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ICP-MS trace element analysis of Song dynasty porcelains from Ding, Jiexiu and Guantai kilns, north China

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Abstract

Bodies of Ding kiln white porcelains and their imitations from Guantai and Jiexiu kilns of the Chinese Song dynasty (960–1279 AD) were analysed for 40 trace elements by inductively coupled plasma mass spectrometry (ICP-MS). Numerous trace element compositions and ratios allow these visually similar products to be distinguished, and a Ding-style shard of uncertain origin is identified as a likely genuine Ding product. In Jiexiu kiln, Ding-style products have trace element features distinctive from blackwares of an inferior quality intended for the lower end market. Based on geochemical behaviour of these trace elements, we propose that geochemically distinctive raw materials were used for Ding-style products of a higher quality, which possibly also underwent purification by levigation prior to use. Capable of analysing over 40 elements with a typical long term precision of <2%, this high precision ICP-MS method proves to be very powerful for grouping and characterising archaeological ceramics. Combined with geochemical interpretation, it can provide insights into the raw materials and techniques used by ancient potters.

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1. Introduction

Ding kiln is one of the most prominent kilns of ancient China [18]. In the 11th and early 12th centuries, it was producing porcelains with the most sophisticated making, setting and firing processes in Song Dynasty (960–1279 AD) China and were approved for palace use [34]. Ding wares, particularly the white porcelains, were so famous and popular in high-end markets that its style and technical innovations were imitated by all kilns

making white porcelains, where white porcelains bearing a Ding-style were keenly produced to meet the great market demand [30]. The strong visual similarity between Ding white porcelains and products from other kilns produced with a Ding style could often confuse the most trained eyes [25]. Therefore archaeological ceramics bearing a Ding style but of an uncertain origin are often just given a generic term of Ding-Type, Ding-Style, or Ding-System white porcelains, as is the case with many other influential Chinese kilns.

In this paper we compare the element compositions of Ding-style white porcelains produced in the Ding, Guantai and Jiexiu kilns in north China to determine if these often visually indistinguishable products can

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be differentiated using ICP-MS trace element analysis. A comparison of Ding-style porcelains and blackwares from the Jiexiu kiln is also discussed.

2. Samples

Among the white porcelain bodies analysed, seven are from the Ding kiln which is in Quyang county ($38^{\circ}36.193'N$, $114^{\circ}40.023'E$), middle Hebei province, and are approximately dated to the 11th to early 12th century; five are imitation-Ding products from Guantai kiln in Cixian County ($36^{\circ}22.57'N$, $114^{\circ}24.805'E$), south Hebei province and are dated to mid 11th to mid 12th century [4]; three are from Jiexiu kiln in Jiexiu county ($37^{\circ}11.064'N$, $111^{\circ}39.491'E$), Shanxi province, neighbouring Hebei, and are approximately dated to early 12th to early 13th century. Guantai kiln is the single most important kiln site making Cizhou-Type wares, which is another very influential style of Song dynasty ceramics made in kilns across north China [19,20], but Guantai kiln still had been, alike the Jiexiu kiln [9], strongly influenced in style and technology by the famous Ding kiln. A good example is production of the imitation-Ding porcelains at Guantai kiln apart from its ordinary products Cizhou-Type wares [24]. All of the white porcelains we analysed demonstrate a typical Ding style featuring exquisite workmanship and a fine, white, thin body. In addition, a Ding-style white porcelain shard (HZ-1) discovered in Hangzhou city ($30^{\circ}22.728'N$, $120^{\circ}20.565'E$), Zhejiang province was also analysed in an attempt to identify its place of manufacture. Hangzhou was one of the most important commercial cities of Song China and served as the Song Dynasty capital after it was defeated by the northern tribes and moved its court to south China. Also analysed for comparison are two Jiexiu blackware shards, which have a coarser and darker body than Jiexiu Ding-style porcelains and thus seem to be for a lower end market.

3. Analytical methods

The glaze of the porcelain shards is completely removed by grinding on a diamond lap. The porcelain bodies are cleaned with Milli-Q water in an ultrasonic bath and then dried. Approximately 50–100 mg of each sample is weighed and digested with distilled HF and HNO₃ acids using high-pressure teflon bombs in an oven at 180 °C for 60 hours. Such a practice ensures dissolution of all minerals in ceramics, particularly refractory minerals such as zircon which can be important hosts for trace elements. The samples are then dried down and redissolved in distilled HCl in the oven at 180 °C overnight. The solutions are transferred to a polystyrene tube and centrifuged. Any remaining

solids are transferred back to the bombs and dissolved in HCl overnight in the oven. If dissolution is complete the solutions are combined and dried down and the sample converted to nitrates by twice adding HNO₃ and drying down. Other sample preparation and analytical procedures used are essentially identical to those of Eggins et al. [5], with modifications described by Kamber et al. [11]. The method uses enriched isotope internal standardisation, external calibration using a natural rock standard, W-2, and rigorous sample washout procedures. Our preferred concentrations for hotplate digestions of W-2 are shown in Table 1. The samples are prepared and analysed with a Fisons PQ2+ICP-MS in the HEPA and charcoal filtered clean laboratories at the Advanced Centre for Queensland University Isotope Research Excellence (ACQUIRE), University of Queensland. The accuracy and precision of our technique can be assessed from the measured concentrations and relative standard deviations for the basalt standard BHVO-1 (an average of 254 analyses of 68 digestions analysed over seven years) and granite standard G-2 (an average of 13 analyses of 5 digestions) which are shown in Table 1. Among the analytical methods applied in ceramic provenance studies the most widely used one today is neutron activation analysis (NAA). For example, 23 elements analysed by NAA were successfully applied to attribute many Korean celadon wares in the British Museum collection to specific kiln sites in Korea [10]. By comparison, over 40 elements can be analysed simultaneously with a long term reproducibility of <2% for many elements using our ICP-MS method. The greater number of elements and high precision and accuracy for ICP-MS analysis give it more potential in grouping and characterising ceramics, and other archaeological materials.

4. Results and discussion

4.1. White porcelains from different kilns

The results of 40 trace elements for all porcelain bodies from Ding and Jiexiu kilns are listed in Table 1. Results for the imitation-Ding samples from Guantai were reported in Li et al. [15]. Concentrations and ratios of selected elements for the Ding-style white porcelains are illustrated in Figs. 1 and 2. Porcelains from Guantai have the highest concentrations of Ti, Sc, V, Cr, Zr, Cs as well as Y and the Rare Earth Elements (REE), whereas porcelains from Jiexiu have the lowest concentrations of these elements. The Ding porcelains have compositions intermediate between Guantai and Jiexiu for these elements and the range in composition for most elements (e.g., Sr, Ba, REE) and trace element ratios is also greater. The ratios of some trace elements

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