PIXE Analysis of Ancient Chinese Porcelain of Hutian Kiln

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ABSTRACT

This paper reports the results of the PIXE analysis on Chinese ancient greenish white porcelain and blue-and-white porcelain produced in Hutian Kiln (Jingdezhen district, Jiangxi province) during 10th–14th centuries. The chemical compositions of porcelain body and greenish white glaze produced from Northern Song (AD 960) to Later Yuan (AD 1320-1368), and that of body, white glaze and underglaze blue of blue-and-white porcelains produced in Ming dynasty (AD 1368-1644) are present. The elemental distributions of blue-and-white porcelains were determined by Scanning Proton Microprobe (SPM). The obtained contents for the porcelains produced in the different dynasties were compared. Details of results are presented and discussed.

Keywords: ancient porcelain; Hutian kiln; chemical composition; PIXE

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1. INTRODUCTION

Hutian kiln (Jingdezhen district, Jiangxi province) is one of the most famous sites in Chinese ceramic history. It lasted for 600 years from 10th to 16th century [1]. Although the blue-and-white porcelain produced in Jingdezhen (including Hutian kiln) have been already studied by EDXRF and PIXE [2, 3], the greenish white porcelain produced in Hutian kiln haven’t been reported yet. The age of two materials (kaolin and chinastone) properly combined to produce porcelain body in Jingdezhen is still argued by some researches [4]. So, it is necessarily to study the chemical compositions of greenish white porcelain, determine the fingerprinting of provenance, date and distinguish precious ancient porcelain ware from a fake. PIXE allows a quick determination of concentrations of multi-elements. It has proved to be an efficient technique for the analysis of archaeological artifacts.

2. EXPERIMENTAL

The PIXE experiments were performed at the NEC 9SDH-2 pelletron tandem accelerator in Fudan University, T.D. Lee Physics Laboratory. The experimental conditions were reported in detail by one

| TABLE 1. The chemical compositions (wt%) of porcelains determined by PIXE |
|------------------------|------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Dynasty               | Measure positions | Al2O3 | SiO2 | K2O | CaO | TiO2 | MnO | Fe2O3 |
| Northern Song (NS)     | Body             | 17.92 | 76.53 | 2.89 | 0.40 | 0.036 | 0.08 | 0.60 |
| (AD 1004-1037)         | greenish white glaze | 13.46 | 67.24 | 1.89 | 14.39 | 0.039 | 0.17 | 0.94 |
| Southern Song (SS)     | Body             | 18.88 | 75.21 | 2.82 | 0.63 | 0.460 | 0.57 | 0.74 |
| (AD 1037-1276)         | greenish white glaze | 13.95 | 66.67 | 1.98 | 14.60 | 0.039 | 0.096 | 1.06 |
| Early Yuan (EY)        | Body             | 17.82 | 76.38 | 2.89 | 0.54 | 0.056 | 0.052 | 0.66 |
| (AD 1279-1320)         | greenish white glaze | 13.38 | 66.48 | 1.81 | 15.78 | 0.033 | 0.117 | 0.83 |
| Late Yuan (LY)         | Body             | 21.33 | 72.21 | 2.83 | 0.52 | 0.150 | 0.055 | 1.26 |
| (AD 1320-1368)         | greenish white glaze | 14.03 | 71.29 | 3.05 | 8.66 | 0.060 | 0.100 | 1.24 |
| Ming (M)               | Body             | 18.48 | 74.58 | 3.41 | 6.79 | 0.033 | 0.082 | 1.34 |
| (AD 1368-1644)         | white glaze      | 13.17 | 72.91 | 4.06 | 6.79 | 0.033 | 0.100 | 1.24 |
|                        | underglaze blue  | 13.43 | 71.61 | 4.21 | 6.34 | 0.640 | 1.05 | 1.44 |

840.1
of authors in literature [3]. The dynasty and major chemical compositions of ancient porcelain measured by PIXE are shown in Table 1. In order to know the elemental pervasion between the white glaze, underglaze blue and body of blue-and-white porcelain, a piece of blue-and-white porcelain potsherds was measured by Scanning Proton Microprobe (SPM), which was performed by one of authors, Dr. M. Jaksic, in the Laboratory for Ion Beam Interactions, Rudjer Boskovic Institute, Bijenicka, Croatia. The elemental distributions of porcelain are shown in Figure 1.

![Figure 1. Elemental distributions of a piece of blue-and-white porcelain potsherd.](image)

(The colors of diagram indicate the concentrations of elements, scanning size is 500x2000 µm²)

3. EXPERIMENTAL RESULTS AND DISCUSSION

Table 1 shows the major chemical compositions of porcelain body, greenish white glaze from Northern Song to Late Yuan Dynasty and that of porcelain body, white glaze and underglaze blue of Ming Dynasty. All data are average values of 5 samples in each dynasty. The major chemical compositions of porcelain body from Northern Song to Early Yuan are similar, but that of Late Yuan period have distinctly different from that of Song and Early Yuan. Such as, the concentration of Al₂O₃ in porcelain body in Late Yuan period is higher than that of Song and Early Yuan, and concentration of SiO₂ in porcelain body of Late Yuan is lower than that. So, we can deduce the age of two materials (kaolin and chinastone) properly combined to produce porcelain body in Jingdezhen was Late Yuan Dynasty. From the information of other archaeometry [5], we can say it is about 1320 years. This conclusion is confirmed by measurement of the minor and trace elements of 168 samples by NAA and multivariable statistical analysis [6]. Compared with greenish white glaze porcelain of Later Yuan and blue-and-white porcelain body fired in Yuan Dynasty in Jingdezhen, there are much similar with the major, minor and trace elements of porcelain body [2, 3].

From Table 1, it can be seen that the major chemical compositions of greenish white glaze of Late Yuan are different from that of Song and Early Yuan, also. Concentrations of K₂O, CaO, and Fe₂O₃ of greenish white glazes of Late Yuan are higher than that of Song and Early Yuan. The variable colors of greenish white glazes are mainly affected by concentrations of manganese oxide and the ferric oxide.

In ancient greenish white porcelain body and glaze, some concentrations of minor and trace elements, such as As, Ba, Co, Cr, Sr et al. are very low, most of them lower than 100 µg.g⁻¹, even lower than 20 µg.g⁻¹. This result is confirmed by NAA also [6]. However, in the modern and fake porcelain body and glaze, they are much higher than that; ever reach more than 100 times of that. This result is in agreement with what is reported by C.T.Yap and S. M. Tang [7, 12]. So, we can consider it as the fingerprinting of provenance and it can be useful to identify precious ancient porcelain from a fake.

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In Ming Dynasty, the productions of Hutian kiln were mainly blue-and-white porcelains. We can also obtain some information of cobalt pigment used for blue-and-white porcelain produced in Hutian kiln. The concentrations of cobalt oxide, manganese oxide and ferric oxide in the pigment, which affect the blue glaze, were obtained by PIXE spectrum measured from the blue glaze. The ratios of MnO/CoO and Fe₂O₃/CoO range from 6.54 to 8.79 and 4.12 to 23.05, respectively. The trace elements concentration of As and Ni measured from blue glaze range from LOD ∼100 µg.g⁻¹ and 607~1216µg.g⁻¹, respectively. These data are in agreement with that of asbolites, produced in Zhejiang, Fujian and Jiangxi province [13].

From Figure 1, we know the elemental distributions of porcelain body, white glaze and underglaze blue are homogeneous, and that a layer thick 5 ~ 10 µm exists between the body and blue glaze. Probably, it is caused by the technology of porcelain production. Concentrations of elements in the white glaze, underglaze blue and porcelain body determined by SPM are in agreement with that of PIXE analyzed.

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