Study on the chemical composition features of Longquan celadon excavated from the Chuzhou site of Huai'an City in Jiangsu Province by EDXRF*

LI Li(李丽)[1,2;1)] FENG Song-Lin(冯松林)[1;2)] FENG Xiang-Qian(冯向前)[1]
XU Qing(徐清)[1] YAN Ling-Tong(闫灵通)[1] MA Bo(马波)[1] HUO Hua(霍华)[3]

[1] Key Laboratory of Nuclear Analysis Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China
[2] Graduate School of Chinese Academy of Sciences, Beijing 100049, China
[3] Nanjing Museum, Nanjing 210000, China

Abstract: A mass of Longquan celadon shards were excavated from the Chuzhou site of Huai'an City in Jiangsu Province, China. These celadon shards were fired during the period of the Late Yuan Dynasty to the Tianshun era of the Ming Dynasty, as identified by archaeologists at Nanjing Museum. In order to research the chemical composition features of this ancient celadon porcelain, energy dispersive X-ray fluorescence (EDXRF) for non-destructive analysis was used to determine the chemical composition of the porcelain body and glaze in these shards. The results indicate that Ti and Fe in the body of Longquan celadon are characteristic elements which can distinguish porcelain produced during the Late Yuan Dynasty from those produced in the Ming Dynasties. The results of the principal component analysis (PCA) show that different body and glaze raw materials were used for the production of porcelain in different periods and the raw materials of the body and glaze are also different for various vessel shapes. The chemical compositions in the porcelain body of civilian ware are slightly different. The imperial and civilian Longquan celadon porcelains produced during the Hongwu era to the Tianshun era of the Ming Dynasty are distinguishable by the MnO, Fe_2O_3, Rb_2O and SrO content in their porcelain glaze.

Key words: Longquan celadon, EDXRF, PCA

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1 Introduction

Chinese ancient celadon began to be fired early in the Late Eastern Han Dynasty (AD 25–220), and the celadon kilns were mainly distributed in South China [1]. The Longquan Kiln is one of the most famous kilns and began to fire celadon in the Southern Dynasties (AD 420–589) and was developed during the Southern Song Dynasty (AD 1127–1279) and the Yuan Dynasty (AD 1271–1368) [2]. In September 2008, a mass of Longquan celadon shards, dating from the late Yuan Dynasty (AD 1325–1368) to the Tianshun (AD 1457–1464) era of the Ming Dynasty (AD 1368–1644), were excavated at the Chuzhou site of Huaian City in Jiangsu Province, China. The provenances of these shards were clearly identified by archaeologists at Nanjing Museum to be the products of Dayao, Longquan Kiln, based on their exterior characteristics. According to the society's developing history, Huai'an City was the hub of water transport in the Yuan, Ming and Qing Dynasties [3, 4]. Huge amounts of Longquan celadon were transported there. After being selected, they were sent to the capital and the defective wares were broke into pieces, therefore, a number of porcelain shards were found in Huai'an City. These porcelain shards consist of imperial and

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

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

civilian wares, and the utensil shapes are of bowl, stem bowl, pot, dish, stem saucer, plate, flower-edge plate and round-edge plate, and so on.

At present, the traditional method for dating ancient Chinese porcelain and distinguishing the imperial ones from the civilian depends on the fact that the shapes and decorations change in different dynasties and wares [5]. However, it is difficult to correctly identify different ancient porcelains using only their visual characteristics because their exterior features vary only slightly or were greatly imitated in later dynasties.

It is well known that the varieties of compositions of major, minor and trace elements in a porcelain body and glaze depend on its raw materials and manufacturing technology [6]. The element information provides important evidence for studying the provenance, date and development of the firing technology of porcelains [7–9]. In this paper, we try to find the elemental features of Chinese ancient celadon porcelains excavated from the Chuzhou site of Huaian City in Jiangsu Province using energy dispersive X-ray fluorescence (EDXRF). The advantage of elemental analysis method is that it can provide high sensitivity, truly simultaneous multi-element, simple and nondestructive analysis. It can be used to determine the elemental concentrations in the porcelain body and glaze [10–12].

2 Experiment

2.1 Samples

Based on the color and decorative glaze patterns, these porcelain shards were identified by archaeologists at Nanjing Museum, most of the shards belong to the products of the Fengdongyan site at the Longquan Kiln. The characteristics of some of the samples were identified to be that of imperial ware from the Fengdongyan site at the Longquan Kiln. In this experiment, eight shapes of wares including bowl, stem bowl, pot, dish, stem saucer, plate, flower-edge plate and round-edge plate were analyzed. The collected samples were divided into 8 groups. Each group consists of fifteen typical shards of ancient celadon, except for the last group which is composed of fourteen pieces of samples. Detailed information about the samples is listed in Table 1. The age of Group 1 is in the late period of the Yuan Dynasty (AD 1325–1368) to the Tianshun era (AD 1457–1464) of the Ming Dynasty (AD 1368–1644), and their exterior characteristics are gray body; the date of Group 2 to 8 is Hongwu era (AD 1368–1398) to Tianshun era of the Ming Dynasty, and their visual characteristics are a light gray body.

Table 1. Detailed information of the samples excavated at the Chuzhou site.

group	utensil	age	number	exterior characteristic
1	bowl	Late Yuan Dynasty to Tianshun era of the Ming Dynasty (AD 1325–1464)	15	Celadon glaze, gray body
2	stem bowl	Hongwu to Tianshun era of the Ming Dynasty (AD 1368–1464)	15	Celadon glaze, light gray body
3	pot	Hongwu to Tianshun era of the Ming Dynasty (AD 1368–1464)	15	Celadon glaze, light gray body
4	dish	Hongwu to Tianshun era of the Ming Dynasty (AD 1368–1464)	15	Celadon glaze, light gray body
5	stem saucer	Hongwu to Tianshun era of the Ming Dynasty (AD 1368–1464)	15	Celadon glaze, light gray body
6	plate	Hongwu to Tianshun era of the Ming Dynasty (AD 1368–1464)	15	Celadon glaze, light gray body
7	flower-edge plate	Hongwu to Tianshun era of the Ming Dynasty (AD 1368–1464)	15	Celadon glaze, light gray body
8	round-edge plate	Hongwu to Tianshun era of the Ming Dynasty (AD 1368–1464)	14	Celadon glaze, light gray body

2.2 EDXRF experiment

A sample of dimensions 30 mm×10 mm was cut from the shard and the cross-section of porcelain strip was polished, then washed three times in an ultrasonic cleaner with deionized water and dried at 105 ℃. The experiments were performed on an EDAX Eagle Ⅲ spectrometer at the Institute of High Energy Physics, CAS, Beijing of China. The spectrometer has a Mo tube and a 125 micron Be window with an incident beam angle of 65° and an emergence angle of 60°. The detector has a liquid-nitrogen-cooled Si(Li) crystal with a resolution of about 160.3 eV at Mn Kα. Due to the limit of the body thickness, the diameter of the X-ray beam spot was selected to be 1 mm. The voltage and the current of the X-ray tube were respectively operated at 40 kV and 250 μA. In order to gain more accurate data, a set of standard reference samples developed by the Institute of High Energy Physics were employed and the homogeneity of the elements in these ceramic reference samples met the requirements for non-destructive quantitative analysis [13]. Several elemental compositions of Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3, CuO, ZnO, Rb_2O, SrO, Y_2O_3 and ZrO_2 were quantified by the fundamental parameter (FP) method [14]. The average values of each elemental composition in the body and glaze are displayed in Tables 2 and 3, respectively. The data of Na_2O and MgO are provided as references because of the poor fluorescence yields and low counting obtained for characteristic X-ray radiation.

Table 2. The average values of each composition in the sample bodies.

group	Na_2O(%)	MgO(%)	Al_2O_3(%)	SiO_2(%)	P_2O_5(%)	K_2O(%)	CaO(%)
1	0.68±0.17	0.35±0.04	18.5±1.7	72.8±1.2	0.052±0.005	4.53±1.08	0.085±0.056
2	0.90±0.21	0.32±0.03	20.8±0.5	70.6±0.8	0.045±0.006	5.15±0.59	0.069±0.034
3	0.88±0.14	0.31±0.05	20.8±0.7	71.0±1.2	0.049±0.005	4.89±0.52	0.083±0.023
4	0.84±0.19	0.29±0.04	20.4±0.5	70.5±0.9	0.051±0.007	5.87±0.64	0.049±0.021
5	0.91±0.12	0.31±0.03	20.4±0.3	71.5±0.4	0.050±0.005	4.65±0.34	0.070±0.020
6	0.81±0.17	0.32±0.04	20.3±1.0	71.1±1.3	0.048±0.006	5.13±0.52	0.064±0.025
7	0.79±0.14	0.33±0.03	18.7±0.8	71.6±1.1	0.046±0.006	6.08±0.23	0.067±0.020
8	0.75±0.15	0.30±0.05	18.5±0.6	72.1±0.8	0.047±0.005	5.93±0.26	0.056±0.017

group	TiO_2(%)	MnO (%)	Fe_2O_3(%)	Rb_2O/ppm	SrO/ppm	Y_2O_3/ppm	ZrO_2/ppm
1	0.37±0.09	0.059±0.031	2.43±0.38	137±27	33±17	28±3	278±25
2	0.15±0.03	0.094±0.029	1.77±0.30	195±16	18±3	41±6	232±14
3	0.14±0.01	0.093±0.016	1.66±0.08	185±15	18±3	45±4	232±10
4	0.16±0.04	0.081±0.013	1.58±0.18	214±18	22±3	38±3	232±10
5	0.14±0.02	0.084±0.021	1.69±0.08	177±9	17±2	46±5	226±9
6	0.19±0.06	0.096±0.019	1.78±0.29	193±14	19±4	40±5	232±15
7	0.23±0.03	0.035±0.009	2.00±0.10	196±8	23±2	40±6	245±12
8	0.21±0.02	0.031±0.005	1.95±0.08	192±9	22±3	38±4	250±25

Table 3. The average values of each composition in the sample glazes.

group	Na_2O(%)	MgO(%)	Al_2O_3(%)	SiO_2(%)	P_2O_5(%)	K_2O(%)	CaO(%)	TiO_2(%)
1	0.49±0.13	0.75±0.09	13.4±0.4	67.9±1.4	0.31±0.04	4.39±0.71	9.55±1.42	0.29±0.05
2	1.02±0.32	0.46±0.08	12.5±0.4	68.1±1.3	0.18±0.02	6.88±1.21	7.74±0.53	0.18±0.02
3	0.95±0.30	0.40±0.06	12.5±0.4	68.0±1.2	0.16±0.02	7.47±1.44	7.58±1.09	0.17±0.03
4	0.95±0.37	0.49±0.09	12.7±0.4	67.2±1.4	0.20±0.03	7.62±1.22	7.64±1.00	0.21±0.05
5	0.77±0.21	0.38±0.07	12.3±0.3	68.8±1.3	0.15±0.01	6.53±0.59	8.20±0.88	0.16±0.02
6	0.82±0.23	0.44±0.09	12.5±0.3	68.4±1.6	0.17±0.04	7.07±0.92	7.57±1.57	0.19±0.03
7	0.58±0.34	0.65±0.08	13.5±0.4	66.6±1.6	0.26±0.04	4.87±1.10	10.43±0.98	0.23±0.02
8	0.47±0.13	0.59±0.09	13.3±0.4	67.5±0.9	0.26±0.02	4.48±0.35	10.47±0.69	0.23±0.03

group	MnO(%)	Fe_2O_3(%)	CuO (%)	ZnO(%)	Rb_2O/ppm	SrO/ppm	ZrO_2/ppm
1	0.94±0.18	1.77±0.29	50±7	103±81	141±18	329±56	263±22
2	0.71±0.06	2.04±0.16	44±7	55±15	183±18	386±54	243±17
3	0.54±0.08	1.98±0.12	44±7	60±16	178±13	348±71	239±33
4	0.71±0.07	2.10±0.15	44±7	89±31	192±12	400±49	242±13
5	0.50±0.05	2.00±0.12	54±9	60±15	172±12	298±50	227±15
6	0.65±0.13	2.02±0.19	46±10	62±23	182±11	392±91	238±17
7	0.85±0.19	1.71±0.10	39±6	93±14	120±6	509±93	247±17
8	0.75±0.08	1.67±0.13	41±4	82±12	117±4	444±65	242±10

3 Results and discussion

3.1 Distinction of a porcelain body fired in the different emperor periods

The analysis data show some element content differences in the porcelain bodies made in the late Yuan Dynasty to the Tianshun era of the Ming Dynasty. As shown in Table 2, the contents of SiO_2, CaO, TiO_2, Fe_2O_3, SrO and ZrO_2 of the porcelain body in Group 1 are higher than those of Groups 2 to 8. The compositions of Al_2O_3, K_2O, Rb_2O and Y_2O_3 in Group 1 are much lower than those of other groups. The contents of Ti and Fe greatly influence the color of the porcelain body. The less the values of Ti and Fe are, the lighter the color of the porcelain body is. Based on the exterior features of these shards, as shown in Table 1, the color of the porcelain body in Group 1 appears gray, while that of Group 2 to 8 is light gray. The average value of Fe_2O_3 in Group 1 is (2.43 ± 0.38)%, while that of Group 2 to 8 varies from (1.58 ± 0.18)% to (2.00 ± 0.10)%. The average content of TiO_2 in Group 1 (0.37 ± 0.09)% is much higher than that of Groups 2 to 8, which are from (0.14 ± 0.01)% to (0.23 ± 0.03)%. The scatterplot of TiO_2 and Fe_2O_3 contents is displayed in Fig. 1. All samples are clearly located in two plot regions. Samples of Group 1 are concentrated in the upper right region while those of Group 2 to 8 are distributed in the lower left region, which shows that different raw materials for making porcelain body were used in the late Yuan Dynasty to Tianshun era of the Ming Dynasty. The concentrations of Ti and Fe can be used to classify these Chinese ancient celadon porcelains into the end of Yuan Dynasty and Ming Dynasty.

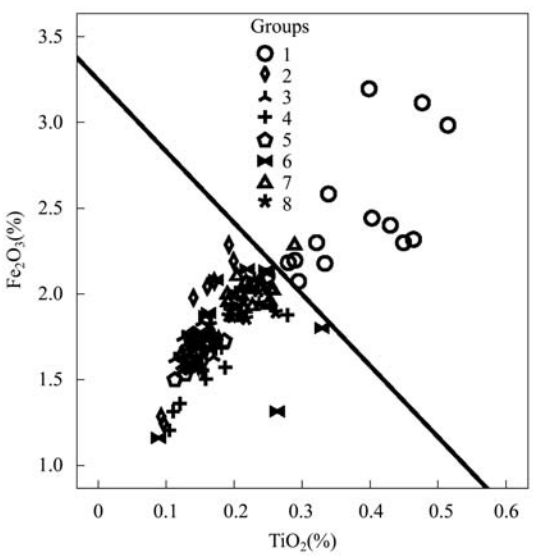

Fig. 1. Scatterplot of TiO_2 and Fe_2O_3 contents in bodies of celadon.

In order to study the pertinence among different wares of these celadon porcelains, principal component analysis (PCA) [15–17] was used to study the experimental data of the samples. The main objective of PCA is to reduce the dimension of the observations through a linear transformation. Low dimensional linear combinations are often easier to interpret and serve as an intermediate step in a more complex data analysis [18]. The results of PCA on the porcelain bodies are shown in Fig. 2. The data of Al_2O_3, SiO_2 K_2O, CaO, TiO_2, MnO and Fe_2O_3 were employed in analysis and the eigenvalue sum of Factor 1 and 2 accounts for 65.7% of the total variance. Three clusters can be clearly seen. Samples of Group 1 located on the upper region are still separated from those of other groups. It means that the speculation that the Group 1 samples were fired in the late Yuan period is reasonable. The data plots of Group 7 to 8 are separately distributed in a small region and those of Group 2 to 6 are widely located in the lower region. The raw materials of Group 7 to 8 were different from those of Group 2 to 6. This means that the kinds of ware are related to the raw materials of the porcelain body.

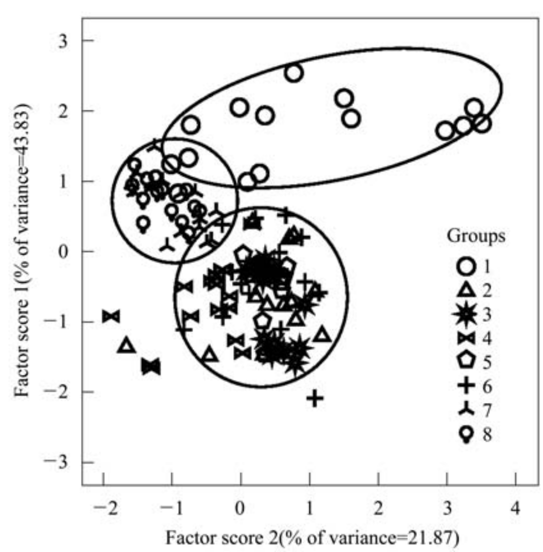

Fig. 2. The analytical result of PCA on all samples.

According to the exterior characteristic of these samples, the wares of Group 1, 3, 5, 7 and 8 belong to civilian porcelain. The contents data of the major element are used for analysis by PCA. The result is shown in Fig. 3. The eigenvalue sum of Factor 1 and 2 is 77.5%. Three sections can be classified: Group 1, Group 7 and 8, Group 3 and 5. A few of the sample plots overlap in Group 1 and Group 7 and

8 because the raw materials and manufacturing technologies are similar. Therefore, the samples of Group 7 and 8 could have be fired in the early Ming Dynasty.

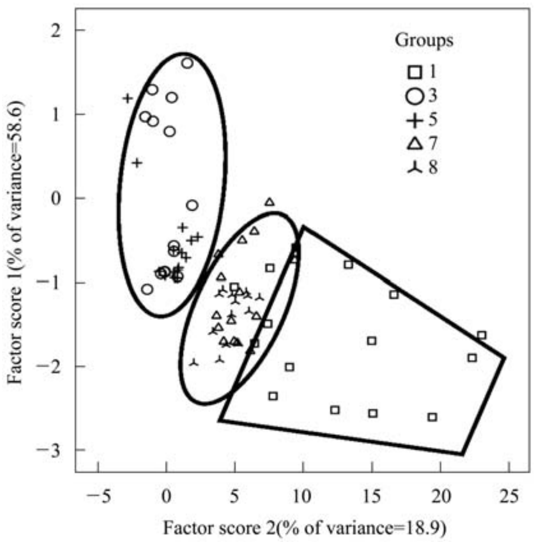

Fig. 3. The analytical result of PCA on civilian porcelain.

3.2 The distinction of porcelain glaze in various groups and differences between imperial and civilian porcelains

The average values of the chemical compositions in porcelain glaze are displayed in Table 3. The composition contents of the glaze in different wares change slightly, which differ from those of the porcelain body, but there are also certain evolutions in the chemical composition of the glaze. The values of Al_2O_3, P_2O_5, CaO, TiO_2, MnO and ZnO elements in Group 1, 7 and 8 are slightly higher than those of Group 2 to 6, but the varieties of K_2O and Fe_2O_3 are opposite. The results are validated in Fig. 4 where the results of PCA in porcelain glaze are shown for porcelain glaze. There are two large clusters in Fig. 4 where the eigenvalue sum of Factor 1 and 2 is equal to 72.7%. The data plots of Group 1, 7 and 8 are scattered in the upper region. It means that the porcelain glaze raw materials in Group 7 and 8 are close to those of Group 1. It also proves that the firing technology was continous and developing. Therefore, the samples of Group 7 and 8 may have been fired in the forepart of the Ming Dynasty. Samples of Group 2 to 6 are distributed in the lower region.

For studying the difference between imperial and civilian wares of Longquan celadon, the content data of compositions in Group 2 to 6 were analysed by PCA, as shown in Fig. 5. According to archaeologists, the Group 2, 4 and 6 samples are imperial wares while Group 3 and 5 are classified

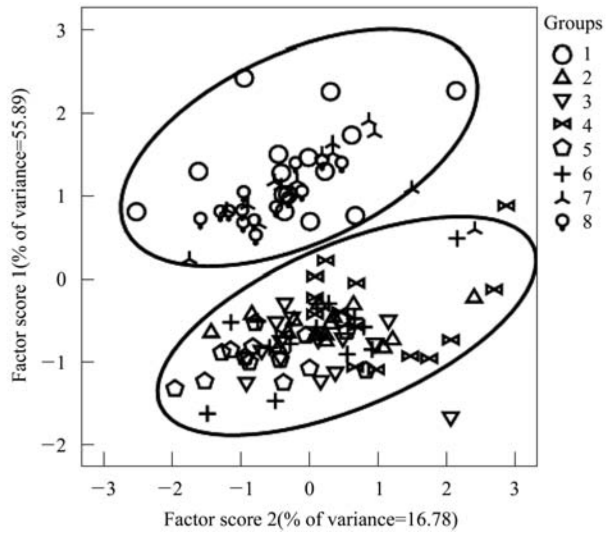

Fig. 4. The analytical result of PCA on the porcelain glaze.

as civilian porcelain. The PCA results of MnO, Fe_2O_3, Rb_2O and SrO are shown in Fig. 5. The eigenvalue sum of Factor 1 and 2 accounts for 71.2 percent of the total variance. Samples of the imperial porcelain are located in the upper regions. That means the ingredients and manufacturing processes of the glaze are strictly controlled for imperial porcelain. These imperial porcelains may have been fired at different times during the Hongwu era to the Tianshun era of the Ming dynasty. Apart from a few plots, most samples of the civilian porcelain are distributed in the lower region. The imperial and civilian wares of Longquan celadon from the Hongwu era to the Tianshun era of the Ming dynasty are distinguished by the contents of MnO, Fe_2O_3, Rb_2O and SrO.

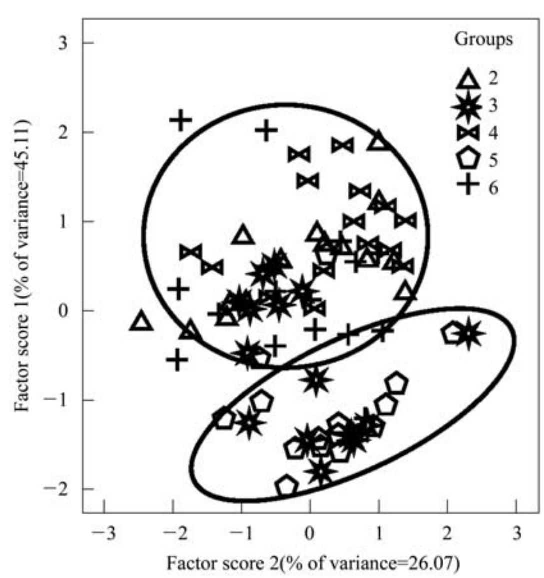

Fig. 5. The analytical result of PCA in the 2 to 6 groups.

4 Conclusions

EDXRF has been used to analyze the elemental compositions in the bodies and glazes of Chinese ancient celadon excavated from the Chuzhou site at Huai'an City in Jiangsu Privince, China. Based on the experimental data, the elemental compositions of the porcelains are various in different periods or wares. Ti and Fe of the porcelain body in Longquan celadon are the characteristic elements which can make a distinction between the late Yuan and Ming Dynasties. The results of PCA indicate that different body and glaze raw materials were used for the production of porcelain in different periods, and the raw body and glaze materials are also different for various vessel shapes. The elemental compositions of the porcelain body of civilian ware are slightly different. The imperial and civilian porcelains of Longquan celadon in the Hongwu era to Tianshun era of Ming dynasty are distinguished by the contents of MnO, Fe_2O_3, Rb_2O and SrO in the porcelain glaze.

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