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Analysis of elemental composition of porcelains unearthed from Waguantan kiln site by PIXE-RBS



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ABSTRACT

A method combining proton-induced X-ray emission spectrometry (PIXE) and Rutherford backscattering spectrometry (RBS) was used to determine the composition of 61 porcelain shards from the Yuan Dynasty (1271–1368 A.D.) unearthed from the Waguantan kiln site at Tianzhu County in Guizhou Province, China. Based on our previous experimental setup, an electron gun device with a LaB_6 crystal cathode was installed to solve the problem created when the incident proton beams generated electric charge accumulations on the surfaces of the insulating porcelain samples, which induced a large bremsstrahlung background. The use of the electron gun has largely eliminated the large bremsstrahlung background and has therefore improved the detection limits for elements, especially for trace elements, and made it possible to determine the origin of the porcelains based on the trace elements. Major and trace elemental compositions of the porcelain bodies and glazes measured by PIXE and RBS were analyzed by the factor analysis method. The factor analysis showed that a few pieces of porcelain with a style similar to the porcelain of the Longquan kiln among the unearthed porcelains from the Waguantan kiln site did not have obvious differences in elemental compositions from other remaining porcelains unearthed from the Waguantan kiln site, indicating that the pieces of unearthed porcelain with the Longquan kiln style did in fact belong to the product fired locally by imitating the model of the Longquan celadon with local raw materials. This result therefore indicated that the Longquan kiln technology that originated from the Five Dynasties (907-960 A.D.) had been propagated to the Waguantan kiln site of Guizhou Province in the Yuan Dynasty.

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1. Introduction

The Waguantan kiln site is located in Tianzhu County of Guizhou Province, China, and was built in the Yuan Dynasty (1271-1368 A.D.). In the winter of 2009, to coordinate with the construction of the Baishi hydropower station in Guizhou Province (a key project), the Guizhou Institute of Cultural Relic Archaeology and the Archaeology Department of Sichuan University organized an archaeological team to conduct a salvage archaeological excavation at the Waguantan kiln site. In the excavation, 14 ash pits, 3 ash troughs and 1 remnant dragon kiln in total were cleaned up. More than 3000 undamaged or repairable porcelains and many porcelain shards were unearthed. The Waguantan kiln site was discovered for the first time in Guizhou Province, and the porcelain samples unearthed at the Waguantan kiln site provide very valuable information [1] for research on the ancient pottery and history of porcelain in China. In particular, a few pieces of the porcelain unearthed from the Waguantan kiln site were very different in style from other porcelains unearthed at this site and had a style similar to the porcelains produced from another famous kiln. For example, a celadon dish from sample No. H3-4 (see Fig. 1d) had a thick dark green glaze layer, an even glaze surface, a fine and smooth feeling to the hand and a strong jade texture, and the celadon dish from sample No. H3-4 was very similar to a celadon dish produced from the Longquan kiln, one of the most famous ancient porcelain kilns in China. The Longquan kiln began operation in the period of the Five Dynasties (907-960 A.D.), ended operation in the period of Emperor KangXi (1661-1722 A.D.) of the Qing Dynasty (1636-1911 A.D.) and was very well known for firing celadon. Some samples unearthed from the Waguantan kiln site are shown in Fig. 1.

According to the traditional identification method for the origin of a porcelain production, namely, a method of typology in which the appearance characteristics for the bodies and glazes, shapes and decorations of porcelains with an unknown origin of production

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are first carefully observed and then compared with the standard porcelains produced at certain kilns to determine the origin of production [2], most of the porcelains excavated at the Waguantan kiln site used a relatively rough fabrication technology and could thus be typologically judged to be produced locally at the Waguantan kiln site (e.g., Fig. 1a and b). A few pieces of unearthed porcelain with an exotic style might belong to the "exotic porcelains" produced at other kilns such as the Longquan kiln (e.g., Fig. 1c and d). However, according to common sense, the exotic porcelains generally appeared at house sites as domestic articles or appeared in tombs as burial objects, but the archaeological place this time was a kiln site for porcelain firing. The geographic location of the Waguantan kiln site is in Tianzhu County of Guizhou Province, while the famous Longquan kiln site is remotely located in Zhejiang Province, China, as shown in Fig. 2. Whether the porcelain products made at the Longquan kiln site were propagated by trade and population migration or whether the porcelain production techniques and art styles were propagated pertains to cultural communication at different levels [3]. Therefore, whether these pieces of porcelain unearthed from the Waguantan kiln site with an exotic style were produced locally is a question that concerned archaeologists.

Currently, in comparison with the traditional identification method for porcelain production origin, the elemental composition analysis techniques have increasingly become powerful methods for porcelain identification. Proton-induced X-ray emission spectrometry (PIXE) [4] is widely applied in archaeological research because of its advantages such as nondestructive testing (in this paper, one of two glazed sides of the samples was destructively removed to analyze the bodies of the samples) and high sensitivity. However, in general, PIXE cannot easily detect the characteristic X-rays of light elements with atomic number Z < 12, while Rutherford backscattering spectrometry (RBS) [5] can verify the existence of those light elements and simultaneously determine the matrix element composition and the incident electric charges needed for the PIXE analysis. Therefore, in this paper, a method of combining PIXE and RBS was employed to perform the elemental composition



Fig. 1. Four porcelain samples unearthed from the Waguantan kiln site. (a) No. H2-2-20: gray body, dark reddish black glaze, bowl, produced locally; (b) No. H2-3-11: gray body, reddish black glaze, bowl, produced locally; (c) No. H2-3-11: gray body, dark green glaze, large dish, suspected to be exotic; (d) No. H3-4: white body, dark green glaze, large dish, suspected to be exotic; (d) No. H3-4: white body, dark green glaze, large dish, suspected to be exotic; (d) No. H3-4: white body, dark green glaze, large dish, suspected to be exotic; (d) No. H3-4: white body, dark green glaze, large dish, suspected to be exotic. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. A map to locate the Waguantan kiln site and the Longquan kiln site.

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