PIXE analysis of proto-porcelain excavated from Tingziqiao kiln site of Deqing (China) (Postprint)

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Abstract

Particle induced X-ray Emission (PIXE) was used to analyze the proto-porcelain excavated from Tingziqiao kiln site of Warring States (475–221 BC) in Deqing County of Zhejiang Province, China. It was found that the porcelain body and glaze differ from each other in recipes. The porcelain clay of high silicon and low aluminum might be used to make the body of proto-porcelain. Lime and plant or wood ashes might be added into the glaze of the proto-porcelain. Cluster analysis was done to reveal the compositional relationship between the proto-porcelain samples.

Full Text

Preamble

PIXE Analysis of Proto-Porcelain Excavated from the Tingziqiao Kiln Site in Deqing, China

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Abstract: Particle-induced X-ray Emission (PIXE) was used to analyze proto-porcelain samples excavated from the Tingziqiao kiln site dating to the Warring States period (475–221 BC) in Deqing County, Zhejiang Province, China. The results revealed distinct compositional differences between the porcelain bodies and glazes, suggesting different raw material recipes. The porcelain bodies exhibited high silicon and low aluminum contents, indicating the likely use of

porcelain clay. The glazes showed high calcium oxide content, suggesting the addition of lime and plant or wood ash. Cluster analysis was performed to elucidate the compositional relationships among the proto-porcelain samples.

Keywords: PIXE, Proto-porcelain, Cluster analysis
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Introduction

Proto-porcelains represent the earliest stage of porcelain production. From October 2007 to March 2008, numerous proto-porcelain artifacts were excavated from the Tingziqiao kiln site in Deqing County, Zhejiang Province, China, dating to the Warring States period (475–221 BC). These artifacts contain valuable archaeological information regarding porcelain origins and manufacturing technology. Determining their chemical compositions is essential for extracting this information. Particle-induced X-ray Emission (PIXE) [1–3] is an efficient technique for analyzing archaeological samples, enabling rapid multi-element determination with ppm-level sensitivity.

At Fudan University, PIXE has been systematically applied to study ancient Chinese pottery and porcelain [4–6]. Recently, we conducted a PIXE investigation of ancient Chinese proto-porcelains. This paper reports our findings on proto-porcelain samples unearthed from the Tingziqiao kiln site. We identified characteristic elemental features specific to these proto-porcelains and explored the compositional relationships among samples to infer manufacturing technologies.

II. Experimental

Eighteen proto-porcelain samples excavated from the Tingziqiao kiln site, coded as DTT303 :1–7 and DTT303 :9–19, were provided by the Institute of Cultural Relics and Archaeology of Zhejiang Province. All samples were jar-shaped with grey bodies and straw-yellow glaze.

PIXE analysis was conducted using the NEC 9SDH-2 3 MV pelletron tandem accelerator at Fudan University. External proton beams of 3 MeV were employed to determine the chemical compositions of proto-porcelain samples positioned 10 mm outside the beam exit window (7.5 µm Kapton film). After energy loss in the Kapton film and air, the protons reached the samples at 2.8 MeV. The beam spot diameter on each sample was 1 mm, and the beam current was 0.05 nA to maintain dead time below 3%. A Si(Li) detector (SGX Sensortech (MA) Ltd, with 150 eV energy resolution FWHM at 5.9 keV) was placed perpendicular to the beam direction to detect X-rays emitted from the sample. X-rays traveled through 15 mm of helium gas before reaching the detector. PIXE spectra were collected using conventional electronics and a multi-channel analyzer. Net counts of characteristic X-ray peaks were obtained after background fitting and subtraction using the GUPIX-96 code [7]. Reference sample GSD-6, whose

elemental contents were determined by Inductively Coupled Plasma Emission Spectrometry (ICP), was used to calibrate PIXE parameters.

The glaze thickness of proto-porcelain samples was not uniform; the thinnest glaze measured approximately 0.1 mm, which is comparable to the projection range of 2.8 MeV protons in porcelain glaze. Such thin locations were unsuitable for glaze chemical composition analysis because protons could penetrate the glaze and reach the body, contaminating the glaze data with body composition information. To avoid this body effect, we selected thick glaze areas larger than the proton beam spot for PIXE measurements.

III. Results and Discussion

Typical PIXE spectra for the body and glaze of sample DTT303 :1 are shown in Fig. 1 [Figure 1: see original paper]. Clear X-ray peaks from Na, Mg, Al, Si, P, K, Ca, Ti, Cr, Mn, and Fe are visible. The concentrations of Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, Cr_2O_3, MnO, and Fe_2O_3 in the porcelain bodies and glazes were obtained from PIXE analysis and are listed in Tables 1 and 2, respectively.

Cluster analysis [8] was applied to investigate compositional relationships among proto-porcelain samples. The chemical compositions from Tables 1 and 2 were used as variables, and samples were clustered stepwise. The clustering results reflect only the compositional relationships based on body or glaze chemistry (i.e., raw materials), independent of ware shape or age. The resulting dendrogram (Fig. 2 [Figure 2: see original paper]) divides samples into Groups 1 and 2, corresponding to porcelain bodies and glazes, respectively. This indicates that bodies and glazes employed different recipes. Body samples cluster more tightly than glaze samples, suggesting smaller compositional variation in bodies compared to glazes.

As shown in Table 1 , body Al_2O_3 and Fe_2O_3 contents range from 13.74%–16.94% and 2.19%–3.29%, respectively, while SiO_2 content ranges from 75.31%–79.89%. This high-silicon, low-aluminum characteristic of proto-porcelain bodies resembles that of porcelain clay [9], which is abundant in southern China, suggesting that such clay was used for proto-porcelain bodies.

Table 2 shows that glaze CaO content (13.56%–23.75%) is substantially higher than K_2O content (1.4%–3.76%), indicating lime addition in proto-porcelain production. Consequently, proto-porcelain glaze is classified as calcium-rich. Glaze P_2O_5 content (0.64%–1.35%) is significantly higher than body P_2O_5 content (0.03%–0.38%), suggesting that plant or wood ash was also added during glaze preparation. Wu et al. [10] reported major compositions for proto-porcelain bodies and glazes from the Fengjiashan kiln site (Warring States period, 475–221 BC) in Deqing County, Zhejiang Province, with average body contents of 15.85% Al_2O_3 and 77.34% SiO_2, and average glaze CaO content of 16.35%, consistent with our results.

The body samples form three sub-clusters. Samples DTT303 :11-B and DTT303 :13-B constitute Sub-cluster 1, characterized by low Al_2O_3 (13.74%–14.16%) and high SiO_2 (79.4%–79.89%). Samples DTT303 :5-B, DTT303 :6-B, DTT303 :7-B, DTT303 :9-B, DTT303 :10-B, DTT303 :18-B, and DTT303 :19-B form Sub-cluster 2, with high Al_2O_3 (16.04%–16.94%) and low SiO_2 (75.31%–76.61%). The remaining body samples cluster as Sub-cluster 3, with intermediate Al_2O_3 (14.4%–15.66%) and SiO_2 (77.04%–78.77%) contents distinct from the other two sub-clusters.

The glaze samples also form three sub-clusters. Samples DTT303 :4-G, DTT303 :10-G, and DTT303 :19-G, with higher CaO (19.56%–23.75%) and lower SiO_2 (53.75%–57.07%), are distinctly separated from other glaze samples. Samples DTT303 :2-G, DTT303 :3-G, DTT303 :5-G, DTT303 :7-G, DTT303 :11-G, DTT303 :12-G, and DTT303 :13-G cluster together due to their relatively low SiO_2 (58.95%–59.9%) and high CaO (16.54%–19.47%) contents. Samples DTT303 :1-G, DTT303 :6-G, DTT303 :9-G, DTT303 :14-G, DTT303 :15-G, DTT303 :16-G, DTT303 :17-G, and DTT303 :18-G form the third sub-cluster, characterized by high SiO_2 (60.95%–63.78%) and low CaO (13.56%–16.32%) contents.

IV. Conclusion

PIXE analysis demonstrates that proto-porcelain bodies and glazes from the Tingziqiao kiln site employed different recipes. High-silicon, low-aluminum porcelain clay was likely used for bodies, while lime and plant or wood ash were added to glazes. Cluster analysis reveals distinct compositional relationships among samples, providing insights into proto-porcelain manufacturing technology.

Acknowledgements

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TABLE 1. Body chemical compositions (wt%) of the DTT303 proto-porcelains from Tingziqiao kiln site

Sample	Al_2O_3	Cr_2O_3	Fe_2O_3	…
DTT303 :1-B	…	…	…	…
…	…	…	…	…

TABLE 2. Glaze chemical compositions (wt%) of the DTT303 proto-porcelains from Tingziqiao kiln site

Sample	Cr_2O_3	Al_2O_3	Fe_2O_3	Fe_2O_3	…
DTT303 :1-G	…	…	…	…	…
…	…	…	…	…	…

Note: Figure translations are in progress. See original paper for figures.