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Data-driven research on chemical features of Jingdezhen and Longquan celadon by energy dispersive X-ray fluorescence

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Abstract

The energy dispersive X-ray fluorescence (EDXRF) is used to determine the chemical composition of celadon body and glaze in Longquan kiln (at Dayao County) and Jingdezhen kiln. Forty typical shards in four cultural eras were selected to investigate the raw materials and firing technology. Random forests, a relatively new statistical technique, has been adopted to identify chemical elements that are strongest explanatory variables to classify samples into different cultural eras and kilns. The results indicated that the contents of Na_2O, Fe_2O_3, TiO_2, SiO_2 and CaO vary in celadon bodies from Longquan and Jingdezhen, which implies that local clay was used to manufacture celadon bodies in Jingdezhen kiln. By comparing the chemical composition in glaze, we find that the chemical elements and firing technology of Jingdezhen kiln are very similar to those in Longquan kiln, especially for Ming dynasty. This study reveals the inheritance between Jingdezhen kiln and Longquan kiln, and explains the differences between two kilns.

Keywords: Celadon; EDXRF; Chemical feature; Longquan; Jingdezhen; Random forests

1. Introduction

Celadon is one of the earliest porcelains in China as well as in the world. With its long history and rich varieties, celadon has attracted a lot of attentions from researchers in archaeology, physics, material science, etc. Longquan kiln, one of the most representative kilns in celadon production, enjoys an important status in Chinese ceramic history [1]. The government in Ming Dynasty invested nationwide labors, resources and capitals in the establishment of imperial kiln in Jingdezhen from Yongle era. Jingdezhen has also became the craftsmen aggregation center and the porcelain manufacturing center in Maritime Silk Road since Yongle era of Ming Dynasty [2]. Jingdezhen kiln was able to make color glaze and whiteware porcelains from Yuan Dynasty and began to make celadon from Tang Dynasty. The demand from commercial activities, foreign trade and imperial reward far stripped the supply of Jingdezhen porcelain [3]. Due to the good quality and unique glaze feature (jade texture) of Longquan celadon, Jingdezhen kiln was trying to imitate Longquan celadon from style, color and pattern. The producing and firing technology of imitated Longquan celadon in Jingdezhen had reached a relative high level in Yongle era of Ming Dynasty (1403–1424), however craftsmen did not master the completely mature firing technology until Yongzheng era of Qing Dynasty (1723–1735) [4]. At present, Longquan celadon has been in depth studied by current archaeologist while the imitated Longquan celadon in Jingdezhen still remains little investigated.

It has been well known that the contents of macro and micro elements in the body and glaze of porcelain are dependent on

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the raw material and firing technology [5,6]. Li et al. [7] used EDXRF to confirm that the raw materials of imperial Longquan porcelain have no obvious changes between Hongwu and Yongle era (1368–1398), and claimed the firing technology has not declined in the Early Ming Dynasty. Zhu et al. [8] show micro elements, e.g. Cr, Sr, Zr in body and Sr, Rb in glaze could be employed as relevant markers for the non-destructive discrimination of the provenance of Xicun and Yaozhou kiln. Wu et al. [9] is a research on the early celadon of Jingdezhen and its initial development. It comparatively analyzed the EDXRF data from Nan and Lantin kiln sites in Jingdezhen and explained the difference in chemical composition and processing characteristics.

In this study, the samples of body and glaze of Longquan celadon in Northern Song, Southern Song, Yuan and Ming Dynasties as well as imitated Longquan celadon in Jingdezhen in Ming Dynasty were examined by the energy dispersive X-ray fluorescence (EDXRF) microprobe. EDXRF is an efficient instrument that combines the merits of X-ray fluorescence spectrometry with the ability to analyze a micro-area. The large chamber size allows for the non-destructive analysis of macro and trace elements on micro-areas of the samples. After obtaining the data, Random forests, a well-established machine learning algorithm, was adopted in the analysis, rather than multivariate statistical methods. If many elements were measured in the experiments, it is very inefficient to find the difference by standard multivariate statistical methods [10]. However, Random forests can return the values that measure the variable importance of explanatory variables in the training data, so only the top-ranked elements need to be investigated. The results of the analysis reveal the inheritance relationship of the celadon from Longquan and Jingdezhen kiln (Fig. 1).

2. Experiment

In this experiment, 40 samples of Longquan celadon in Northern Song, Southern Song, Yuan and Ming Dynasties as well as imitated Longquan celadon in Jingdezhen civilian kilns in Ming Dynasty are collected. They include 7 samples of Longquan celadon in Northern Song Dynasty (LQ-BS-1～LQ-BS-7), 8 samples of Longquan celadon in Southern Song Dynasty(LQ-NS-1～LQ-NS-8), 9 samples of Longquan celadon in Yuan Dynasty(LQ-Y-1～LQ-Y-9), 3 samples of Longquan celadon in Ming Dynasty(LQ-M-1～LQ-M-3) and 13 samples of imitated Longquan celadon in Jingdezhen in Ming Dynasty(FLQ-M-1～FLQ-M-13). The photographs of samples are shown in Fig. 2.

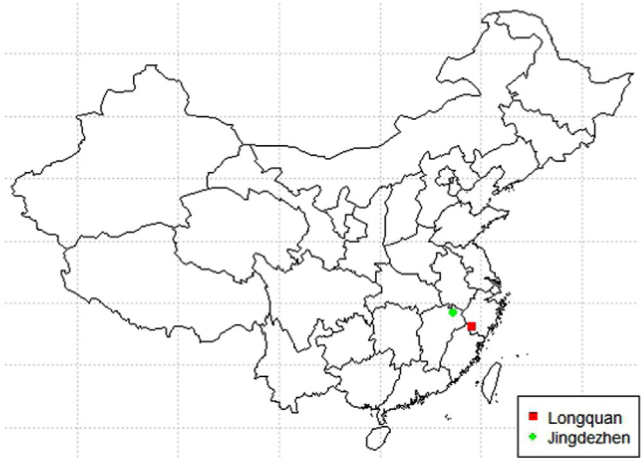

Fig. 1. The locations of Longquan kiln (Dayao County) and Jingdezhen kiln.

The samples were cut and cleaned in an ultrasonic bath and then dried before testing. Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer (EAGLE-III) was used to detected body and glaze compositions. The analysis was executed at 50 kV and 200 μA voltage–current of the X-ray tube, with a vacuum optical route and dead time was around 25%. The detector is a liquid-nitrogen-cooled Si (Li) crystal with Rh window, and the beam spot was 300 μm. The software employed for spectrum retraction and analysis was the program VISION32, associating with the instrument. Quantitative analysis was operated by calibration curve method. The calibration samples were from a set of reference samples (13 pieces) with known chemical compositions, provided by the Shanghai Institute of Ceramics of the Chinese Academy of Science (SICCAS). The analytical results were in Tables 1 and 2.

The firing temperatures of the typical samples were estimated from the inflection point of the thermal expansion curves (Table 3) and measured by DIL 402C Thermal Dilatometer of the German NETZSCH Instrument Company. Water absorptions were tested through boiling method.

3. Results and discussion

3.1. Random forests and variable importance

Random forests, an increasingly popular nonparametric methodology, is an extension of classification and regression trees (CART) method [11]. It grows many classification trees or regression trees and thus has the name “forests”. Every tree is built using a deterministic algorithm, and the trees are different in two aspects: first, at each node, a best split is chosen from a random subset of the predictors rather than all of them; second, every tree is built using a bootstrap sample of the observations. The remaining sample, the so-called “out-of-bag” (OOB) sample, which contains approximately one-third of the observations, are then used to estimate the prediction accuracy. A key feature of random forest is its ability to measure variable importance [12]. Variable importance reflects the degree of association between a given explanatory variable and the response variable. More details about random forests and its wide applications can be found in [13,14].

In this research, the contents of chemical elements are the explanatory variables and the categories of eras and kilns are the response variable. By using *randomForest* Package in R language [15], we performed random forests method to do classification of celadon samples. Mean decrease in accuracy (MDA) and mean decrease in Gini index (MDG), two values that random forests method returns after constructing classification trees, can be used to identify chemical elements that differ most significantly among groups of samples in different

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