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PIXE analysis of ancient Chinese Qing dynasty porcelain ☆

Cheng Huansheng [a,*], He Wenquan [a], Tang Jiayong [a], Yang Fujia [a], Wang Jianhua [b]

[a] *T.D. Lee Physics Laboratory, Department of Physics II, Fudan university, Shanghai, 200433, China*
[b] *Peking Palace Museum, Peking, 100009, China*

Abstract

The major and minor chemical compositions and trace element content of white glaze made in Qing dynasty at kuan kiln have been determined by PIXE. Experimental results show that trace element contents Rb–Sr–Zr are useful to distinguish the place of production of ancient porcelain. In the porcelain from different kilns situated in a same province, the trace element contents can be different from each other. Determining and comparing the major and minor compositions and trace elemental concentrations in white glaze by PIXE technique, we can distinguish a precious Qing dynasty porcelain made at kuan kiln from a fake.

1. Introduction

PIXE has proved to be an efficient technique for the analysis of archaeological artifacts. It allows a quick multi-elemental determination of concentrations. In 1979 we have studied in our laboratory a pair of famous 2500 year old swords using an external beam [1]. By analyzing the glaze on the sword guard-ring, the oldest K–Ca glass in China was found. The technique was also used to study the hair of a 3200 year old preserved mummy [2]. We also have applied IBA (PIXE, NRA, RBS) for the characterization of metal and the treatment applied 2200 years ago to enhance the resistance of an arrowhead [3]. In the past two years, nuclear techniques such as PIXE, RBS, NR, micro PIXE, etc., have been used at Fudan University to systematically study ancient Chinese pottery and porcelain, through chemical composition and trace element analysis. We expect to find a realizable method in authenticity, i.e., to distinguish a precious ancient porcelain from a fake. China has a long history of porcelain production. In the past dynasties of China there were some famous kilns at which famous porcelains through the ages were produced. Among them the porcelains made in Ming dynasty (1368–1643) and Qing dynasty (1644–1911) at kuan kiln (located at Jingdezhen, Jiangxi Province) are most famous. The art grade of the porcelain manufacture reached the top position. Of course, there are not lots of such products existing. Recently many fake ancient Chinese porcelains have appeared on the market. In the paper, the major and minor chemical compositions and trace elemental concentrations in white glaze manufactured in the Qing dynasty at kuan kilns (official) are presented.

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* Corresponding author. Fax +86 21 5493232, e-mail hsche@fudan.ihep.ac.cn.

2. Experiment

2.1. Samples

The details are described in Table 1. All the samples studied were produced in Qing dynasty at kuan kiln (Jingdezhen, Jiangxi Province) and differentiated by specialists in Chinese ancient porcelain. We have not found the sample made in the Shun-Zhi (1644–1661) and Yong-Zheng (1723–1735) emperor period.

Table 1
Description of the analyzed ancient porcelain

Sample No.	emperor	Madding age	Type of porcelain shard
1	Kang-Xi	1662–1722	Blue and white glaze bowl
2	Qian-Long	1736–1795	Wucai glaze bowl
3	Jia-Qing	1796–1820	Blue and white wucai glaze bowl
4	Dao-Guang	1821–1850	Blue and white glaze bowl
5	Xiang-Feng	1851–1861	White glaze bowl
6	Tong-Zhi	1862–1874	Yellow glaze bowl
7	Guang-Xu	1895–1908	Blue and white glaze bowl
8	Xuan-Tong	1909–1911	Plastering red glaze bowl

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2.2. Experiments

The experiments were performed at the NEC 9SDH-2 pelletron tandem accelerator in Fudan University, T.D. Lee Physics Laboratory. The studied sample was set in a cylindrical chamber with the diameter of 40 cm. in which the vacuum is maintained at 10^{-7} Torr by a turbo pump. A Si (Li) detector (165 eV FWHM at 5.9 KeV) placed at 90° relative to the beam direction, was used to detect the X-ray emitted from the sample. A collimated 1.0 MeV proton beam with diameter of 1.5 mm was incident on the sample. We used a beam current of 1–3 nA keeping the counting rate lower than 1 kc/s to measure the elements having $11 < z < 26$. This range includes most of the major elements in the case of ceramics. Heavier elements were analyzed with a beam of 2.5 MeV protons, using a 110 μm Al foil to absorb most of the low energy X-ray produced by the major elements. When we studied the large porcelain sample, the external beam PIXE technique was used. This set is at the end of this beam line. A kapton film with thickness of 10 μm is used to isolate the vacuum of beam tube and atmosphere, but this set is not sensitive to the X-rays from light elements Na and Mg because of the atmosphere absorption.

In order to monitor precisely the incident proton charge on the measured sample, the Rutherford Backscattering Spectrum (RBS) technique was utilized to measure the number of protons scattered from a thin Au film (10^{-2} μm) coated on self-supporting C film (10 μg/cm^2). The thin Au/C film was located up stream of the target. The measured results for major and minor chemical composition were compared to those of the reference sample whose chemical composition was determined by ICP method.

3. Experimental results and discussions

Figs. 1 and 2 show a typical PIXE spectrum, the X-ray energy ranges are from 1–8 keV and 6–19 keV respectively. The measured main and minor chemical components are listed in Table 2. In order to easily compare our experimental results with those from other authors, in Table 2 we present the composition of porcelain with the clay matrix. Because the clay matrix of the Chinese porcelain is well known, from the elemental determination with PIXE, the corresponding oxides can be determined. In order to show the difference of chemical composition between glaze and body, the chemical composition of body for sample No. 5 (Xian-Feng porcelain Body) is also included in Table 2. From Table 2 we can see that during the period of the Qing dynasty the chemical composition of white glaze does not change in an important way for kuan kiln porcelain. For all the studied samples the contents of SiO_2 are among 73–75 wt.%, and the concentrations of Al_2O_3 are between 13.3 and 16.5 wt.%. The content of CaO decreases from Kang-Xi to Tong-Zhi, its data are 3.64 wt.% and 2.2 wt.% respectively, although a little bit of increase appears for sample No. 7. The contents of K_2O show the trends of increasing from Kang-Xi to Guang-Xu and Xuan-Tong. The chemical composition of body for sample No. 5 is in good coincidence with that of sample No. C27 in Ref. [4] which was determined by ICP.

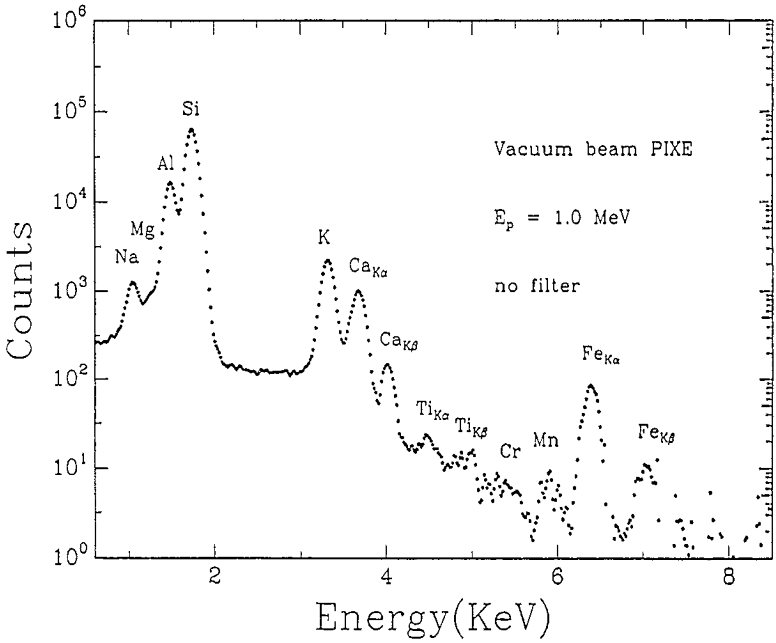

Fig. 1. A PIXE spectrum from an ancient white glaze (up to 8 keV).

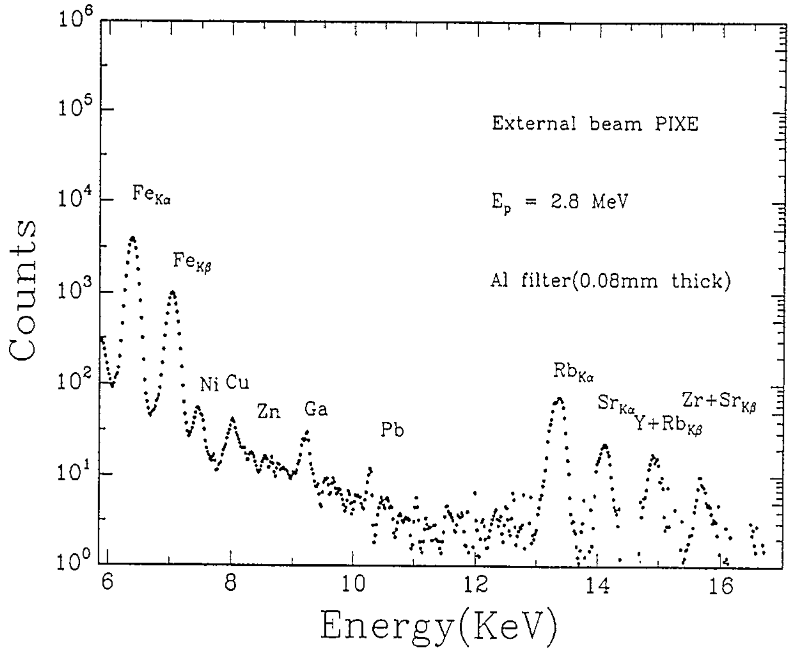

Fig. 2. A PIXE spectrum from an ancient white glaze (6–19 keV).

For all the measured samples the chemical compositions of white glaze are also in reasonable agreement with that of sample No. C14, C15 and C17 in Ref. [4]. It confirms that the measured results by PIXE are correct.

The contents of trace element Ni, Zn, Ga, Pb, Y, Rb, Sr and Zr are listed in Table 3. In contrast, the results from a modern white and blue bowl made in Jianxin kiln, Jingdezhen (1993) are also listed in Table 3. For samples

Table 2
The main and minor chemical composition (wt.%) determined by PIXE

No.	Na_2O	K_2O	MgO	Al_2O_3	SiO_2	CaO	TiO_2	MnO	Fe_2O_3	P_2O_5	SO_2	Cl
1	1.60	3.82	0.52	13.22	75.42	3.64	0.03	0.08	1.58	0.00	0.05	0.00
2	1.09	4.04	0.44	14.01	75.44	3.04	0.13	0.13	1.61	0.00	0.05	0.02
3	1.12	4.22	0.56	13.26	75.81	3.60	0.00	0.06	1.36	0.00	0.00	0.00
4	1.49	4.64	0.55	13.02	74.19	3.93	0.05	0.07	1.92	0.00	0.00	0.05
5	1.43	4.32	0.42	15.04	74.90	2.19	0.02	0.05	1.49	0.00	0.00	0.00 glaze
	1.16	3.39	0.50	22.74	70.60	0.60	0.09	0.05	0.83	0.00	0.03	0.03 body
6	1.19	4.14	0.36	16.57	74.23	2.20	0.07	0.09	1.15	0.00	0.00	0.00
7	2.06	4.20	0.75	15.72	73.03	2.59	0.05	0.06	1.30	0.17	0.00	0.00
8	1.49	4.26	0.11	13.90	77.21	1.90	0.00	0.04	0.97	0.00	0.00	0.00

Table 3
The trace element contents determined by PIXE (ppm)

No.	Cr	Ni	Cu	Zn	Ga	Pb	Br	Rb	Sr	Y	Zr
1	42.0	80.0	44.0	17.0	51.0	14.0	0.0	537.0	85.0	0.0	85.0
2	66.0	67.0	67.0	11.0	57.0	815.0	0.0	690.0	155.0	0.0	155.0
3	46.0	52.0	73.0	12.0	53.0	2478.0	8.0	580.0	75.0	0.0	75.0
4	41.0	55.0	128.0	7.0	44.0	0.0	5.0	505.0	95.0	0.0	95.0
5	36.0	50.0	36.0	7.0	33.0	16.0	0.0	479.0	149.0	0.0	149.0
6	40.0	60.0	65.0	9.0	45.0	4950.0	0.0	498.0	107.0	0.0	107.0
7	19.0	63.0	60.0	15.0	37.0	30.0	4.0	427.0	104.0	0.0	104.0
8	30.0	57.0	44.0	10.0	43.0	740.0	0.0	474.0	123.0	0.0	123.0
9	10.0	68.0	45.0	986.0	32.0	13.0	0.0	535.0	29.0	0.0	24.0

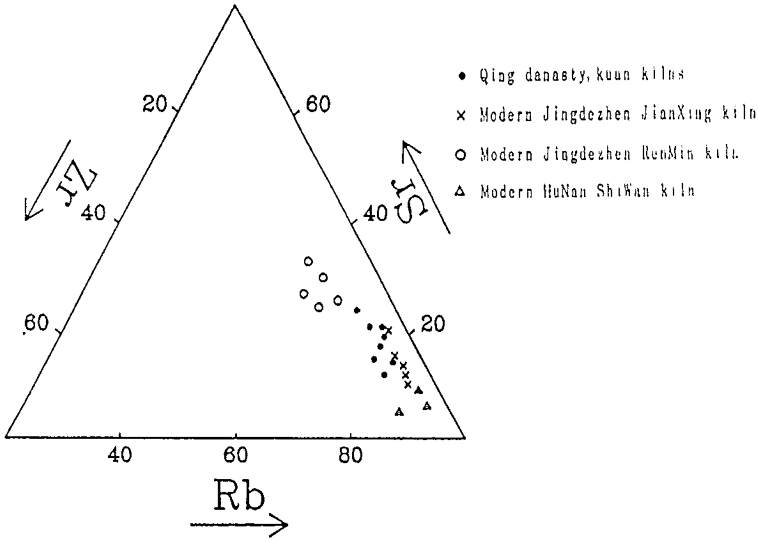

Fig. 3. Rb–Sr–Zr diagram.

No. 2, No. 3, No. 6 and No. 8, Pb is present in the white glaze with a concentration of more than 700 ppm. Table 1 shows that the samples 2, 3 and 8 are lead containing color glaze. During the procedure of firing color glaze, the lead partial pressure was very high, a lead layer deposited on the white glaze surface and diffused into it. Our RBS measurement of the white glaze indicates that the thickness of the layer with Pb is about 200 nm. For all the measured ancient samples the contents of Zn are lower than 20 ppm, but for those of most modern factories in Jingdezhen, the concentrations of Zn are higher than 0.1% in the white glaze. This result is in agreement with that of Yap [5]. We also determined the Zn content in the white glaze made in other 15 modern porcelain kilns, most samples contain Zn with 0.1 wt.%. Only few kiln's porcelain wares don't contain Zn in the white glaze, for example Shiwan (Hunan). Fortunately, their content ratios of major elements (SiO_2/Al_2O_3 and K_2O/CaO) are different from those of Qing dynasty porcelain.

The concentration of trace element is useful to distinguish the production location of pottery and porcelain [6]. We assume total contents of Rb, Sr and Zr are 100%,

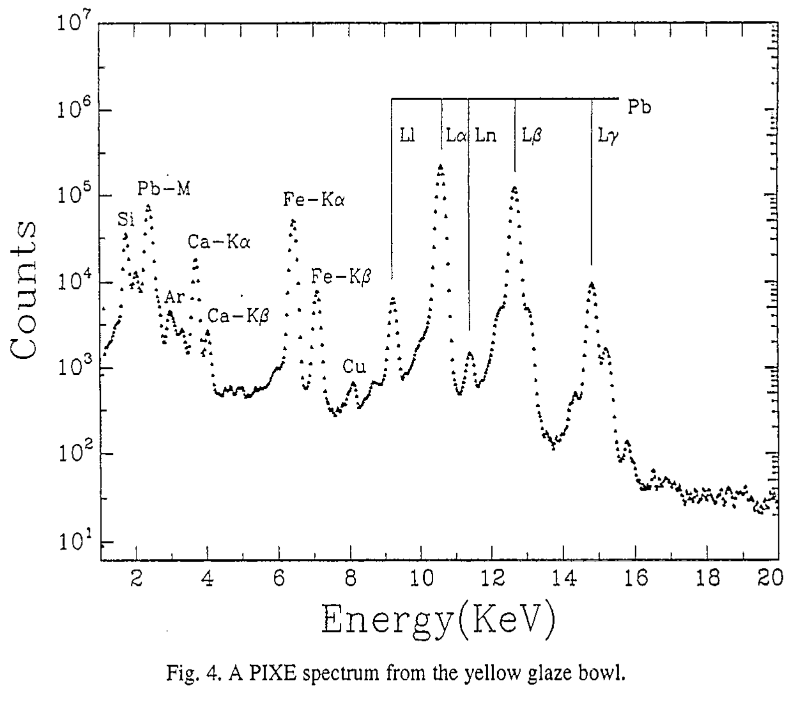

Fig. 4. A PIXE spectrum from the yellow glaze bowl.

$C_{Rb} + C_{Sr} + C_{Zr} = 100\%$, then we obtain the Rb–Sr–Zr diagram showing in Fig. 3. It shows that all the studied samples are clustered in a small area. In Fig. 3 we also plotted the results of three samples in ShiWan (Hunan Province, 1993). They are positioned at the bottom right in Fig. 3. For the samples of Jianxin kiln and Renming kiln in Jingdezhen, they are site at the above and right of ancient porcelain respectively. From Fig. 3 we can see that the samples of modern Jingdezhen Renmin kiln and Shiwan kiln (Hunan Province) depart from those of Qing dynasty kuan kiln. It makes it easy to distinguish each other. The samples from modern Jingdezhen Jianxing kiln are very close to that of Qing dynasty kuan kiln, it is very hard to distinguish each other by this way. But as we have mentioned above, the contents of Zn in all the white glaze of modern Jingdezhen kiln are much higher than those of Qing dynasty kuan kiln. This result also indicates that samples from different kilns in the same province may contain the trace elements with different concentration. Determining and comparing the major and minor chemical compositions and trace elemental concentrations in white glaze by PIXE, we can distinguish a precious Qing dynasty porcelain made at kuan kiln from a fake.

We also would like to mention that in the Qing dynasty yellow glaze bowls and dishes were specially made for the emperor (with yellow glaze on both sides) and empress (with white glaze inside, for example, sample No. 6 in Table 1) only. PIXE analysis indicates all the yellow glaze are rich in lead as shown in Fig. 4.

4. Summary

The major and minor chemical compositions and trace element contents of white glaze made in Qing dynasty at kuan kiln have been determined by PIXE. Experimental results show the trace element contents Rb–Sr–Zr are useful to distinguish the productive place of ancient porcelain. For the porcelain from different kilns situated in same province, the contents of trace element may be different from each other. Determining and comparing the major and minor chemical compositions and trace elemental concentrations in white glaze by PIXE, we can distinguish a precious Qing dynasty porcelain made at kuan kiln from a fake.

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