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A Study of Provenance and Dating of Ancient Chinese Porcelain by X-Ray Fluorescence Spectrometry

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In order to extend the scope of employing major elements to study the evolution process of manufacturing techniques, we employed minor and/or trace elements to study provenance and dating and to distinguish fake from original Chinese pottery and porcelain by energy-dispersive x-ray fluorescence (EDXRF) spectrometry. In summarizing our previous work, 85 typical Chinese white porcelain objects from Jingdezhen, Dehua and Hebei (Xing, Ding and Cizou), were measured by EDXRF and further analysed statistically. We found discriminate functions for the provenance of samples among Jingdezhen, Dehua and Hebei and also samples among Xing, Ding and Cizou in Hebei. We also derived functions for dating samples among Yuan, Ming and Qing of Jingdezhen blue and white porcelain, and samples between Song to Yuan and Ming periods of Dehua white porcelain. Element ratios are suggested to be employed in all of the discriminate functions in order to minimize measurement errors and to form a fast, non-destructive, comparable and reliable method for provenance and dating of ancient porcelain.

INTRODUCTION

China is one of the earliest pottery manufacturing areas (about 10 000 years ago[1,2]) and was the first country to produce porcelain (about 2000 years ago[3]). In this long time period, ancient Chinese potters had produced many kinds of pottery and porcelain wares in different kiln sites in successive periods. Some of them are very attractive with a high reputation not only in China but also overseas. Unfortunately, many of these objects are not documented scientifically. The true facts hidden behind these treasures can be obtained by correct scientific measurements and studies. Two questions are particularly important. The first is concerned with the manufacturing techniques and evolution of the manufacturing process[4–11] and the second with provenance and dating.[12–22] In answering these two questions, the chemical composition of ancient objects is usually required. The first question only requires the determination of the major elements whereas the second necessitates the determination of minor and/or trace elements. In the determination of chemical composition, x-ray fluorescence (XRF),[14–19,21,23] proton induced x-ray emission (PIXE),[24] atomic absorption spectrometry (AAS),[9] neutron activation analysis (NAA)[25] and wet chemical analysis are mostly employed, but only XRF and PIXE are non-destructive, fast, multi-element techniques which analyse the surface layer and determine major and minor and also some trace elements in thin and thick samples of all sizes and forms.[26] It is this reason that makes XRF and PIXE widely applicable in the non-destructive study of ancient relics, because they do not require even a small amount of powder to be removed from ancient treasures, unlike other methods. We shall focus our attention on the study of provenance and dating by non-destructive XRF of trace elements.

Young[27] employed wavelength-dispersive x-ray fluorescence (WDXRF) spectrometry to study Chinese blue and white porcelain (1300–1900 AD) in 1956. Since then, much work[14–19,21,23,28] has been carried out, and satisfactory provenance and dating results have been obtained by employing WDXRF and energy-dispersive x-ray fluorescence (EDXRF) spectrometry to measure major, minor and trace elements in Chinese porcelain. Yap and Tang[14–17] employed EDXRF to identify blue and white Chinese imperial porcelain of pre-World War II from modern fakes of post-World War II. Yu and Miao[18,19] also studied blue and white Chinese porcelain after the Ming Dynasty from several kiln sites and excavation sites in China by non-destructive EDXRF. Both groups have obtained fast, non-destructive and reliable discriminate results, but there are still some points that require further study, as follows. (1) Not much work has been carried out on studying Jingdezhen blue and white samples before the Ming Dynasty or on studying other kinds of Chinese porcelain wares from different kilns and different time periods except Jingdezhen blue and white wares. (2) Different measurement conditions (including x-ray collimated area, measurement current and voltage, correction method and standard sample) always make measurements difficult to compare with each other. (3) Not much work has been carried out on provenance and dating by studying the elemental composition of the body. The body is usually produced by local materials in different kiln sites

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and time periods and it can supply much more information for identifying the provenance and dating than that of the glaze.[11] (4) Although the element ratios in blue areas of Jingdezhen blue and white porcelain can supply some information for identifying some specific samples, care should be taken in using data from these blue areas because the Mn/Co ratios and other element ratios are determined not only by cobalt materials but also by glaze materials which covered the blue paint. Different cobalt materials and different glaze materials usually have different Mn/Co and other element ratios. It has been found that potters employed several kinds of cobalt materials[29,30] and different glaze materials[11] in the same dynasty in Jingdezhen.

After element measurement by EDXRF, deriving the best 'fingerprint' and discriminate function is also very important. For the provenance and dating of Chinese porcelain, many kinds of statistical analysis methods have been involved, including correspondence analysis,[10] discriminate analysis,[22,31] fuzzy analysis[11] and principal component analysis.[21,32–35] The discriminate functions are expressed by one to three elements (or oxides)[14–19,36] or several combined elements (or oxides)[21,22,31–35] or element (or oxide) ratios.[37,38] Considering the measurement process and coefficients that influence the intensity of x-ray fluorescence, the 'fingerprint' of the element ratios concerned may be the most convenient, reliable and fast way to deduce provenance and date.

In order to overcome these disadvantages and obtain fast, non-destructive and comparable data for building a reliable database and to derive discriminate functions not only for blue and white Chinese porcelain but also for most other Chinese pottery and porcelain, a concerted plan is needed. For this reason, a programme called Aided Joint Method for Determining the Provenance and Dating of Chinese Pottery and Porcelain by EDXRF (AJMDPD-EDXRF) (supported by the City University of Hong Kong, grant number 7000648) has been established. Many scientists from museums and related institutions in China are involved in this programme. Major, minor and some trace element contents for a large number of typical fragments from different kiln sites and supplied by archaeologists are successively determined and stored in a database for further use. In order to find the best 'fingerprint' for different groups of samples, a statistical analysis software package is also being developed. In this paper, we summarize our previous work[21,31,34,35] on the study of provenance and dating.

Provenance and dating study by element characterization is based on the hypothesis that pottery and porcelain from different kiln sites or same kiln site but different time periods of manufacture, is usually made using different raw materials and/or batch compositions that make the products have their own specific chemical composition. Is this correct? In ancient times (usually before 1900 AD), it was very difficult to transport raw materials from one place to another in China, so potters usually employed local materials to manufacture pottery and porcelain and also employed specific raw materials and/or batch composition in certain time periods,[11] which provides a very good scientific basis for employing element characterization in provenance and dating studies. However, one should note that the chemical composition difference between samples from different kiln sites is usually much greater than that between samples from the same kiln but different time periods, because a change of emperor did not influence the raw materials and/or batch composition significantly. In other words, the accuracy of provenance is usually better than that of dating by XRF.

STATISTICAL DATA

At the beginning of our programme, Chinese archaeologists supplied some typical and famous Chinese white porcelain fragments from Jingdezhen in Jiangxi, Dehua in Fujian and Xing, Ding and Cizou in Hebei (the last three groups of fragments are called 'Hebei' below). The geographical locations of these kiln sites can be found in Fig. 1. We employed EDXRF in the City University of Hong Kong to measure major, minor and trace element contents of their bodies and glazes, and revealed the differences between samples in different locations and time periods individually with different statistical methods.[31,34,35] Unfortunately, the element differences among these three groups of white porcelain were not studied. Here we quote the trace element contents (some of them have been transferred from oxide contents) of these bodies from our previous work[31,34,35] and employ statistical analysis to find the provenance and dating discriminate functions for them.

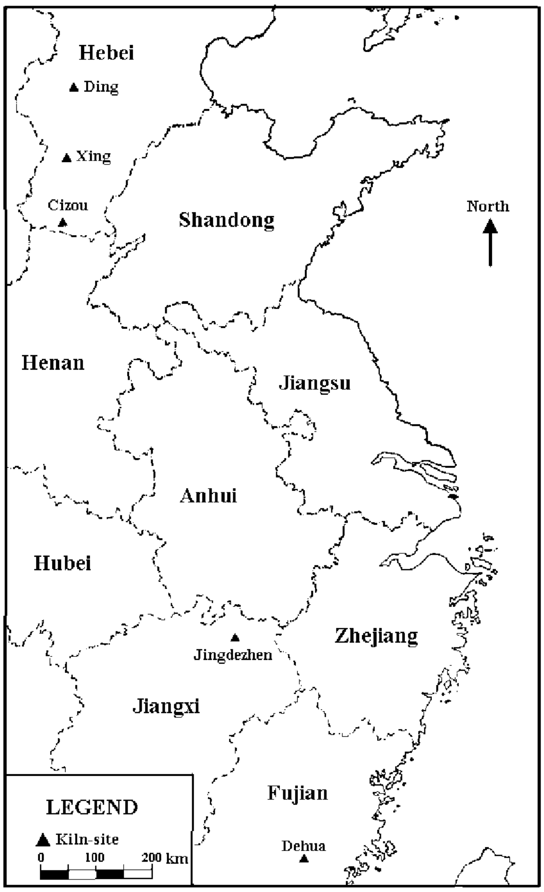

Figure 1. Map of the areas considered.

PROVENANCE AND DATING OF CHINESE WHITE PORCELAIN FROM JINGDEZHEN, DEHUA AND HEBEI

In the study of provenance and dating by XRF, it is difficult to compare the data from different researchers and institutions because the differences in equipment, measuring conditions, standard samples, etc., strongly influence the measurement results. Differences in results of ±10 to ±20%, or even more, between instruments always occur in trace element measurements (see Ref. 35, Table 1; a detail analysis of XRF measurement was described by Mommsen *et al*.[39]). This makes it difficult to exchange data between researchers. In order to reduce and eliminate the influence of these difficulties, we suggest the use of element ratios as statistical data for finding their discriminate functions even though we used the same equipment. Here, the first question that arises is which element should be chosen as the element to compare with others.

Using correspondence and discriminate analysis (mathematical methods can be found in Ref. 40) to treat the data from different kiln sites or the same kiln site but different time periods in order to find which elements are the best fingerprints for separating samples of interest (called BF), and which element is the worst one with almost the same mean and standard deviation for the samples of interest (called WF), we can divide the element contents of BF by the element content of WF for each of the samples of interest because the element content of WF has almost no influence on the cluster result divided by the contents of BF, and further the ratio of BF with WF can reduce and eliminate the above difficulties.

Using discriminate analysis to treat the data on element ratios further, we can obtain the discriminate functions of provenance and dating for different samples.

Provenance study

Functions for discriminating white porcelain from Jingdezheng, Dehua and Hebei. Chinese white porcelain from Jingdezhen, Dehua and Hebei can be distinguished from each other by the following functions (see Fig. 2): $Zr/Rb = 1.29$ and/or $0.79\,(Rb/Y + Zr/Y) = 6.00$.

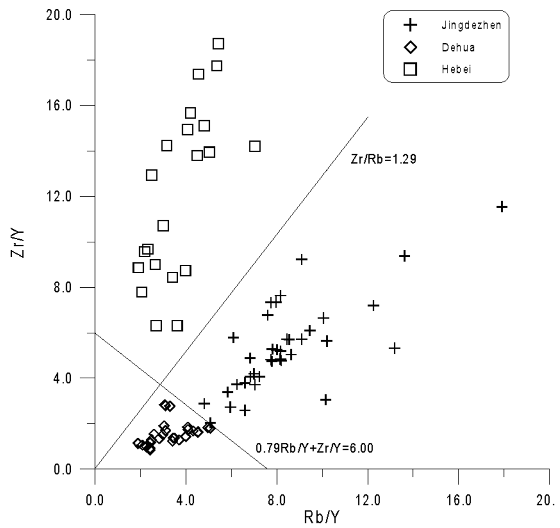

Figure 2. Scatter diagram for Chinese porcelain bodies from Jingdezhen, Dehua and Hebei.

Figure 2 shows that all of the Hebei, Jingdezhen and Dehua sample points are located in their own specific areas individually: Hebei, $Zr/Rb > 1.29$; Jingdezhen, $Zr/Rb < 1.29$ and $0.79\,(Rb/Y+Zr/Y) > 6.00$; and Dehua, $0.79\,(Rb/Y + Zr/Y) < 6.00$.

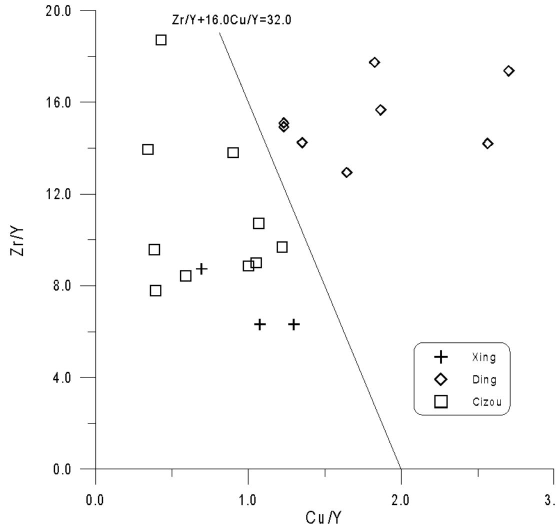

Figure 3. Scatter diagram for white porcelain bodies from Xing, Ding and Cizou kiln in Hebei.

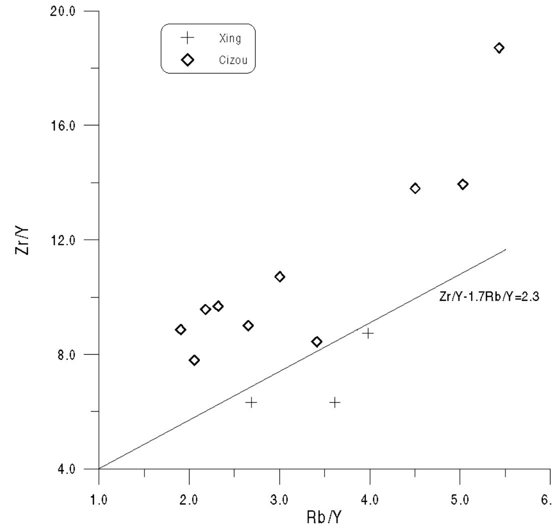

Figure 4. Scatter diagram for white porcelain from Xing and Cizou kiln.

Functions for discriminating white porcelain from Xing, Ding and Cizou in Hebei Province. From Figs 3 and 4, we can see that the samples from Xing, Ding and Cizou can be separated from each other by the following functions: $Zr/Y + 16.0Cu/Y = 32.0$ and/or $Zr/Y - 1.7Rb/Y = 2.3$.

If $Zr/Y+16.0Cu/Y > 32.0$, then the sample may belong to Ding, otherwise Cizou or Xing (see Fig. 3). For Xing and Cizou white porcelain, Xing samples belong to the area where $Zr/Y - 1.7Rb/Y < 2.3$ and Cizou in the area where $Zr/Y - 1.7Rb/Y > 2.3$.

Dating study

Functions for discriminating the Jingdezhen Blue and White Porcelain from the Yuan (1279–1368 AD), Ming (1368–1644 AD) and Qing (1644–1911 AD) periods. The functions for discriminating the Jingdezhen samples from different time periods can be found in Fig. 5, which shows the following results.

The samples from the Yuan Dynasty are located in two different areas, one (Cr/Rb > 0.3 and Zr/Rb > 0.72) includes the samples produced in what is called Min Yao [Y.D.(P)], which did not produce wares for the emperor, and another (Cr/Rb > 0.3 and Zr/Rb < 0.58) includes the samples produced in what is called Guan Yao [Y.D.(I)], which only produced wares for the emperor. The samples from the Qing period are located in the area of Cr/Rb < 0.3. Differing from those of Yuan and Qing samples, Ming data points are scattered in a larger area, but most of them (about 90%) are located in a long and thin area ($0.58 <$ Zr/Rb < 0.72), except for two samples coded JMI14 and JMI15.

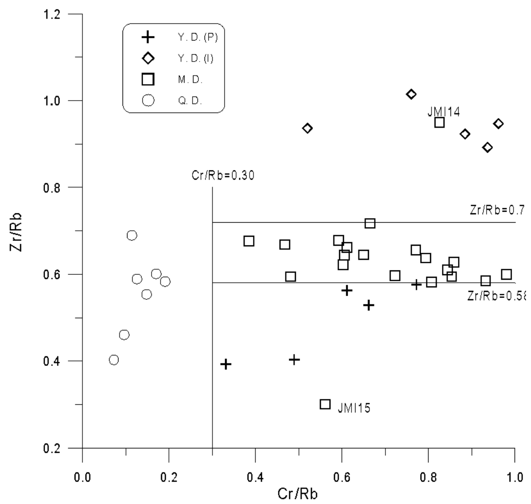

Figure 5. Scatter diagram for Jingdezhen blue and white porcelain bodies from Yuan (Y.D.), Ming (M.D.) and Qing (Q.D.) perlods.

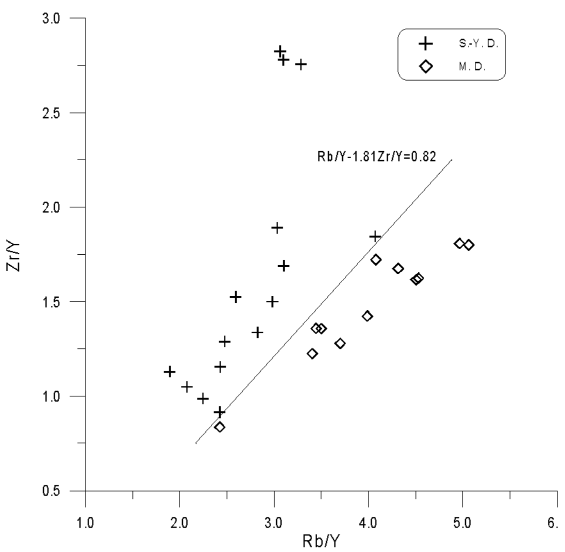

Figure 6. Scatter diagram for Dehua white porcelain body from Song to Yuan (S.-Y.D.) and Ming (M.D.) periods.

Functions for discriminating the Dehua White Porcelain from Song to Yuan (960–1368 AD) and Ming (1368–1644 AD) period. Figure 6 shows that all of the Ming samples are located in the area where $Rb/Y - 1.81Zr/Y < 0.82$ and the samples from Song to Yuan periods in the area where $Rb/Y - 1.81Zr/Y > 0.82$.

DISCUSSION

Except for two samples (JM14 and JM15, see Fig. 5) of blue and white Jindezhen porcelain from the Ming period, all of the other samples can be identified successfully with regard to their provenance and manufacture periods by their discriminate functions. This means that the groups of samples we have studied have different chemical characterizations statistically, which are determined by their manufacture materials and/or batch composition.

Although the samples of Xing and Cizou cannot be separated from each other in Fig. 3, their characteristics in element contents are still obvious in Fig. 4. This observation reveals that although each group of samples usually has different characteristics of element content, sometimes it is difficult to show all of the differences among different samples in just one figure. It is necessary to find their difference according to their element ratios by statistical analysis.

There were only three Xing samples in our study. It is possible that the function for discriminating Xing and Cizou will change if we include more Xing samples. It is necessary to measure more Xing samples in the future and to find their discriminate function.

Two of the Ming samples coded JMI14 and JM15 are located far away from most of the Ming data points, one in the area of Y.D.(I) and another in Y.D.(P). Why is this so? There are three possibilities: (1) measurement errors; (2) mis-classified group by archaeologist; (3) imitation Yuan Dynasty style products. These possibilities need to be investigated further.

For a real ware to be measured for identification regarding its provenance and date by EDXRF, the influence of curved surface and distance should be corrected in order to compare the measurement results with those in the database which were obtained on a flat plane. We suggested using an outer mark film on the surface of a ware as a standard which is analysed before measurement of the sample itself.[41]

CONCLUSION

With the exception of the function for discriminating the samples of Xing and Cizou (the number of Xing samples was too small to find the discriminate functions with other samples), the other functions presented in this paper can distinguish successfully the provenance and dating of the samples examined.

The use of element ratios in the discriminate functions can provide fast, non-destructive and reliable answers in the study of provenance and dating by XRF because it reduces or eliminates the influence of equipment, measurement conditions and errors with standard samples.

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