# Nondestructive analysis on ancient porcelain of Longquan Kiln in Zhejiang Province by WDXRF*

FENG Song-Lin(冯松林)[1;1)] FENG Xiang-Qian(冯向前)[1]
ZHU Ji-Hao(朱继浩)[1] XIE Guo-Xi(谢国喜)[1] YAN Ling-Tong(闫灵通)[1]
LI Li(李丽)[1] LI Gang(李刚)[2] SHEN Qiong-Hua(沈琼华)[2]

1 (Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China)
2 (Zhejiang Province Museum, Hangzhou 310007, China)

**Abstract** Nuclear analytical technique is an efficient method in study of rarity cultural relic for its advantage of nondestructive analysis. Longquan celadon is one kind of the most important ancient porcelain in China. In order to determine the inner provenance property and age's characteristic of ancient Longquan porcelain, ten components in porcelain body and glaze were measured by the Wave Dispersive X-ray Fluorescence (WDXRF). Multivariates Statistical Analysis was used to analyze the experiment data. The results showed that the chemical compositions in porcelain body of three typical kilns were similar. The difference of components in porcelain glaze can be used to identify the provenance and age.

**Key words** WDXRF, nondestructive analysis, ancient Longquan porcelain, provenance property, ages characteristic

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## 1 Introduction

X-ray Fluorescence (XRF)[1], Proton Induced X-ray Emission (PIXE)[2] and Synchrotron Radiation X-ray Fluorescence (SRXRF)[3] can be used to nondestructive analyze the elemental composition of samples. This excellence could not be substituted by other analytic methods. These analytic techniques were widely applied in biology, material, geology, agriculture and archaeology[4] for its advantage of nondestructive analysis. Wavelength dispersive X-ray Fluorescence (WDXRF) is clipping, handy and economical multi elemental analytic method. The elemental concentration of $Z \geqslant 11$ can be determined by this method. Especially, it is suite to original position and nondestructive analyze the chemical composition in body and glaze of rarity ancient small porcelain ware.

Longquan Kiln locates Longquan county of Zhejiang Province. It began to fire celadon porcelain since Former Northern Song (960—1127 A.D.) and is famous for its distinctive glaze color in China and other countries. It reached at the height of power and splendour since Later Southern Song (1127—1279 A.D.) to Ming Dynasty (1368—1644 A.D.). Longquan Kiln of Yuan Dynasty (1271—1368 A.D.) and Ming Dynasty was final illustrious period in celadon history of China. Longquan Kiln was consisted of about thousand kilns sites which distributed in the region of Longquan County. Dayao Kiln site which made from one hundred and twenty-six porcelain kiln sites was the most history, art and scientific importance one of Longquan Kiln. It began to fire celadon porcelain since Five Dynasty (907—960

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1) E-mail: fengsl@ihep.ac.cn

A.D.) and closed at Qing Dynasty (1644—1911 A.D.). It was announced as the one of most important cultural relic site of nation and rigorously protected by government. At present, the ancient porcelain of typical Longquan Kiln site has not been systemically scientific studied. Therefore, we have no representational and statistical analytic data to identify the ancient Longquan ware which was handed down from ancient times and excavated from city ruins and mausoleums. The provenance and age's characteristic of ancient Longquan porcelain produced in different kiln site and various history periods can be described by using the experimental data of chemical composition in body and glaze. It would offer the scientific criterion for distinguishing provenance, age and fakemnet. Otherwise, it is very useful to study the manufacture technology, rise and fall of porcelain phylogeny.

## 2 Samples and experimental

In this paper, 144 pieces sherds of celadon porcelain produced in three typical Longquan kilns sites were offered by Zhejiang Province museum. Forty-three pieces sherds of Longquan Dayao Kiln site were produced in the period from Southern Song to Yuan Dynasty. Forty-eight pieces sherds of Longquan Jincun Kiln site were fired in Later Northern Song. Fifty-three pieces sherds of Longquan Xikou Kiln site were manufactured in the period from Southern Song to Yuan Dynasty. A small strip of about 10 mm × 20 mm was cut down from porcelain sherd. The incision section of the sample was polished for nondestructive analysis of Wave Dispersive X-ray fluorescence (WDXRF). The strip specimen was washed in ultrasonic cleaner with tap water and deionized water respectively, and then baked in 80℃for 8 hours. In order to reduce the effect results from the inhomogeneous of elemental distribution in body and glaze, these samples of porcelain body thickness were less than 5 mm and surface was too bend to satisfy the measuring requirement. The X-ray spot of ϕ5 mm was used to measure the porcelain body due to the limitation of body thickness. The X-ray spot of ϕ10 mm was used to analyze the porcelain glaze. In this case, ten pieces samples of Dayao, eleven pieces specimen of Jincun and five samples of Xikou were selected to be analyzed by WDXRF in our experiment.

The WDXRF experiment was performed at the XRF-1800 in Tsinghua University, Beijing of China. The conditions of the experiment are: Voltage of X-ray tube is 40 kV, Current of X-ray tube is 70 mA. Almost all the sample bodies were thicker than 5 mm and their glaze surface was larger enough. The X-ray beam can directly irradiate on the transverse section and glaze surface to determine the elemental composition in the specimen. Ten elemental compositions of $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $TiO_2$, MnO, $K_2O$, $Na_2O$, CaO, Cu and Zn were determined under these conditions. The average values of each elemental composition in porcelain body and glaze are displayed in Table 1 and Table 2.

Table 1. The average contents of chemical composition in body of three Longquan Kilns.

| Kiln site | Ages | Body color | Glaze color | $SiO_2$(%) | $Al_2O_3$(%) | $K_2O$(%) | CaO(%) | $TiO_2$(%) |
|---|---|---|---|---|---|---|---|---|
| Dayao | Southern Song to Yuan Dynasty | Hoariness | Blue | 67.4±1.6 | 28.2±1.1 | 3.09±0.44 | 0.028±0.021 | 0.068±0.010 |
| Jincun | Later Northern Song Dynasty | Grey | Blue with light yellow | 73.0±1.2 | 23.8±1.3 | 1.86±0.26 | 0.024±0.009 | 0.186±0.040 |
| Xikou | Southern Song to Yuan Dynasty | Grey | Blue with light brown | 68.2±5.6 | 25.7±1.1 | 2.04±0.20 | 0.033±0.023 | 0.172±0.057 |
| Kiln site | Ages | Body color | Glaze color | MnO(%) | $Fe_2O_3$(%) | $Na_2O$(%) | Cu/ppm | Zn/ppm |
| Dayao | Southern Song to Yuan Dynasty | Hoariness | Blue | 0.048±0.022 | 0.86±0.08 | 0.40±0.09 | 2.2±0.8 | 12.5±5.0 |
| Jincun | Later Northern Song Dynasty | Grey | Blue with light yellow | 0.013±0.007 | 0.97±0.18 | 0.13±0.04 | 5.0±0.7 | 10.4±3.8 |
| Xikou | Southern Song to Yuan Dynasty | Grey | Blue with light brown | 0.023±0.013 | 1.03±0.05 | 0.18±0.08 | 2.1±0.8 | 14.3±2.6 |

Table 2. The average contents of chemical composition in glaze of three Longquan Kilns.

| Kiln site | Ages | Body color | Glaze color | $SiO_2$(%) | $Al_2O_3$(%) | $K_2O$(%) | CaO(%) | $TiO_2$(%) |
|---|---|---|---|---|---|---|---|---|
| Dayao | Southern Song to Yuan Dynasty | Hoariness | Blue | 72.2±1.1 | 17.9±0.8 | 3.42±0.29 | 4.54±0.53 | 0.049±0.009 |
| Jincun | Later Northern Song Dynasty | Grey | Blue with light yellow | 71.6±2.0 | 18.3±1.1 | 2.12±0.16 | 6.63±1.17 | 0.092±0.064 |
| Xikou | Southern Song to Yuan Dynasty | Grey | Blue with light brown | 73.8±2.0 | 17.6±1.2 | 3.14±0.43 | 4.00±0.49 | 0.055±0.011 |
| Kiln site | Ages | Body color | Glaze color | MnO(%) | $Fe_2O_3$(%) | $Na_2O$(%) | Cu/ppm | Zn/ppm |
| Dayao | Southern Song to Yuan Dynasty | Hoariness | Blue | 0.32±0.13 | 0.87±0.09 | 0.70±0.16 | 5.3±1.2 | 14.7±5.1 |
| Jincun | Later Northern Song Dynasty | Grey | Blue with light yellow | 0.41±0.11 | 0.73±0.28 | 0.18±0.05 | 11.0±3.5 | 14.5±7.3 |
| Xikou | Southern Song to Yuan Dynasty | Grey | Blue with light brown | 0.17±0.06 | 0.85±0.39 | 0.40±0.12 | 4.9±2.2 | 9.6±0.8 |

As shown in table1, the average content of $SiO_2$ of porcelain body in Jincun was (73.0±1.2)% which is the highest one of three typical Longquan Kiln. It was closed to each other for Dayao Kiln and Xikou Kiln. The mean values of $Al_2O_3$ and $K_2O$ in body of Dayao were the highest ones. They reached (28.2±1.1)% and(3.09±0.44)% respectively. The lowest ones of these two chemical composition occurred in the porcelain body of Jincun Kiln. They were (23.8±1.3)% and(1.86±0.26)% respectively. The concentrations of CaO in porcelain body of three typical Longquan Kiln were nearly lower, but it was relatively slight high for Jincun. The average contents of $TiO_2$ and $Fe_2O_3$ in body of Dayao were (0.068±0.010)% and (0.86±0.08)% respectively, they were the lowest ones. There were no evident differences between Jincun and Xikou Kilns. The concentrations of MnO and $Na_2O$ in body of Dayao were the highest ones. They were (0.048±0.022)% and (0.40±0.09)% respectively. The lowest ones occurred in porcelain body of Jincun Kiln. The content of Cu in porcelain body of Jincun Kiln was slight higher than that in Dayao and Xikou. The average contents of Zn were close to each other for three typical Longquan Kilns.

According to the discussion as above, the average concentration of $SiO_2$ in porcelain body of Jincun Kiln produced in Northern Song was the highest, as $Al_2O_3$, $K_2O$, CaO, MnO and $Na_2O$ were the lowest ones. The mean values of $Al_2O_3$, $K_2O$, MnO and $Na_2O$ in porcelain body of Dayao Kiln produced in the period from Southern Song to Yuan Dynasty was relatively higher than other two kilns. The average contents of CaO and $Fe_2O_3$ in porcelain body of Xikou Kiln produced in the period from Southern Song to Yuan Dynasty was relatively higher.

## 3 Results and Discussion

There were no evident differences of average concentration of $SiO_2$ and $Al_2O_3$ in the porcelain glaze of three Longquan Kilns as shown in Table 2. The average contents of $K_2O$ and $Fe_2O_3$ in glaze of Dayao and Xikou Kiln were similar, but it was higher than that of Jincun Kiln. The mean magnitudes of CaO and $TiO_2$ in glaze of Jincun were the highest one, it was close to each other two kiln. The highest average concentration of MnO in glaze was (0.41±0.11)% which occurred in Jincun Kiln as it was the lowest (0.17±0.06)% in Xikou Kiln. The highest magnitude of $Na_2O$ was (0.70±0.16)% which occurred in glaze of Dayao Kiln, as the lowest one was (18±0.05)% in Jincun Kiln. The average content of trace element Cu in porcelain glaze of Jincun Kiln was (11.0±3.5) ppm, it was obvious higher than that of other two kilns. The magnitude of trace element Zn indicated that it was approached in both of Dayao and Jincun Kiln, but it was higher than that of Xikou.

According to the discussion as above, the average contents of $SiO_2$ and $Al_2O_3$ in glaze of three Longquan Kilns were similar. The mean magnitude of CaO, $TiO_2$, MnO and Cu in glaze Jincun increased the highest as that of $K_2O$, $Fe_2O_3$ and $Na_2O$

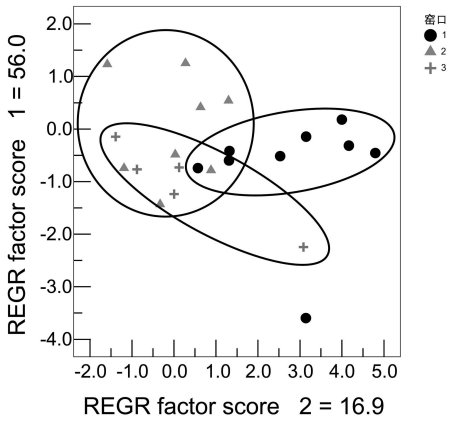


Fig. 1. 1: Dyao 2: Jincun 3: Xikou PCA scatter plot of total data in body.

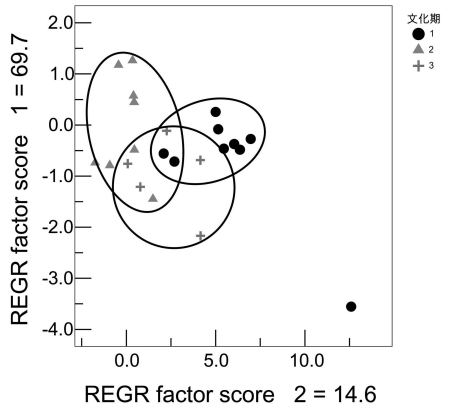


Fig. 2. 1&3: Southern Song to Yuan 2: Later Northern Song PCA scatter plot of main composition in body.

decreased to the lowest. The average concentration of $Na_2O$ in glaze of Dayao reached the highest. The average concentration of CaO, MnO, Cu and Zn in porcelain glaze of Xikou Kiln were the lowest ones.

Principal Component Analysis (PCA)[5] is used to study the provenance and ages characteristic of elemental composition in body and glaze of ancient Longquan porcelain. The outcome of total data in porcelain body of three Longquan Kiln was shown as Fig. 1. It can be observed that the samples points tend to separate as they overlapped each other. The result of main composition $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $TiO_2$, MnO, $K_2O$, $Na_2O$ and CaO in the body was shown as Fig. 2. The sample points of Dayao Kiln in period from Southern Song to Yuan Dynasty and Jincun Kiln in Later Northern Song were clearly separated. The data points of Xikou Kiln in period from Southern Song to Yuan Dynasty were crossed with that of other tow kilns. It was similar with that of Fig. 1. Both results of Fig. 1 and Fig. 2 indicated that the raw materials of porcelain body in different age were closed to each other for three typical Longquan Kilns sites. Therefore, there is no obviously distinction has been found in experiment.

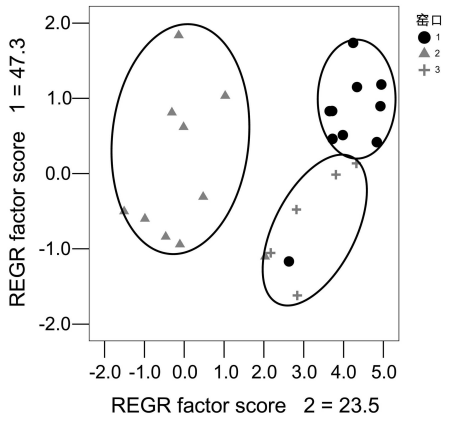


Fig. 3. Dyao 2: Jincun 3: Xikou PCA scatter plot of total data in glaze.

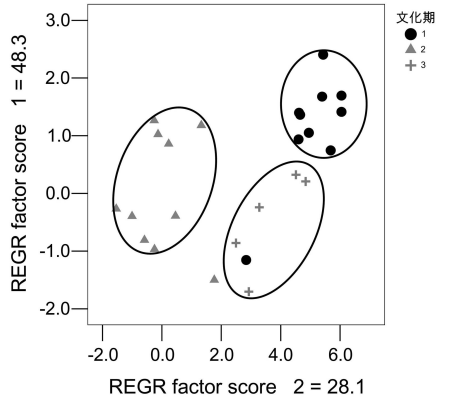


Fig. 4. 1&3: Southern Song to Yuan 2: Later Northern Song PCA scatter plot of main composition in glaze.

The outcome of total data in porcelain glaze was shown as Fig. 3. The sample points of three typical Longquan Kiln distributed respectively in various region. Only one sample point of Dayao and Jincun overlapped in the region of Xikou Kiln. It indicated that raw material of glaze were various for the three typical Longquan Kiln. The obvious difference of provenance characteristic has been observed. This was the scientific criterion to identify the ancient Longquan porcelain. The ages characteristic of main composition $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $TiO_2$, MnO, $K_2O$, $Na_2O$ and CaO in the glaze was shown as Fig. 4. The data points of both Southern Song Later Northern Song distributed in three separated region. Its property was similar with Fig. 3. Both results of Fig. 3

and Fig. 4 indicated that the raw material of porcelain glaze in different age were different to each other for three typical Longquan Kilns. Therefore, this is very valuable scientific criterion to identify the ancient Longquan porcelain.

## 4 Conclusion

The average conten of $SiO_2$ in porcelain body of Jincun Kiln produced in Northern Song was the highest, as $Al_2O_3$, $K_2O$, CaO, MnO and $Na_2O$ were the lowest ones. The average concentrations of $Al_2O_3$, $K_2O$, MnO and $Na_2O$ in porcelain body of Dayao Kiln produced in the period from Southern Song to Yuan Dynasty was relatively higher than other two kilns. The average contents of CaO and $Fe_2O_3$ in porcelain body of Xikou Kiln produced in the period from Southern Song to Yuan Dynasty was relatively higher.

The average contents of $SiO_2$ and $Al_2O_3$ in glaze of three Longquan Kilns were closed to each other. The mean magnitude of CaO, $TiO_2$, MnO and Cu in glaze of Jincun increased the highest as that of $K_2O$, $Fe_2O_3$ and $Na_2O$ decreased to the lowest. The average concentration of $Na_2O$ in glaze of Dayao reached the highest. The average concentration of CaO, MnO and Cu in glaze of Xikou were the lowest ones.

Both results of total data and main element indicated that the raw material of porcelain body in different kiln and ages were closed to each other for three typical Longquan Kilns sites. Both results of total data and main element indicated that the raw material of porcelain glaze in different provenance and age were different to each other for three typical Longquan Kilns. It is very valuable scientific criterion to identify the ancient Longquan porcelain.

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