10 mm × 10 mm. On the coin, the two crossed-strokes of the character 'wu (武)' of *wuzhu* connect in curve. Its surface is bluish black, the edges are black and most of the regions, as shown in Figure 1, are green. All of the chemical reagents are of analytical purity.

### 2.2. Preparation of verdigris

5 mL  $\text{CuSO}_4$  solution (0.5 mol/L) and 6 mL  $\text{Na}_2\text{CO}_3$  solution (0.5 mol/L) were poured separately

into two small beakers. The two beakers were heated for a few minutes in water at 50 °C. Then  $\text{CuSO}_4$  solution was poured into  $\text{Na}_2\text{CO}_3$  solution under stirring. The reaction mixture was stirred at 960 rotations per minute at 50 °C for two or three days until precipitated completely, and the resulting precipitates were filtrated and washed with distilled water several times until no sulfate ions could be detected from the filtrate. Next, the precipitates were dried at 100 °C and then cooled at room temperature. Finally we retained the product for future use.

### 2.3. Instruments

**Raman microscopic spectra** of samples were obtained on a LabRAM Aramis (Horiba Jobin Yvon, HJY) using laser 532 nm radiation. The resolution was better than  $1 \text{ cm}^{-1}$ , and 20 scans per sample within 300 s. The best horizontal spatial resolution of confocal microscopy was 1  $\mu\text{m}$ . The best longitudinal depth resolution was 2  $\mu\text{m}$ . The amplification factor of the objective lens was 50. The spot size was 1.3  $\mu\text{m}$  in diameter, while the size of the sampling spot was 1.33  $\mu\text{m}^2$  and longitudinal spatial resolution was 2  $\mu\text{m}$ . The laser power at the surface of the sample was 8 mw. Signal acquisition time was 10 s.

X-ray photoelectron spectroscopy details: ThermoFisher Scientific company (USA) ESCALAB 250 type, X-ray Source was Monochromated Al K $\alpha$  200 W, sampling spot size, 650  $\mu\text{m}$ . Pass Energy, 200 eV for survey and 30 eV for high resolution scans. Lens Mode, LargeAreaXL. Analyser Mode, CAE.

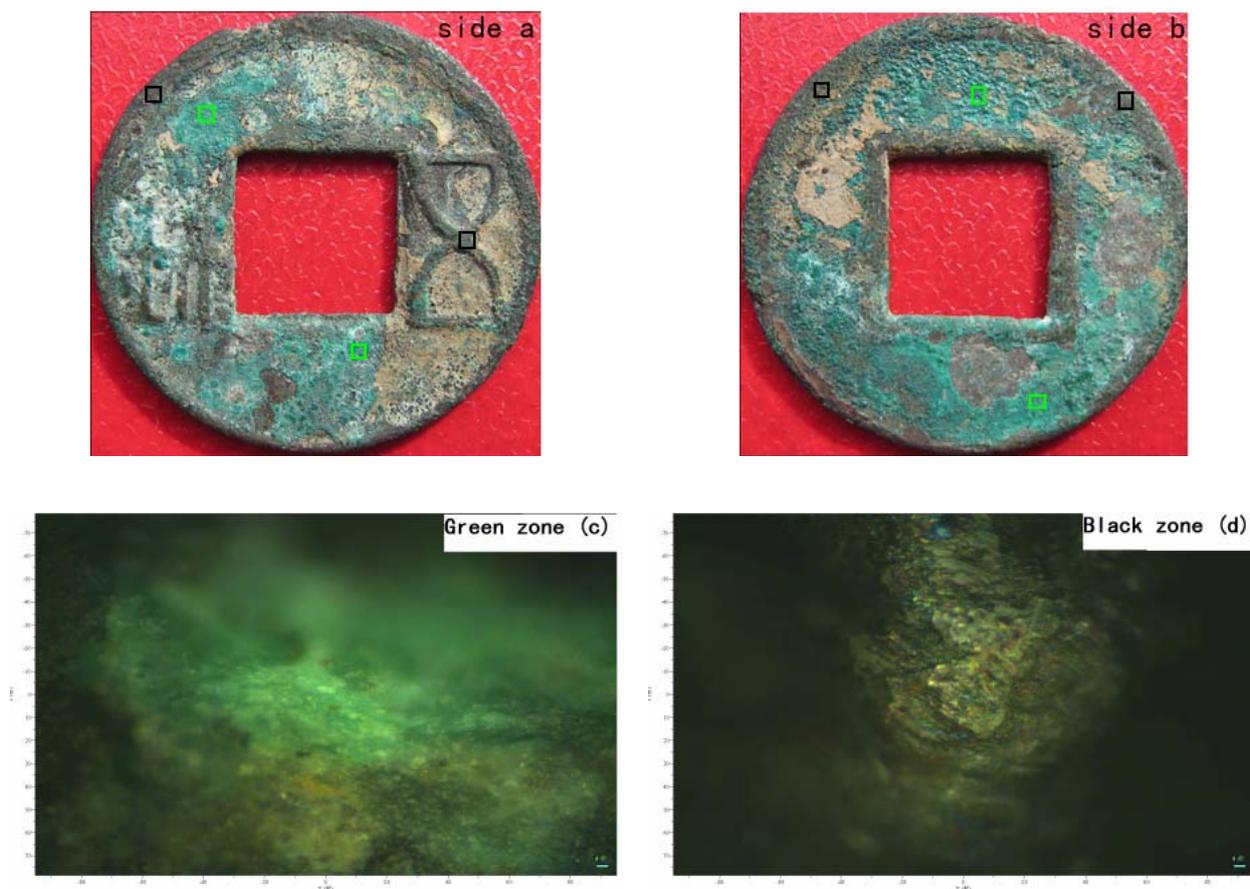
Energy dispersive spectroscopy (EDS): Hitachi FESEM S-4800 with Horiba EMAX 350 type, and the areas of the sampling point are shown in the Figure 5.

## 3. RESULTS AND DISCUSSION

### 3.1. Raman microscope spectra of the coin

Copper coin and the sampling points are shown in Figure 1. As it can be seen, the coin was badly corroded. Micrographs of green and black sampling areas are shown in Figure 1.

Raman spectra of green and black sampling areas on the surface of the coin are shown in Figure 1 and Raman shifts observed and the possible assignments are listed in Table 1. From the

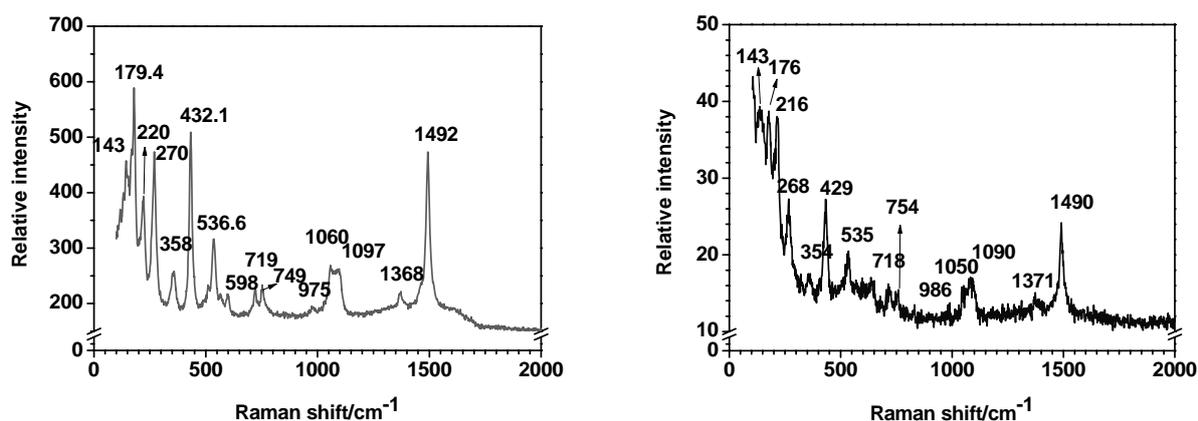


**Figure 1.** Side (a) and (b) photographs of *Sui Wu Zhu* coin and micrographs of green (c) and black (d) sampling areas for Raman. Black and green squares refer to the sampling sites.

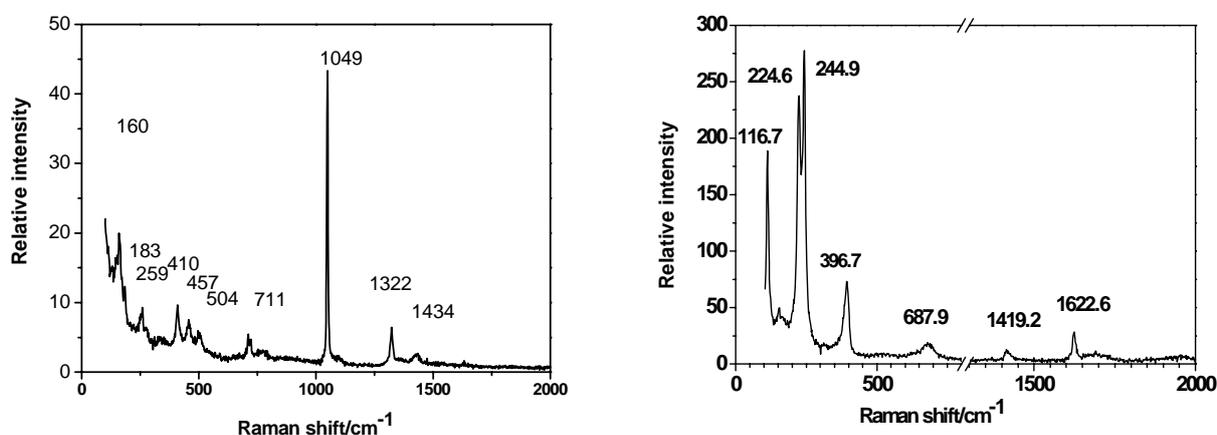
**Table 1.** Possible assignments of Raman shifts of the samples.

Raman shifts/cm <sup>-1</sup>	Possible assignments	Refs.
143	PbO	[4, 9]
176/179.4; 268/270; 363/358; 429/432.1; 535/537; 718-754/719-749; 1050-1090/1060-1095; 1490/1492	CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub> : double peak at 718-754/719-749 from bending vibration in the plane of CO <sub>3</sub> <sup>2-</sup> , or deformation and warping; double peak at 1050-1090/1060-1095 from symmetric stretching vibration of carbonate ion at around 1066 cm <sup>-1</sup> caused by the vibration coupling and Fermi resonance; single peak at 1490/1492 from antisymmetric stretching vibration of carbonate (strong).	[8]
216/220	Cu <sub>2</sub> O	[7]
598 (Black)	CuPbSO <sub>4</sub> (OH) <sub>2</sub> : asymmetric deviational vibration of sulfate;	[8]
975/986	CuPbSO <sub>4</sub> (OH) <sub>2</sub> : symmetric stretching vibration of sulfate.	[3, 7, 8, 10]
1368/1371	PbCO <sub>3</sub> : symmetric stretch (w) of carbonate.	[4]

Notes: Δv/Δv means the Raman shift in green/black areas, respectively.



**Figure 2.** Raman spectra of Chinese ancient copper coin: Green (left) and Black (right) areas.



**Figure 3.** Raman spectra of Lab-prepared  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (a) and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Analytical reagent) (b).

Figure 2(a), it can be seen that main Raman shifts ( $\text{cm}^{-1}$ ) in the green area were observed at 143, 179.4, 220, 270, 358, 432.1 (strong), 537, 598, 719 & 749 (double peaks), 975, 1060 & 1097 (double peaks), 1368 and 1492 (strong/main peak). Main Raman shifts ( $\text{cm}^{-1}$ ) in black area were observed at 143, 176, 216, 268, 362.8, 429 (strong), 535, 718 & 754 (double peaks), 986, 1050 & 1090 (double peaks), 1371 and 1490 (strong/main peak). Raman peak of black area was remarkably lower than that of green area in intensity.

The Raman spectrum of basic cupric carbonate made in the laboratory is shown in Figure 3(a), which fits well with the Raman spectra of copper coin in green areas. Raman spectra of verdigris, including  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  and  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$

has also been reported in reference [4]. It can be found that Raman shifts of the two spectral lines fit well with that of basic cupric carbonate  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ , which means the corrosion products, both in the green and black areas, mainly contain basic cupric carbonate ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ).

In addition, the main Raman shift of pure cupric oxide ( $\text{Cu}_2\text{O}$ ) occurs at  $220 \text{ cm}^{-1}$  [4]. The same Raman shift can be observed from green area in Figure 2. So it is obvious that the green area contains  $\text{Cu}_2\text{O}$ . In the green areas, the Raman peak located in  $598$  and  $975 \text{ cm}^{-1}$  should be separately attributed to  $\text{SO}_4^{2-}$  from  $\text{PbSO}_4$  in asymmetric deviational and symmetric stretching vibrations. According to reference [7], the main peaks of  $\text{CuPbSO}_4(\text{OH})_2$  were 163, 230, 326, 345, 594, 968 (main peak) and  $1019 \text{ cm}^{-1}$ , which prove

the above judgments. In Figure 2, the weak peak located at  $1368\text{ cm}^{-1}$  (green area) and  $1371\text{ cm}^{-1}$  (black area) should be attributed to asymmetric stretching vibration of carbonate, which fits with the Raman spectra of lead carbonate ( $1051$  &  $1054$  (double peak),  $1287$ ,  $1366\text{ cm}^{-1}$ ) in reference [4], which further confirms that the green and black areas contain lead carbonate. The  $\text{CO}_3^{2-}$  symmetry stretch is Raman active and the Raman peak is at  $1510\text{--}1390\text{ cm}^{-1}$  (C=O) and  $1089\text{ cm}^{-1}$  (C-O). At the same time, vibrational coupling and Fermi resonance cause the double peak effect [8]. The  $\text{SO}_4^{2-}$  symmetric stretching modes with Raman activity were observed in  $950\text{--}1000\text{ cm}^{-1}$  region, which corresponds to the peak at  $975\text{ cm}^{-1}$  from  $\text{CuPbSO}_4(\text{OH})_2$ . It has been reported that Raman spectrum of lead oxide has a main peak at  $145\text{ cm}^{-1}$  [4], which can be found in both green and black areas in Figure 2. Hence, the conclusion can be drawn that the copper matrix and the corrosion both contain lead oxide.

The reference material, copper chloride  $\text{CuCl}_2$  dehydrate (+99%), was analyzed using Raman microscope as shown in Figure 3(b). The peaks were located at  $116.7$ ,  $224.6$ ,  $244.9$ ,  $396.7$ ,  $687.9$ ,  $1419.2$  and  $1622.6\text{ cm}^{-1}$ . However, they do not match with the spectra as shown in Figure 2. Hence, it is inferred that there is no  $\text{CuCl}_2$  in the sample.

From the color and the Raman data, the conclusion can be drawn that the major constituents of green area were  $\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$ , and small amounts of  $\text{Cu}_2\text{O}$ ,  $\text{CuPbSO}_4(\text{OH})_2$ ,  $\text{PbCO}_3$  and  $\text{PbO}$  which are not green. The coin is green, as the amount of chemical substances which are not green is too little to change the color of copper corrosion. Also a judgment based on Raman peak intensities can be made that the amount of  $\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$ ,  $\text{Cu}_2\text{O}$ ,  $\text{PbCO}_3$  and  $\text{PbO}$  in black area is smaller than in green area. Both the areas contain sulfate, which is further proven by the elementary analysis in XPS and EDS, presented later on. Furthermore, tin was the major constituent of bronzes. The stannic oxide  $\text{SnO}_2$  covering on the surface of bronze produced by corrosion bestows bronze with good protective ability. However, Raman signal of  $\text{SnO}_2$  was not observed herein and also tin could not be detected in the experiment later. This might indicate that tin does not exist in the

tested samples or is too low in content to be detected because the Raman signal of stannic oxide on the surface of the bronze is very weak.

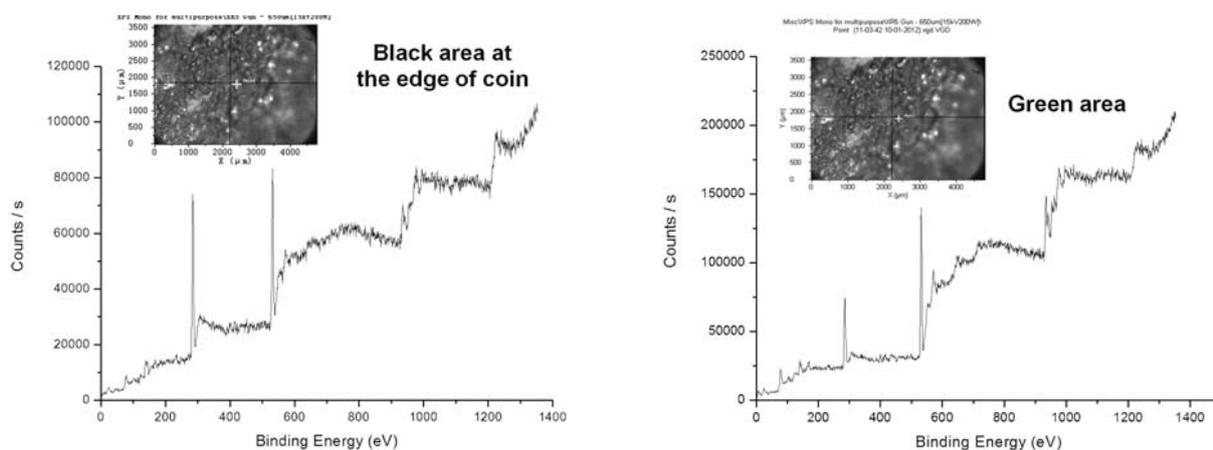
### 3.2. Photoelectron spectroscopy analysis (XPS)

Photoelectron spectroscopy has deeper detecting depth than Raman microspectroscopy, and the two methods are complementary to each other, such that more accurate analytical information could be obtained. Figure 4 shows the XPS of the samples, and the results are summarized in Table 2. It can be seen that the elements in the black and green parts on the copper surface display an obvious difference in percentage. In the green areas, the contents of S, O and Cu are larger than that of the black areas except C. But the content of Pb in the two areas is similar. Cu might be enriched on the surface in the corrosion process. The copper coin surface was seriously corroded, and Raman spectra above show that the corroded layer of the coin contains lead oxide besides copper oxide. Existence of the element Pb in Table 2 fully proves the Raman analysis. Secondly, Sn failed to be detected which is in agreement with the result of Raman spectrum. It shows that the copper coin was manufactured with Cu-Pb, and not with Cu-Sn alloy.

It had been proved that adding Pb into material used to cast bronze Buddha could improve the fluidity of alloy solution in the bronze smelting process and enhance the definition and the dimensional accuracy of the texture on the casting surface [5]. This copper coin was made from Cu-Pb alloy, perhaps in order to make the coins refined in outline, and furthermore to inhibit the corrosion during use, or to keep manufacturing costs low. It reflects that the social productivity level was low in that period.

### 3.3. Energy dispersive spectroscopy (EDS)

Five and three sampling points in the green and black parts, respectively, were selected for EDS. The result of each sampling site is the average of five replicates. Figure 5 (a) and (b) show a typical sampling point and EDS spectra of green and black parts, respectively. The contents of these elements are shown in Table 3. In four points of green area, iron is detected, and all points contain copper and oxygen, and three points are detected to have lead. The average content of copper (mass percent) is close to 30.6%, while lead is only



**Figure 4.** XPS of Chinese ancient copper coin. The sampling points of green and black areas are showed in Figure 1.

**Table 2.** Assignment of XPS of samples and amounts of elemental components (atomic percent: At. % and mass percent:  $\omega\%$ ).

Elements	Green area			Black area		
	Peak/eV	$\omega\%$	At. %	Peak/eV	$\omega\%$	At. %
C1s	284.95	29.25	48.43	284.65	52.35	70.83
O1s	531.75	28.59	35.5	531.8	20.95	21.26
S2p	168.6	14.77	9.17	168.9	9.42	4.78
Cu2p3	934.85	19.7	6.17	934.3	10.13	2.57
Pb4f	138.75	7.5	0.72	139.4	7.15	0.56

3.26%. The surface verdigris layer contains Mg, Al, Fe, Si, S, K, etc., but their contents are all less than 5%.

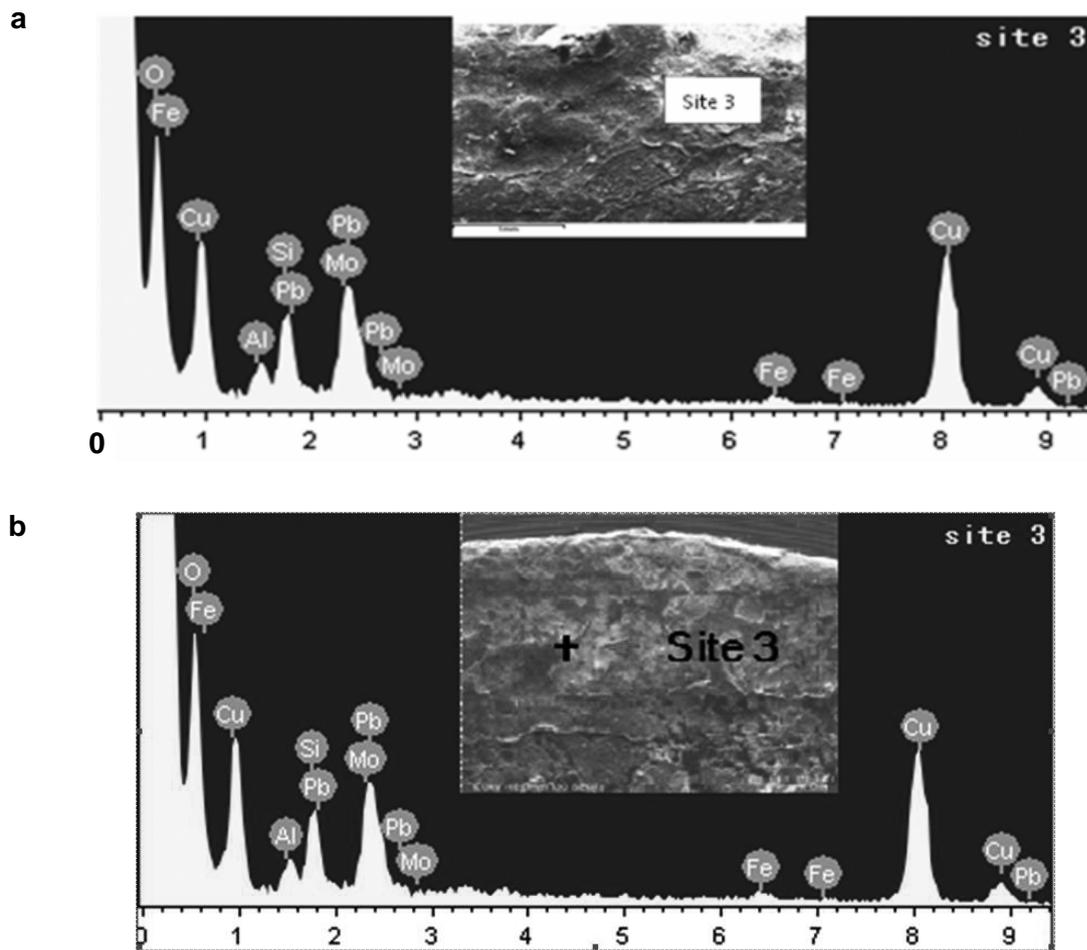
In the three sampling points of the black area, copper and lead are detected. The average contents (mass percent) of copper and Pb are 23.4% and 13.4%, respectively, as shown in Table 3. The content of Pb in the green area is obviously lower than that in the black area. The results are consistent with that of XPS or Raman spectrum. In the black area, the contents of carbon and oxygen are close to 30%. The content of sulfur is a little lower, but slightly higher than that in the green area. In the black areas, other elements such as Al, Si, Fe, Ca, K, Cl, etc. are detected as well.

### 3.4. Discussion

The reliable results on the components of the surface and matrix elements near surface were

obtained by the combination of three non-destructive analytical methods. The contents of Cu or Pb tested by XPS are both less than those tested by EDS. The differences in the results from the three methods should be understandable, which may be because of the error of the methods or the slight differences in the sampling points. In addition, it probably also originated from different penetration depths of the matrix. Based on those reasons, Cu-Pb should be the matrix component near the surface of the coin.

It can be seen from the results from EDS that the contents of elements and even types of elements vary somewhat largely with points at different locations, proving the non-uniformity of the coin. For example, some points contain Pb, but others do not; the content of Pb is high in some parts, but in other parts it is low. So it may be speculated that the corrosion metal center could be divided



**Figure 5.** EDS (a) green and (b) black areas.

**Table 3.** Assignments of EDS of samples and amounts of elemental components (atomic percent: At. % and mass percent: ω%).

Areas	Elements	ω%	At. %
White areas	C, K	18.9 ± 8.4	29.7 ± 12.4
	O, K	40.7 ± 12.2	63.2 ± 11.3
	S, K	0.71 ± 0.42	1.02 ± 0.51
	Cu, K	30.6 ± 6.9	10.6 ± 3.9
	Pb, M	3.26 ± 2.7	0.42 ± 0.35
Black areas	C, K	29.1 ± 9.5	50.0 ± 9.5
	O, K	27.0 ± 0.31	36.1 ± 6.0
	S, K	3.49 ± 0.23	2.31 ± 0.25
	Cu, K	23.4 ± 4.5	8.02 ± 2.8
	Pb, M	13.4 ± 8.0	1.47 ± 1.1

into lead areas of  $\text{PbCO}_3/\text{CuPbSO}_4(\text{OH})_2/\text{PbO}$  and lead-free areas. It may be further proved by heterogenetic metallographic structures, as shown in Raman micrographs in Figure 1. Pb ions leave from a droplet through the porous corrosion layers. Then they are replaced by deposited Cu which is sequentially oxidized to  $\text{Cu}_2\text{O}$ , giving the corrosion process progression  $\text{Pb} \rightarrow \text{Cu} \rightarrow \text{Cu}_2\text{O}$  [4]. On the other hand, to a certain extent, matrix heterogeneity of copper coin may reflect the smelting, casting and productivity level of that period.

The source of iron, silicon, and aluminum is uncertain. It may have been introduced in the metal smelting process or the natural corrosion process. It may also have been introduced by the contact among the coins and the soil in which they were buried. After several exposures of radiation, the color of some parts of the green regions became slightly shallow. It is speculated that it may be because of the radiation evaporation or loss of surface species, such as water. But the mass of the coin is not significantly reduced. So the radiation exposure may have lead to slight change of verdigris in structure.

#### 4. CONCLUSION

The non-destructive analysis by Raman microscopy, X-ray photoelectron spectroscopy and X-ray energy dispersive spectroscopy shows that the *Sui wuzhu* is a copper-lead alloy. The green area mainly contains verdigris, lead sulfate/lead carbonate, and cuprous oxide. Copper matrix is heterogeneous in composition and metallographic structure. To a certain extent, it reflects the smelting and casting level at that period. The non-uniformity of the matrix and the differences of corrosion environment resulted in the formation of heterogeneous corrosion on the copper surface. The results might also be significant in understanding Chinese ancient cultures and exploring ancient social issues [11, 12, 13].

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