# Study on trace element of Yue ware unearthed at different kiln sites

WU Juan (吴 隽), LI Jiazhi (李家治), GUO Jingkun (郭景坤),

(Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China)

XU Kai (徐 锴) and CHEN Baolin (陈宝林)

(Shanghai Institute of Metrology and Testing Technology, Shanghai 200000, China)

Received January 14, 1999

**Abstract** The contents of trace element of Yue ware excavated in Shaoxing, Shanglinhu, Shangyu kiln sites and Hangzhou palace were analyzed by NAA technique. The data of trace element compositions were treated by statistical analysis. It is found that the sources of raw materials used in Shaoxing, Shanglinhu, Shangyu kiln sites are different and stable. Especially the discriminant function predicted for porcelain bodies provides high discriminatory power according to production site. It shows that Yue ware specimens excavated in Hangzhou palace were fired in Shanglinhu. It indicates the special function of trace element in the studies on site identification.

**Keywords:** NAA, Yue ware, trace element, statistical analysis.

The dating and siting of ancient ceramics has always received considerable attention. In addition to determining the date and site by vessel shape, ornament and size etc., chemical composition analysis has been increasingly employed in attempt to identify ancient ceramics. However, the major element compositions of the same type of raw material from different regions are similar to each other, and the recipes of some kinds of ceramics often include two or more types of raw materials. Then the major element composition of artifacts is not only dependent on the composition of each kind of raw material itself but also on the proportion of different raw materials. Undoubtedly in these cases, site identification from major element composition becomes more difficult. In contrast, trace element compositions of raw materials with different sources have a distinctive signature respectively, and in general, trace element composition has nothing to do with the quality of wares. It is not necessary and possible for ancient potters to control it. In this way trace element composition can give more reliable predictions for dating and siting studies.

Celadon is widely recognized as the earliest porcelain invented in China and even in the world. It was first produced during the East Han dynasty (206—220 B.C.), and Yue ware manufactured in Cixi, Shangyu, Shaoxing city, Zhejiang Province, China, has remained one of the most important representatives of Chinese ancient ceramics for a long time. As a result of similar appearance and major element composition, it is difficult to determine provenance of these Yue ware artifacts fired at different production sites. In this paper, 26 specimens of Yue ware excavated at Cixi, Shangyu, Shaoxing and Hangzhou city, were selected from reliable strata and were chosen for being typical and representative of the respective sites. The element compositions for all samples were analyzed by NAA, and some new and important information was obtained.

## 1 Experiment

Neutron active analysis is now well established as a powerful tool for analyzing the trace element composition of ancient ceramics. It provides a wide breadth of elements with good precision and accuracy. Especially the analytical result is not influenced by the homogeneity of the materials of ceramic sample.

All samples were cleaned by alcohol and dried. Then the glazes were separated from the bodies of samples. After separating, both bodies and glazes of samples were powdered to a fine powder (200 mesh) in an agate mill. Then the powered samples were sealed and irradiated with neutron in the Reactor of Shanghai Institute of Metrology and Testing Technology. The standard sample was Chinese soil standard GSS-4 and American coal fly ash standard 1663A.

## 2 Multivariate statistical analysis

As a result of the different kinds of ancient ceramics, production place and the development of manufacturing techniques etc., the chemical compositions of ancient ceramics are very complicated. Especially when trace elements were applied in the studies on ancient ceramics, it is difficult to directly describe the variety in the composition by graph. Multivariate statistical analysis is a practical statistical method for treating multi-factors questions; Cluster, Correspondence and Discriminant analyses are some of the most commonly used statistical methods for the studies of ancient ceramics.

### 2.1 Correspondence analysis

Correspondence analysis is a method which extracts most of information using the fewest factors (composed of some weighted variables)——$F_1$, $F_2$ and $F_3$ etc. It can show not only correlation among all samples, but also correlation between significant variables and samples. The data of trace element composition for all sample bodies were treated with Correspondence analysis. Three principal factors ($F_1$, $F_2$ and $F_3$), summarizing 90% of the total variability, were selected and a 3D-scatter is used to convey more statistical information (see figure 1).

### 2.2 Discriminant analysis

Discriminant analysis is a powerful method of distinguishing sample groups. Instead of looking for natural groupings in the data it produces functions that separate known groupings. To group samples more clearly, trace element compositions for all sample bodies and glazes were treated using the stepwise discriminant technique capable of selecting significant variables.

Setting the $F$-value to 2 for selecting and removing variables respectively, the discriminant functions predicted for bodies of Yue ware excavated at three kiln sites are

$$S_1 = -1\,135 - 23.5\text{As} + 2.92\text{La} - 7.334\text{Cs} + 262.72\text{Eu} + 0.91\text{Mn} + 9.94\text{Rb} - 108\text{Sb} - 11.65\text{Sc} - 171\text{Tb} + 15.9\text{Th}, \quad (1)$$

$$S_2 = -937 - 19.94\text{As} + 1.01\text{La} - 3.63\text{Cs} + 270\text{Eu} + 0.9\text{Mn} + 9.5\text{Rb} - 72.3\text{Sb} - 16.22\text{Sc} - 158\text{Tb} + 12.16\text{Th}, \quad (2)$$

$$S_3 = -618.6 - 16.22\text{As} + 2.46\text{La} - 5.05\text{Cs} + 173\text{Eu} + 0.683\text{Mn} + 7.05\text{Rb} - 73.38\text{Sb} - 5.1\text{Sc} - 115.41\text{Tb} + 10.61\text{Th}. \quad (3)$$

Setting the $F$-value to 2.22 for selecting and removing variables respectively, the discriminant

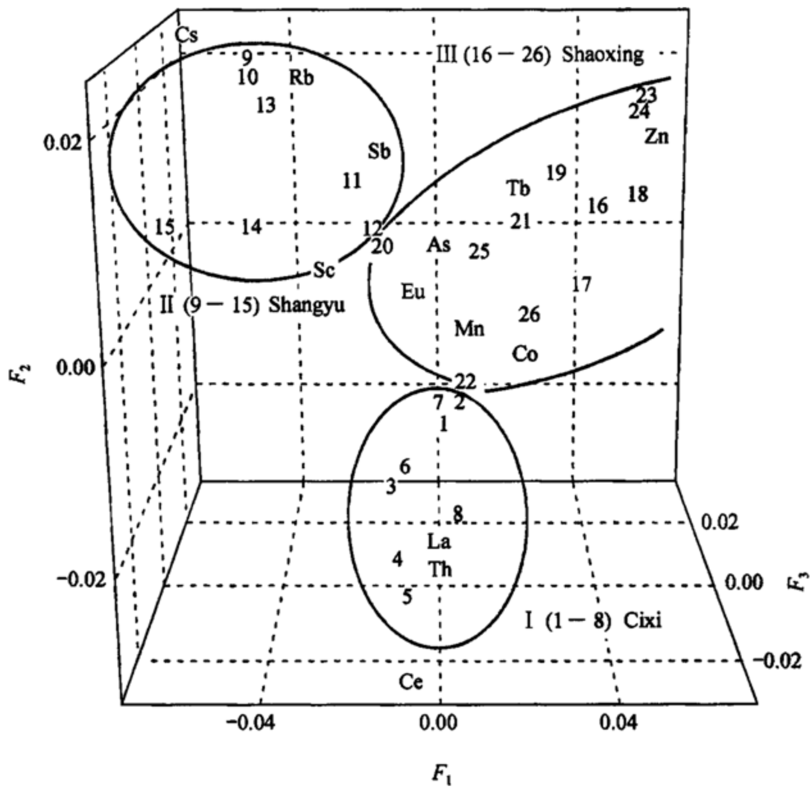


Fig. 1. $F_1$, $F_2$ and $F_3$ factor loading's diagram of Yue ware bodies from different kiln sites.

functions predicted for glazes of Yue ware excavated at three kiln sites are

$$S_1 = -130.55 - 1.05\mathrm{Cs} + 13.91\mathrm{Hf} + 0.55\mathrm{Rb} + 12.28\mathrm{Sc} + 0.21\mathrm{Zn}, \quad (4)$$

$$S_2 = -156.54 - 3.71\mathrm{Cs} + 29.6\mathrm{Hf} + 0.16\mathrm{Rb} + 2.24\mathrm{Sc} + 0.28\mathrm{Zn}, \quad (5)$$

$$S_3 = -139.44 - 1.36\mathrm{Cs} + 14.31\mathrm{Hf} + 0.1\mathrm{Rb} + 17.88\mathrm{Sc} + 0.07\mathrm{Zn}. \quad (6)$$

Any unknown sample can be classified in this way: As, La, Cs, Eu, Mn, Rb, Sb, Sc, Tb, Th, Hf, Zn represent the element concentrations, when the As, Ca, Cs, Eu, Mn, Rb, Sb, Sc, Tb and Th concentrations in sample bodies or Cs, Hf, Rb, Sc and Zn concentrations in sample glazes are substituted into eqs. (1)—(3) or (4)—(6). The group function $S_x$ that delivers the highest value indicates the group the sample most probably belongs to ($S_1$—Cixi Shanglinhu, $S_2$—Shangyu, $S_3$—Shaoxing).

The relative discriminatory power of the variables employed was assessed by the approximate Bartelette $\chi^2$ distribution:

$$\chi^2 = -\ln V[(N-1) - (L+M)/2], \ r \text{ (degree of freedom)} = L(M-1),$$

where $N$ is the number of samples; $L$, number of variables employed; $M$, number of groups; $V$, Wilks statistical value.

As $N$, $L$, $M$ and $V$ for all sample bodies equal 26, 10, 3 and 0.001 435 respectively, $\chi^2 = 121$. Concerning all sample glazes, in similarity, $\chi^2 = 39.8$. Referring to tables of $\chi^2$ distribution value, $\chi^2_{0.005}(r)$, $\chi^2_{0.005}(20) = 40 < 121$, $\chi^2_{0.005}(10) = 25 < 39.8$. This clearly shows that the discrimination functions for sample bodies and glazes are effective. Furthermore, table 1 shows the results of discrimination for all known samples where 100% of the original cases for sample bodies are correctly classified, and except for Shaoxing, 100% of the original cases for sample glazes are also correctly classified. This also demonstrates the validity of discriminant functions.

Table 1 The results of discrimination for all known samples

| | I (Cixi) | | II (Shangyu) | | III (Shaoxing) | |
|---|---|---|---|---|---|---|
| | Body | Glaze | Body | Glaze | Body | Glaze |
| Total | 8 | 4 | 7 | 3 | 11 | 8 |
| Correct classification | 8 | 4 | 7 | 3 | 11 | 7 |
| The ratio of correct classification | 100% | 100% | 100% | 100% | 100% | 87.5% |

2.3 Cluster analysis

Cluster analysis is the statistical method of grouping samples according to their similarities and differences. The data of trace element composition for 15 specimens of Yue ware glazes excavated at Shangyu, Shaoxing and Shanglinhu city, Zhejiang Province, were treated using cluster analysis. Fig. 2 shows the analytical result.

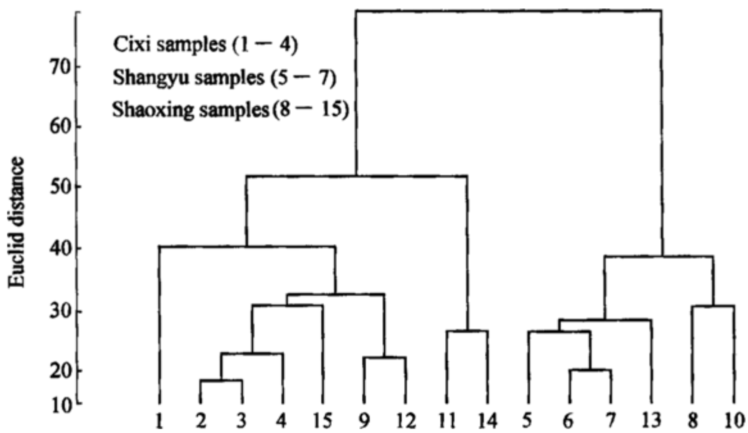


Fig. 2. The result of clustering analysis.

## 3 Discussion

3.1 Characteristic distribution of trace elements for Yue ware bodies from different production places

The invention of Yue ware related closely to the abundance of porcelain stone in southern China, because porcelain stone was the only raw materials used for porcelain production. The early porcelain artifact produced in southern China was a kind of quartz-mica ceramics. The early studies on Yue ware shows that site identification from major element composition is difficult. However, as shown in fig. 1, as far as trace element composition is concerned, there is a clear separation of samples from different production places. All samples may be divided into three groups: samples from Cixi (Shanglinhu), Shangyu and Shaoxing. Group 1 is close to Th, Ce and La but not to Cs, Zn etc. According to principles of Correspondence analysis there are higher Th, Ce, La contents and lower Cs, Zn contents in sample bodies from Shanglinhu compared to other groups. Similarly, Zn, Co, As and

Tb contents in sample bodies from Shaoxing are lower than in any other groups, Cs, Rb and Sb concentration in sample bodies from Shangyu is relatively high and Th, Ce and Co concentration is relatively low. Table 2 lists the mean and variance of characteristic element concentration in sample bodies from different production places. Because porcelain stone was used as the only raw materials for porcelain production, it indicates that the different trace element composition patterns mainly depend on the origin of raw materials used.

Table 2 Mean and variance of characteristic elements concentration in sample bodies from different production places

| | Cixi(Shanglinhu) | | Shangyu | | Shaoxing | |
|---|---|---|---|---|---|---|
| | Mean/$\mu g \cdot g^{-1}$ | Variance | Mean/$\mu g \cdot g^{-1}$ | Variance | Mean/$\mu g \cdot g^{-1}$ | Variance |
| Ce | 134 | 32 | 107 | 286 | 109 | 46 |
| Co | 5.69 | 0.33 | 4.13 | 0.82 | 6.48 | 1.85 |
| Cs | 10.14 | 1.01 | 22.21 | 57 | 10.29 | 3.96 |
| As | 2.07 | 1.36 | 2.46 | 0.51 | 2.67 | 1.03 |
| Rb | 143 | 11.87 | 156 | 184 | 120.7 | 142 |
| Th | 25.4 | 4.27 | 19.39 | 8.67 | 18.64 | 8.42 |
| Sb | 0.786 | 0.006 | 1.82 | 0.226 | 1.27 | 0.059 |
| Tb | 1.17 | 0.06 | 1.33 | 0.066 | 1.89 | 0.21 |
| La | 73.45 | 9.5 | 66.44 | 23.5 | 64.27 | 17.89 |
| Eu | 1.65 | 0.013 | 1.74 | 0.095 | 1.99 | 0.055 |
| Mn | 313 | 406 | 287 | 896 | 348 | 694 |
| Sc | 10.2 | 0.421 | 12.7 | 1.14 | 12.3 | 1.6 |
| Zn | 70.95 | 53.43 | 53.19 | 75 | 94.77 | 265 |

### 3.2 Characteristic distribution of trace elements for Yue ware glazes from different production places

It is widely recognized that the glazes of Yue ware was made from porcelain stone, wood-ash or limestone. There are more factors that lead to a variety of trace element compositions. When divided with Euclidian distance 45, all samples can be grouped into three categories (fig. 2). The first contains all the samples unearthed in Cixi (Shanglinhu) and some unearthed in Shaoxing. The second only contains the samples unearthed in Shaoxing. The third contains all the samples unearthed in Shangyu and some unearthed in Shaoxing. The samples excavated in Cixi (Shanglinhu) and Shangyu are different from that excavated in Shaoxing. They lie in different subcategories. In contrast, the dispersiveness of trace element composition of different sample glazes from Shaoxing was very large. The samples from Shaoxing lie in different subcategories. Table 3 lists the mean and variance of characteristic elements concentration in porcelain glazes from different places (see table 3). With the same recipe, the different composition patterns relate more to the origin of raw materials. The dispersiveness of trace element composition of different sample glazes from Shaoxing shows that the ancient potter may employ the raw materials with different sources. Because fewer of the raw materials were required for glaze manufacture, and Cixi (Shanglinhu), Shangyu and Shaoxing are near to one another, it is possible for ancient potters in Shaoxing to use the porcelain stone, limestone or wood-ash from Shanglinhu and Shangyu. Therefore, the compositions of some samples are similar to that from Shanglinhu or Shangyu.

### 3.3 Site identification of Yue ware

According to different patterns of trace element composition, the discriminant functions predicted for Yue ware bodies from different sites were established (see eqs. (1)—(3)). When the data of characteristic element concentrations were substituted for the fragments of secret color ware unearthed in Hangzhou palace (HY1—7, see table 4), $S_1$ delivers the highest value for each sample (see table 5). Undoubtedly, these tributary wares were fired in Shanglinhu.

Table 3 Mean and variance of characteristic elements concentration in sample bodies from different production places

| | Cixi (Shanglinhu) | | Shangyu | | Shaoxing | |
|---|---|---|---|---|---|---|
| | Mean/$\mu g \cdot g^{-1}$ | Variance | Mean/$\mu g \cdot g^{-1}$ | Variance | Mean/$\mu g \cdot g^{-1}$ | Variance |
| Cs | 4.61 | 2.71 | 12.49 | 12.03 | 6.5 | 1.19 |
| Hf | 5.97 | 0.24 | 7.93 | 0.023 | 6.27 | 0.38 |
| Rb | 74.39 | 5.43 | 92.8 | 9.98 | 65.25 | 56 |
| Sc | 8.48 | 0.21 | 9.5 | 0.07 | 10.81 | 0.5 |
| Zn | 121.5 | 208 | 36.77 | 52 | 76 | 1 262 |

Table 4 The contents of characteristic elements in ware bodies excavated in Hangzhou palace/$\mu g \cdot g^{-1}$

| | HY1 | HY2 | HY3 | HY4 | HY5 | HY6 | HY7 |
|---|---|---|---|---|---|---|---|
| As | 1.38 | 3.25 | 3.29 | 2.31 | 2.7 | 2.81 | 2.33 |
| La | 73.04 | 63 | 56.58 | 70.58 | 61.91 | 92.21 | 71.64 |
| Cs | 11.31 | 14 | 10.33 | 10.14 | 11.63 | 12.51 | 14.07 |
| Eu | 1.7 | 1.74 | 1.48 | 1.93 | 1.61 | 2.82 | 1.8 |
| Mn | 311.8 | 310 | 338.4 | 346.7 | 329.1 | 320.7 | 367 |
| Rb | 151.1 | 151.5 | 147.3 | 145.1 | 170.9 | 158.8 | 153.9 |
| Sb | 0.81 | 0.85 | 0.7 | 0.84 | 0.87 | 1.07 | 0.95 |
| Sc | 10.6 | 11.19 | 10.83 | 10.71 | 10.61 | 13.7 | 11.66 |
| Tb | 1.26 | 1.02 | 1.25 | 1.24 | 1.42 | 2.13 | 1.38 |
| Th | 22.92 | 24.47 | 23 | 24.14 | 23 | 22.18 | 22.39 |

Table 5 The discriminant results of the specimens excavated in Hangzhou palace

| Sample | $S_1$ | $S_2$ | $S_3$ | Discrimination |
|---|---|---|---|---|
| HY1 | 1 133 | 1 093 | 1 038 | Shanglinhu |
| HY2 | 1 096 | 1 078 | 1 010 | Shanglinhu |
| HY3 | 988 | 978 | 933 | Shanglinhu |
| HY4 | 1 164 | 1 127 | 1 056 | Shanglinhu |
| HY5 | 1 223 | 1 205 | 1 101 | Shanglinhu |
| HY6 | 1 301 | 1 248 | 1 166 | Shanglinhu |
| HY7 | 1 142 | 1 122 | 1 049 | Shanglinhu |

## 4 Conclusion

1) Although the major element composition of specimens from different production places show similarity, differences in trace element composition indicated that the origin of the raw materials utilization is different in spite of the same type of raw materials. Except that the raw materials used to manufacture Shaoxing porcelain glazes were probably obtained from different sites, Yue ware produced in Cixi (Shanglinhu) and Shangyu had long-term stable source of raw materials respectively. It means that these sites abound in the raw materials for porcelain production.

2) Yue ware produced at different sites can be classified based on trace element composition. Especially the discriminant function predicted for porcelain bodies provides high discriminatory power according to production site. Besides different types of ceramics artifact, the same type of ceramics

artifact produced at different sites can be classified according to the content of characteristic element too. It accounts for the special function of trace element in the studies on site identification.

3) It was proved that the fragments of Yue ware with good quality excavated in Hangzhou palace were produced in Cixi (Shanglinhu) by discriminant function according to trace element composition. It indicates that Cixi (Shanglinhu) was a very important producer of porcelain ware at that time and also verified great praise of ancient people for the secret color porcelain produced in Cixi (Shanglinhu). This is the first time to directly identify the provenance of secret color porcelain using science and technology method.

## References

1 Chinese Silicate Society, *History of China Pottery and Porcelain* (in Chinese), Beijing: Wenwu Publishing House, 1996, 338.

2 Luo, H. J., *Studies on Basis of Ancient Chinese Ceramics Physical-chemistry and Application of Multivariate Statistical Analysis* (in Chinese), Shanghai: Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1991.

3 Luo, J. Y., Xin, Y., *Economic Statistics and Forecast*, Beijing: Tsinghua University Press, 1985, 248.

4 Deng, Q. Z., Li, J. Z., Zhang, G.Z. et al., Studies on science and technology of Shaoxing yue ware, in *Proceedings of the International Symposium on Science and Technology of Ancient Ceramics* (*ISAC*'95) (in Chinese), Shanghai: Shanghai Scientific Technical Publishers, 1995, 172.