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Nondestructive Analysis of Celadon Unearthed from Xiangzhou Kiln in Anyang by Portable Spectrometer

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Abstract:

Xiangzhou kiln was an important kiln in northern China from the Northern Dynasty to the Sui and Tang Dynasties. To investigate the locality features and glaze-making technique of the celadon produced in Xiangzhou kiln, this study used portable X-ray fluorescence spectrometer to conduct non-destructive testing on chemical element composition of some celadon and a small amount of white porcelain glaze layer, decorative slip and porcelain body excavated in Xiangzhou kiln in 2009. The data shows that the artifacts unearthed in the kiln site are high-temperature calcium-glazed porcelain; most of the celadon-glazed porcelain belong to unselected porcelain. The level of potassium content in the glaze will affect the firing state, and the level of titanium content in the glaze will affect the glaze browning or bluing. The kiln workers used decorative slip with similar composition as porcelain body to improve the celadon product quality and achieve the effect of body protection and whitening. The results show that it is feasible to use portable X-ray fluorescence spectrometer to study the provenance of porcelain, which provides a real and reliable database for the future provenance analysis of porcelain in Sui Dynasty, and provides scientific data for the research on the raw material preparation technology of Xiangzhou kiln porcelain.

Keywords*: Xiangzhou kiln, Sui Dynasty, Northern China, portable X-ray fluorescence spectrometer, Chemical composition.*

I. INTRODUCTION

Anyang, one of China's eight ancient capitals, is located at the junction of Henan, Hebei and Shanxi provinces. It has a very important geographical location, a long history and rich archaeological resources. Since the discovery of Xiangzhou kiln site on the south bank of the Anyang Bridge on the Huan River in Anyang City in 1974, four archaeological excavations have been carried out [1]. Several archaeological excavations have basically clarified the creation and continuation era, layout, technical characteristics, and artifacts types of Xiangzhou kilns. Xiangzhou kiln was founded in the Northern Dynasties. The Sui and Tang dynasties were the most prosperous period for the development of Xiangzhou kiln, during which, it became one important kiln for firing celadon in the northern region at that time [2]. Xiangzhou kiln was also an early kiln for firing white porcelain at that time. The artifacts fired in Xiangzhou kiln boast various types, superb firing skills, extraordinary decorative techniques, distinctive era and geographical features. Moreover, it is also one kiln for large-scale white porcelain firing in the history of ancient Chinese ceramics development, reflecting high-level development of human economy, culture and politics at that time [3].

The research materials of this paper are based on the third archaeological excavation of Xiangzhou kiln site [4]. Portable XRF was used to conduct non-destructive analysis and research on relevant samples, which increases the understanding of the raw material preparation process of porcelain produced in Xiangzhou kiln, and also provides a stable and reliable database for studying the provenance of porcelain in Sui Dynasty.

II. MATERIALS AND METHODS

2.1 Materials and Methodology

2.1.1 Materials

In this analysis, the recoverable integrity devices in the H1, H2 and H4 ash pits were selected for component analysis and testing. A total of 256 pieces of porcelain were selected, including 249 pieces of celadon porcelain. According to different firing states and different glaze colors, celadon porcelain was divided into: 14 pieces of smoked celadon porcelain, 22 pieces of brown celadon porcelain, 118 pieces of ordinary celadon porcelain, 64 pieces of Low fired celadon porcelain and 31 pieces of yin-yellow celadon porcelain. 7 pieces of white glaze porcelain were also selected for testing and compared with the test results of celadon porcelain.

2.1.2 Methodology

When analyzing the chemical composition of the porcelain samples, the detection experimental instrument was NITON XL3t portable X-ray fluorescence spectrometer produced by Thermo Fisher, the analysis mode was the ore copper/zinc mode under the "soil & ore" mode. The time was 65 seconds, and eleven chemical elements, such as Al_2O_3, SiO_2, K_2O, CaO, TiO_2, MnO, Fe_2O_3, Rb, Sr, Zr, and Pb, were selected for analysis. The test parts were the porcelain glaze layer, the porcelain body and the decorative slip.

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III. EXPERIMENTAL RESULTS and DISCUSSION

3.1 Experimental Results

This detection experiment using portable X-ray fluorescence spectrometer is divided into four parts. The first part is to detect the chemical composition of the glaze layer of the Xiangzhou kiln celadon samples; the second part is to detect the glaze layer chemical composition of the white porcelain samples; the third part is to select the artifacts with more exposed decorative slip from the celadon samples of Xiangzhou kiln, and then detect its body, glaze and decorative slip; the fourth part is to detect the chemical composition of some celadon and white porcelain bodies.

According to the portable XRF analysis results, eleven chemical compositions including Al_2O_3, SiO_2, K_2O, CaO, TiO_2, MnO, Fe_2O_3, Rb, Sr, Zr, and Pb were selected for analysis. TABLE I lists the mean and standard deviation of element composition of glaze layer of Xiangzhou kiln samples according to different firing states and different glaze colors.

TABLE I. Mean and standard deviation (Wt%) of the glaze chemical composition of the experimental samples of Xiangzhou kiln porcelain

TYPE	**MEAN and DEVIATION**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**Zr**	**Sr**	**Rb**	**Pb**
SMOKED CELADON(N=14)	MEAN	6	4	1	8	0	0	2	0	0	0	0
	SD	1.919	8.731	0.278	1.906	0.045	0.014	0.692	0.003	0.005	0.001	0.013
BROWN CELADON(N=	MEAN	6	4	1	7	0	0	2	0	0	0	0
	SD	2	8	0	1	0	0	0	0	0	0	0
ORDINARY	MEAN	7	4	1	1	0	0	1	0	0	0	0
	SD	2	9	0	2	0	0	0	0	0	0	0
LOW FIRED	MEAN	5	3	0	7	0	0	1	0	0	0	0
	SD	1	8	0	2	0	0	0	0	0	0	0
YIN-YELLOW	MEAN	5	4	1	9	0	0	1	0	0	0	0
	SD	1	8	0	2	0	0	0	0	0	0	0
WHITE GLAZED	MEAN	7	5	0	1	0	0	0	0	0	0	0
	SD	0	2	0	0	0	0	0	0	0	0	0

3.2 Discussion

3.2.1 Instrument Feasibility Analysis and Judgment

In the chemical composition of Xiangzhou kiln porcelain, Zr (zirconium), Sr (strontium), and Rb (rubidium) are rare earth elements. Seen from the test results, rare earth elements in the experimental samples have a content of less than 0.1%. The content of rare earth elements in porcelain is not controlled by ancient kiln workers, but is mostly affected by the provenance of the raw materials for making porcelain, which can be used to study the provenance of ancient porcelains [5]. The porcelain glaze test data of the samples shows that the rare earth elements of the samples are relatively consistent, with little fluctuation. The glaze layer of the celadon samples has relatively consistent content of rare earth elements with that of white porcelain samples. It is speculated that the porcelain glaze materials of Xiangzhou kiln site came from the same place. Due to the lack of comparison of porcelain kiln sites in the same period, in order to prove the feasibility of portable X-ray fluorescence spectrometer in the study of the provenance of porcelain, 10 samples were randomly selected from the test results, and XRF detection data of porcelain flake samples from Yaozhou kiln, Yue Kiln and Ru Kiln selected from the porcelain specimen bank of the College of Archaeology and Museology of Peking University were processed and the social statistics software SPSS18.0 was used to conduct multivariate statistical research on the analysis results [6]. The analysis results were plotted as a scatter plot (Figure 1).

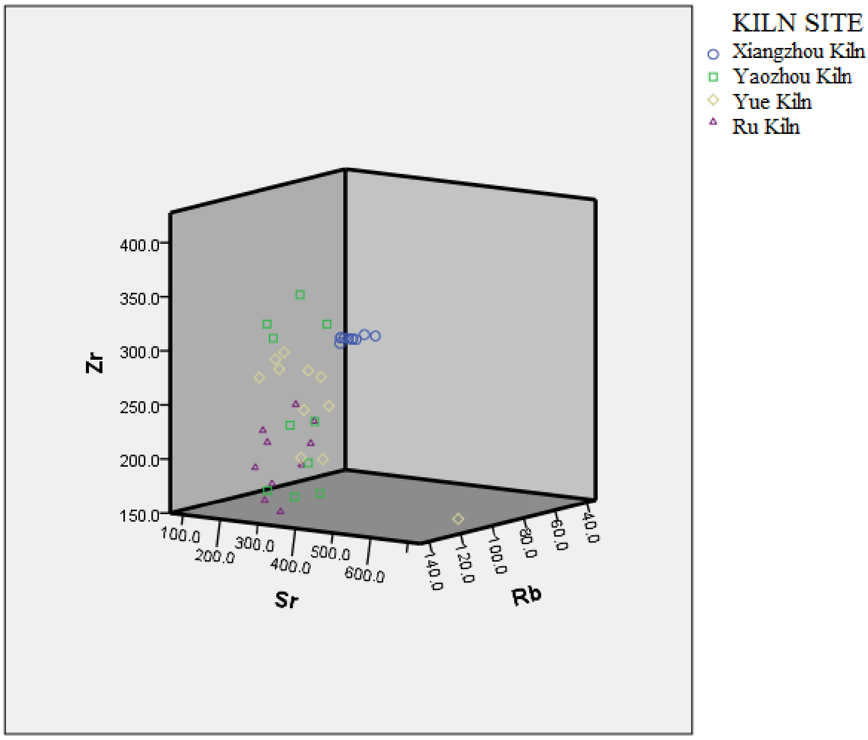

Fig 1: statistical analysis results of Yaozhou kiln, Yue kiln, Ru kiln and some celadon porcelains

3.2.2 Analysis on the flux chemical composition in the glaze layer of Xiangzhou kiln porcelain

Pb (lead), CaO (calcium oxide) and K_2O (potassium oxide) in the detected porcelain samples are used as fluxes, which reduces the firing temperature of the fetal glaze in the porcelain firing [7]. As shown in Figures 2 and 3, the content of Pb (lead) in the sample is extremely low, the average content of K_2O (potassium oxide) is 1.2%, and the average content of CaO (calcium oxide) is as high as 9.2%, indicating that porcelain glaze of Xiangzhou kiln porcelain samples is high temperature calcium glaze, rather than low temperature lead glaze. Therefore, it is inferred that the products produced by Xiangzhou kiln are all porcelain.

According to the different firing temperature, firing state and glaze color of Xiangzhou kiln porcelain products, the experimental samples are divided into three groups. The first group is raw fired celadon porcelain samples and yin-yellow celadon glazed porcelain samples, whose firing temperature is low. The second group consists of celadon samples, browned celadon samples and smoked celadon samples, whose firing temperature is higher. The third group consists of white porcelain samples, which are compared with the celadon samples.

It can be seen from TABLE I and Figure 2 that, in the first group of samples, the raw fired sample has 0.97% potassium oxide on average and yin-yellow sample has 1.11% potassium oxide on average. In the second group of samples, celadon sample has 1.29% potassium oxide on average, brown sample has 1.33% potassium oxide on average, and smoked sample has 1.67% potassium oxide on average. The three celadon samples with low firing temperature in the first group have significantly lower average content of potassium oxide than the three celadon samples with high firing temperature in the second group. It can be speculated that potassium oxide content affects the firing state and quality of Xiangzhou kiln porcelain to some extent. The content change of potassium oxide in the glaze is mainly reflected in the proportion of flux raw materials in the glaze formula. It can be speculated that Xiangzhou kiln celadon has immature flux formula, and the level of potassium oxide may affect the firing quality of Xiangzhou kiln celadon.

The average content of potassium oxide in white glaze samples is 0.91%, which is lower than that of celadon products; the average content of calcium oxide is 10.33%, which is higher than that of celadon samples. It is speculated that white porcelain of Xiangzhou kiln has different flux formula compared to celadon.

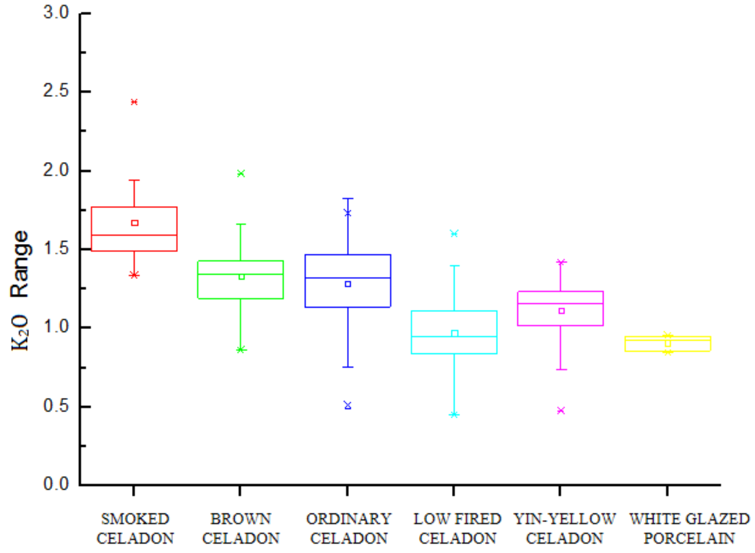

Fig 2: Box diagram of flux K_2O content in Xiangzhou kiln glaze

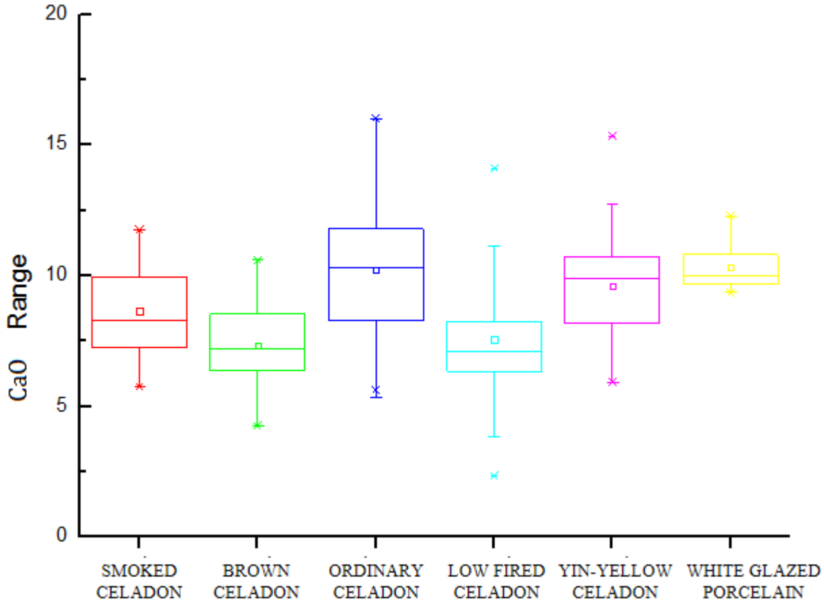

Fig 3: Box diagram of flux CaO content in Xiangzhou kiln glaze

3.2.3 Chemical composition analysis of color formers in the glaze layer of Xiangzhou kiln porcelain

TiO_2 (titanium dioxide), MnO (manganese oxide) and Fe_2O_3 (iron trioxide) are color formers in the glaze, which play a decisive role in the hue of the body glaze [8]. Considering low content of manganese oxide in the glaze, manganese oxide is not discussed here. As shown in Figures 4 and 5, there are significant differences in the content of colorants in the porcelain samples of different glaze appearances.

Nigle Wood's experiments show that the celadon glaze with more than 0.2% titanium oxide is grayish and greenish [9]. The reduction of titanium oxide content in celadon glaze renders more pure celadon color. As shown in Figure 4 and TABLE I, for the two types of celadon products with low firing temperatures in the first group: the average content of titanium dioxide in the raw fired samples is 0.36%, that in yin-yellow samples is 0.36%, which is much lower than that of the three types of celadon products with higher forming temperature in the second group. The average content of titanium dioxide in celadon samples is 0.397%, that in brown samples is 0.45%, and that in smoked samples is 0.4%. White porcelain samples have 0.17% titanium dioxide on average, which is much lower than that of raw fired celadon with low firing temperature.

As shown in Figure 5 and TABLE I, white porcelain samples have 0.85% iron trioxide on average. In the first group of samples, raw fired samples have 1.95% iron trioxide on average, yellow samples have1.8% iron trioxide on average, yin-yellow samples have1.92% iron trioxide on average. In the second group of samples, celadon samples have 1.64% iron trioxide on average, brown samples have 2.04% iron trioxide on average, smoked samples have 2.26% iron trioxide on average. White porcelain samples have much lower average content of iron trioxide than the five types of celadon samples; ordinary celadon samples have much lower average content of iron trioxide than the other four celadon samples.

To sum up, white porcelain samples have much lower average content of iron trioxide and titanium oxide than the five types of celadon samples. It can be speculated that the white porcelain of Xiangzhou kiln is fired at high temperature with a low-titanium and low-iron color-forming formula, but the content of color former in white porcelain is generally low, resulting in white body and transparent glaze in appearance. The celadon samples tested this time are the products of the Xiangzhou kiln in its heyday, but the Xiangzhou kiln belongs to early northern celadon kiln site, and the color former has unstable formula according to the test results. It is speculated that the porcelain-making technology of the Xiangzhou kiln was imperfect at that time.

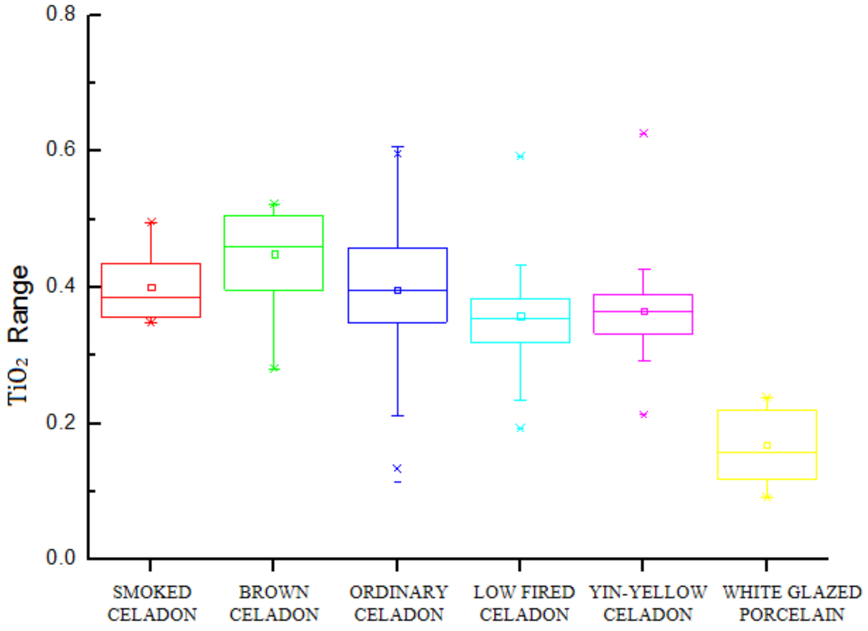

Fig 4: Box diagram of TiO_2 content of color former in Xiangzhou kiln glaze

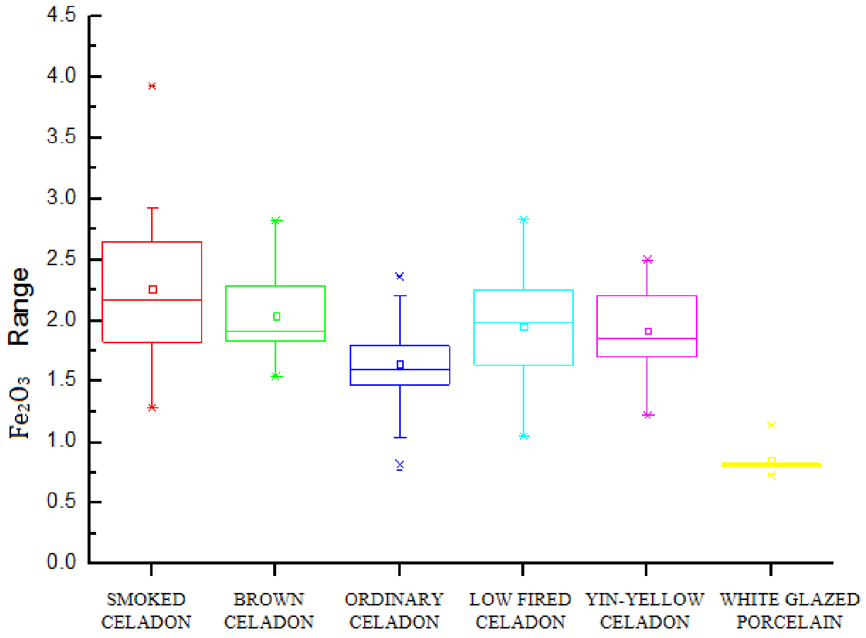

Fig 5: Box diagram of Fe_2O_3 content of color former in Xiangzhou kiln glaze

3.2.4 Analysis on Chemical Composition of Decorative Slip from Xiangzhou Kiln

Decorative slip is a kind of mud made of processed porcelain clay with high aluminum content and low iron content, which is applied between the glazes of the porcelain body. Kiln workers apply decorative slip between the body glaze and on the rough surface of the porcelain body to improve the product quality, enrich the porcelain decoration, and finally achieve the purpose of changing the color [10]. When kiln workers in northern China kilns in the Sui Dynasty applied decorative slip to porcelain, they often chose white raw materials with high aluminum, low iron content or no iron to improve the surface smoothness of the porcelain body, brighten the porcelain glaze color, so that the porcelain glaze color gets light and almost white, thus achieving the effect of fine work despite coarse material [11].

Figure 6 is plotted according to the test results of celadon samples applied with decorative slip. As shown in the figure, the average contents of rare earth elements Zr (zirconium), Sr (strontium) and Rb (rubidium) in the celadon glaze layer are 0.27%, 0.12% and 0.005%, respectively. The average contents of rare earth elements Zr, Sr and Rb in the porcelain body are 0.03%, 0.007%, and 0.006%, respectively, and the average contents of rare earth elements Zr, Sr and Rb in the decorative slip are 0.03%, 0.007%, and 0.006%, respectively. Decorative slip has similar content of rare earth elements as the porcelain body, indicating that the raw materials of decorative slip and porcelain body are from the same source, and porcelain glaze layer, porcelain body and decorative slip have relatively low and stable rare earth content, which provides the basis for applying the detection data herein to the research on the provenance of porcelain in the Sui Dynasty.

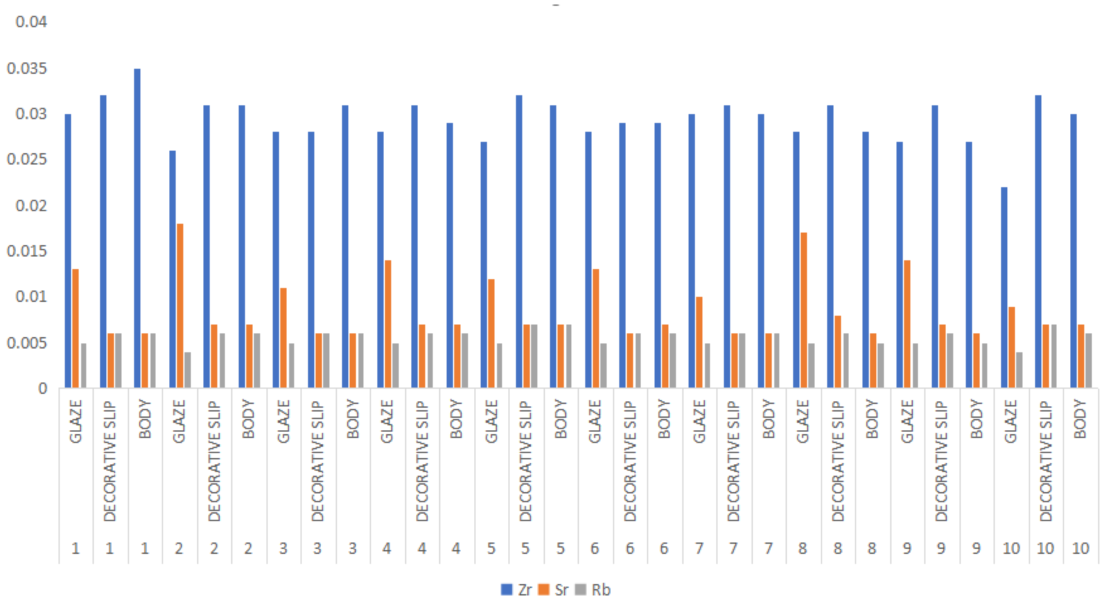

Fig 6: Histogram of the content of rare earth elements Zr, Sr and Rb in the body, glaze and decorative slip of Xiangzhou kiln celadon samples

Figures 7 and 8 show that the average Al_2O_3 content of celadon glaze layer, porcelain body and decorative slip are 6.8%, 13.28% and 13.57% respectively. The average contents of Fe elements in color formers of celadon glaze layer, porcelain body and the decorative slip are 1.32%, 0.98% and 0.8%, respectively. The average contents of Ti elements in color formers of celadon glaze layer, porcelain body and decorative slip are 0.24%, 0.5% and 0.5% respectively. Mn element in color formers is detected in some celadon glaze, but is basically not detected in porcelain body and decorative slip. Celadon decorative slip and porcelain body have very close aluminum oxide content and color former elements. The celadon decorative slip has the lowest iron content and the highest aluminum oxide content, which proves that decorative slip of the Xiangzhou kiln celadon uses white raw materials with high aluminum and low iron content. The color former in the detected samples has the highest iron content among the three elements Fe, Mn and Ti, which makes the celadon glaze lighter and proves the grey body characteristics of Xiangzhou kiln's celadon.

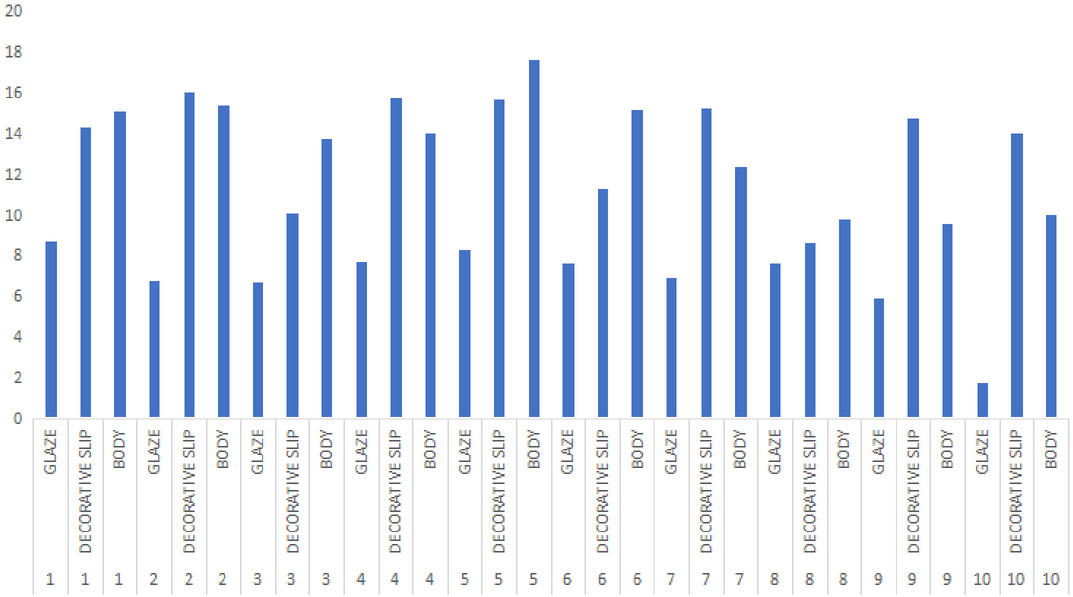

Fig 7: Histogram of Al_2O_3 content in body, glaze and decorative slip of Xiangzhou kiln celadon samples

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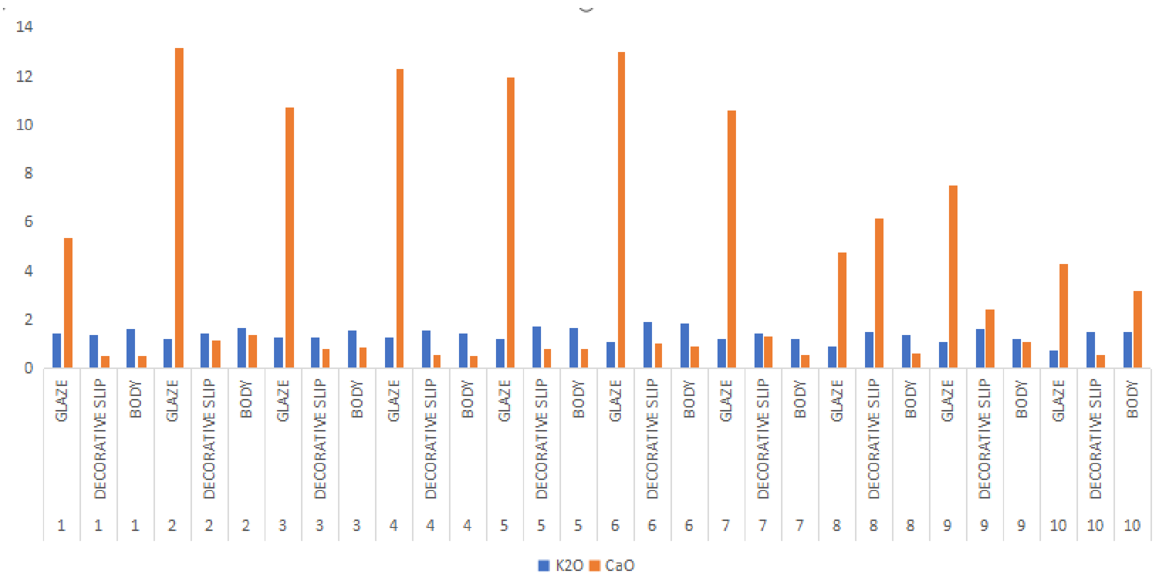

Fig 8: Histogram of the content of Fe, Mn and Ti elements in the body, glaze and decorative slip of Xiangzhou kiln celadon samples

Figure 9 shows that the average content of element Ca is 6.69%, 0.76% and 1.1% respectively in celadon glaze layer, porcelain body and decorative slip. The average content of element K is 0.96%, 1.26% and 1.27%, respectively in flux of celadon glaze layer, the porcelain body and the decorative slip. Decorative slip and porcelain body has similar flux element content. Figure 9 shows that flux Ca element content is the highest in glaze and the lowest in decorative slip, which proves that the decorative slip of Xiangzhou kiln celadon is not fetal glaze, and the raw material of the decorative slip is similar to that of the porcelain body.

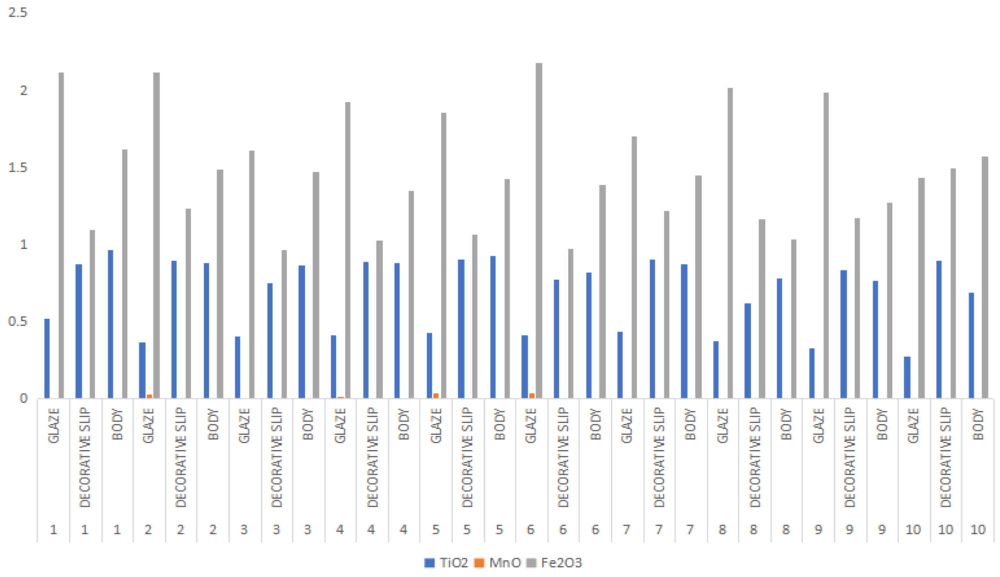

Fig 9: Histogram of the content of Ca and K elements in fluxes in the body, glaze and decorative slip of Xiangzhou kiln celadon samples

To sum up, decorative slip has similar chemical composition as porcelain body. It can be speculated that decorative slip of Xiangzhou kiln celadon is a mud made from high-aluminum and low-iron porcelain body raw materials, rather than fetal glaze, which has porcelain coloration effect.

IV. CONCLUSION

In this paper, a portable spectrometer is used to conduct non-destructive analysis and research on the elemental composition of porcelain glaze, body and decorative slip in various Xiangzhou kiln samples, and the following conclusions can be drawn:

First, SPSS18.0 was used to conduct multivariate statistical analysis on the trace element data of glaze layer of celadon samples in the celadon kiln sites such as Xiangzhou kiln, Yaozhou kiln, Yue kiln and Ru kiln. The portable spectrometer is feasible in the study of the provenance of porcelain, and the detection data of the celadon unearthed from the Xiangzhou kiln site will also provide a real and reliable database for the future provenance analysis of celadon in the Sui Dynasty.

Second, the porcelain clay products in the kiln site are all made of high-aluminum and low-silicon materials, which are the characteristics of typical northern porcelain bodies. The glaze flux of the kiln site products has extremely low lead content, which can be ignored, but it has the highest calcium oxide content and relatively high potassium oxide content. It can be inferred that the Xiangzhou kiln products are not lead-glazed pottery with low temperature lead glaze, but calcium-glazed porcelain with high temperature calcium glaze.

On the other hand, most of the tested samples are unselected porcelain with certain firing defects because they are located in the kiln site. Through p-XRF detection and analysis, flux potassium oxide K_2O in the celadon raw-fired low-temperature samples has lower average content than celadon-fired high-temperature samples. It is speculated that immature use of flux potassium oxide greatly impairs the quality of celadon products. Color former of raw fired samples has lower average content of titanium oxide TiO_2 than normally fired samples; celadon samples have much lower average content of ferric oxide than the other five types of samples. It is speculated that the color former formula of celadon porcelain is immature, and the titanium oxide content in the glaze affects the browning or bluing of the glaze surface. The Xiangzhou kiln site was an early northern celadon kiln site in the Sui and Tang Dynasties. Based on the test results of the fluxes and color formers of the Xiangzhou kiln celadon, it is speculated that the porcelain making technology of the Xiangzhou kiln was immature.

Chemical composition analysis of the fetal glaze interlayer shows that the kiln workers of Xiangzhou kiln consciously used glazing raw materials with small coloring components such as iron in order to produce high-quality celadon. In order to increase the rate of finished celadon products and improve the surface finish of the body, the mud prepared with high-aluminum and low-iron porcelain clay is used to make decorative slip to achieve the effect of body protection and whitening.

The most special seven white glaze samples unearthed in the kiln site provide new clues for studying the development law of white porcelain in the Sui Dynasty and the provenance of white porcelain in northern China. The white glaze porcelain has small color former content, exhibiting white body and transparent glaze. Finally, this paper conducts a non-destructive analysis on celadon produced in Xiangzhou kiln by using a portable X-ray fluorescence spectrometer. The results show that the artifacts unearthed in the Xiangzhou kiln site are high-temperature calcium-glazed porcelain; most of the celadon-glazed porcelain belong to unselected porcelain. The level of potassium content in the glaze will affect the firing state, and the level of titanium content in the glaze will affect the glaze browning or bluing. The kiln workers used decorative slip with similar composition as porcelain body to improve the celadon product quality and achieve the effect of body protection and whitening. The results show that it is feasible to use portable X-ray fluorescence spectrometer to study the provenance of porcelain, which provides a real and reliable database for the future provenance analysis of porcelain in Sui Dynasty, and provides scientific data for the research on the raw material preparation technology of Xiangzhou kiln porcelain.

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