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Elemental analyses on porcelains of Tang and Song Dynasties excavated from Yongjinwan zone at Jinsha site

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ABSTRACT

The work presented here carried out elemental analyses on 60 porcelain shards of Tang and Song Dynasties, unearthed from Yongjinwan zone at Jinsha site, Sichuan, China, using a combination of PIXE and RBS methods. Six shards from Liulichang kiln site and 6 from Shifangtang kiln site were also analyzed as reference materials. The factor analyses for the elemental compositions in the bodies and glazes of the total 72 porcelain shards have been performed to explore their similarities and differences. Combining the results of factor analyses on elements in bodies and glazes and the classification by traditional archaeological criteria, the provenances for most of shards unearthed from Yongjinwan zone in Jinsha site could be determined. Majority of shards with a Qiong-kiln style were found as products of Liulichang kiln, this is consistent with Yongjinwan's geographical location and social environment, i.e., Yongjinwan was a suburban settlement nearest to Liulichang kiln in ancient times. Although both products of Liulichang kiln and Shifangtang kiln belonged to Qiong-kiln system and they shared a similar appearance such as red body and celadon glaze, there were distinct differences in chemical composition which could be unraveled by PIXE-RBS measurements and factor analysis. There were no apparent differences of chemical compositions for the same kinds of body and glaze between Tang and Song Dynasties, which may suggest that raw materials and production techniques for the same kinds of body and glaze continued between Tang and Song Dynasties. The chemical characteristics for each kind of body and glaze and the correlations between element composition and porcelain appearance were also obtained in this work.

1. Introduction

The Jinsha site of Chengdu Plain in Sichuan province, China, known for the discovery of the Solar Divine Bird, which has been taken as a symbol of Chinese cultural heritage, was considered as the center of the ancient Ba-Shu Culture of Sichuan. Yongjinwan zone, located at the center of the Jinsha site, 700 m east of the sacrificial area and 4 km northwest of outside rampart, on the south bank of Modihe River, was a well-preserved suburban settlement and covered the period from Qin Dynasty to Qing Dynasty (221 BCE-1912 CE). In the excavated area, which extended over 1375 m^2, 60 ash pits, 64 ash troughs and 9 tombs in total were found during the excavation conducted by a joint archaeological team from School of History and Culture of Sichuan University and Chengdu Institute of Archaeology in 2005 [1]. Strata 2B and 2C among different archaeological strata in residential areas have attracted the most attention of archaeologists, not only because the largest amount of porcelain finds were unearthed from these two layers, but also they correspond to the Tang Dynasty and Song Dynasty, two of the most prosperous dynasties in Chinese history. Furthermore, porcelain finds utilized for everyday domestic use and then usually excavated in residential areas can tell us more information about various aspects of ancient people's daily life than those used for burial ceremonies and then discovered in burial sites. In the excavation of strata 2B and 2C, more than 830 utilitarian commodities, mainly shards of bowls, cups and dishes, were found in a fragmentary state, and occasionally entire or repairable porcelains were also excavated.

All porcelain finds were classified preliminarily during the excavation by archaeologists into groups according to traditional archaeological stratigraphy and typology. In the viewpoint of archaeological stratigraphy, items discovered in stratum 2C dating from the middle Tang Dynasty (618–907 CE) to the Five Dynasties (907–960 CE) were labelled as Period 2C here; and items in stratum 2B fairly representative of the period between the middle Northern Song Dynasty (960–1127 CE) and Southern Song Dynasty (1127–1279 CE) were labelled as Period 2B. Relatively more porcelains were found in the Period 2B than that in the Period 2C. On the basis of typological characteristics such as shape, glaze, colors and decorations, these porcelain items have been divided into the following categories: a few shards with exotic

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characteristics, only in Period 2B, were attributed to three famous imperial kilns located in other province, namely Yaozhou kiln in Shanxi Province, Jingdezhen kiln in Jiangxi Province and Longquan kiln in Zhejiang Province; several shards with some distinctive features could be confirmed to be produced in three folk kilns located in Chengdu Plain, namely Cifeng kiln in Pengzhou city, Yutang kiln and Jinfeng kiln in Dujiangyan city; and all the remaining porcelains were just labelled as Qiong kiln-System.

It was noteworthy that the Qiong kiln-System is not a specific kiln but a generic name of many kilns in Chengdu Plain. Also called Qionglai kiln, Qiong kiln is a famous folk kiln site located in Qionglai city. Qiong kiln wares, particularly the celadon porcelains, were so famous and popular that its style and techniques were imitated by other kilns in Chengdu Plain, where porcelain commodities with a Qiong-style were extensively produced to satisfy the great market demand. The strong visual similarity between Qiong porcelains and products from other kilns produced with a Qiong-style could often confuse the experienced experts. Consequently, these porcelains with a Qiong style but of an uncertain origin are just given a general name of Qiong kiln-System [2]. The production of Qiong kiln-System lasted from the beginning of the 4th century until the 13th century, with a production peak during the Tang Dynasty (618–907 CE) and the Five Dynasties (907–960 CE). The main products of Qiong kiln-System are utilitarian and household wares, among which a kind of oil-burning lamp with high oil utilization efficiency had been praised in many masterpieces of ancient poets such as Lu You, one of the most famous poets in ancient China. Qiong kiln-System includes many kiln sites, among which Shifangtang kiln is the largest and most influential, and Liulichang kiln is the nearest to Yongjinwan zone. The graphical location of Yongjinwan zone and aforementioned kiln sites in Chengdu Plain are shown in Fig. 1.

Although some documentary reports about porcelains of Qiong kiln-System are available, relevant scientific investigations are scarce. It is necessary to proceed with detailed laboratory analysis so that new relevant aspects for these porcelains can be unraveled. Currently, elemental analysis followed by multivariate statistical analysis can distinguish different groups with similar chemical profiles, which are assumed to correspond to the same provenance, supporting or refuting hypotheses put forward by archaeologists. During past years, a simultaneous proton induced X-ray emission (PIXE) and Rutherford backscattering spectrometry (RBS) analysis was employed to analyze the samples of ancient porcelains in our laboratory [3–5]. Among the instrumental techniques which can be applied for elemental analysis on porcelains, PIXE has been proven to be a very useful analytical technique because it combines the advantage of non-destructive determinations of a wide range of elements simultaneously with high sensitivity and accuracy; and the RBS in such kind of work was used to indirectly determine the incident charges which is necessary for quantitative PIXE analysis and to verify the existence/non-existence of lighter elements ($Z < 12$) that PIXE usually cannot analyze.

This work is the first systematic PIXE-RBS elemental analysis for porcelain of Qiong kiln-System, being the first stage of an ongoing project aiming to initiate a compositional database and establish reference materials for porcelains produced and circulated in Chengdu Plain. With the elemental results given by scientific analyses, some new recognitions about these porcelains may be acquired. The provenance results based on elemental analysis and multivariate statistical analysis can be a complement to the preliminary classification by archaeologists through traditional typology. Whether the products of Qiong kiln-System could be classified further into subgroups representative of different kiln sites is of interest to archaeologists. The most likely sources of those porcelains attributed to Qiong kiln-System unearthed from Yongjinwan zone are Liulichang kiln and Shifangtang kiln, the nearest one and the largest one, respectively. In order to determine whether these Qiong kiln-System products came from Liulichang kiln or Shifangtang kiln, two groups of porcelains unearthed from these two kiln sites and dated back to the Period 2C and Period 2B, were also sampled with the assistance of Chengdu Institute of Archaeology. We also seek to investigate whether the porcelains corresponding to the two periods (i.e., Period 2C and Period 2B) could be distinguished by chemical analysis. If distinguishable chemical composition groups can be observed among products of the two different periods for the same kiln site, then evolution about production of porcelains in these kilns could be discussed, and more importantly, chemical analyses would prove to be able to aid in the chronological classification of porcelains produced in Chengdu Plain. Moreover, a distinct chemical characteristics for different styles of body and glaze may also help us to identify correlation between element composition and porcelain appearance.

2. Samples and methods

2.1. Sample preparation

Sixty porcelain shards from Yongjinwan zone, 6 porcelain pieces from Liulichang kiln site (LLC) and 6 porcelain pieces from Shifangtang kiln site (SFT) were sampled for the elemental analysis using PIXE-RBS. According to traditional typological criteria, these 60 porcelain shards unearthed from Yongjinwan zone were catalogued into following groups: Yutang kiln (YT), Cifeng kiln (CF), Jinfeng kiln (JF), Yaozhou kiln (YZ), Jingdezhen kiln (JDZ), Longquan kiln (LQ), and Qiong kiln-System (QS). The archaeological information of all 72 samples and their exterior features are listed in detail in Table 1.

To make it easier to mount the samples on a specifically designed sample holder in the target chamber, a piece of sample about $1\text{ cm} \times 2\text{ cm}$ in dimension was cut from these shards, and a maximum of 12 samples of this size can be run in each batch. To determine elemental composition of the bodies of the porcelain samples, the glaze of one side was completely removed by grinding and then polished to obtain a smooth surface. To determine accurately elemental composition of glazes, those samples with smooth or low curvature surfaces and well preserved glaze layer were selected, and a calibrated metallographic microscope supported by software Motic Image Plus 2.0 ML, set at $100\times$ magnification, was used to observe the cross section of each sample to measure the thickness of glaze. The thinnest glaze thickness of all the samples was about 50 μm, which was larger than the analysis depth (~ 30 μm) of 2 MeV protons in the porcelain glazes. Thus glazes of these sample were suitable for analysis by PIXE with a 2 MeV proton beam. Moreover, each sample was cleaned with brush and washed successively with deionized water and high-purity acetone in an ultrasonic bath, dried in a drying oven for 12 h at 105 °C, and then stored in a vacuum dryer for PIXE-RBS analyses.

2.2. PIXE-RBS experiments

Simultaneous PIXE and RBS measurements for these 72 porcelain shards were performed using 2 MeV proton beam generated by the Van de Graaff accelerator at Institute of Nuclear Science and Technology, Sichuan University [3,4]. The target chamber was electrically insulated from surrounding beam lines, and the vacuum was controlled at $\sim 2 \times 10^{-4}$ Pa during experiments. The proton beam was perpendicular to the sample surface, and the beam spot size was about 2–3 mm in diameter and could be adjusted manually using two sets of slits located at the beam line to keep the dead time less than 2% for PIXE and less than 4% for RBS. During the manufacture of porcelain, raw material handling processes, including screening, elutriating and refining, had to be done carefully, therefore the elemental composition in porcelain could be regarded as homogeneous.

The RBS spectra were recorded by a semiconductor Au-Si surface barrier detector (Beijing Nuclear Instruments Factory, Beijing, China) with a collimator of 2 mm in diameter, and placed in the target chamber at an angle of 165° with respect to the incident beam direction. The Au-Si detector had a sensitive area of 8 mm in diameter and a depletion depth of 300 μm when operated at a bias voltage of +200 V. The PIXE