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Study on ancient Chinese imitated GE ware by INAA and WDXRF

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Abstract

Imitated GE ware was one of the most famous products of Jingdezhen porcelain field in Ming dynasty (AD 1368–1644). The exterior features of its body and glaze are very marvelous. Black foot, purple mouth and crazing glaze are the main features of imitated GE ware. Until now, the key conditions of resulting these features are not clearly identified. In order to find the critical elements for firing these features, instrumental neutron activation analysis (INAA) and wavelength-dispersive X-ray fluorescence (WDXRF) were used to determine the element abundance patterns of imitated GE ware body and glaze. The experimental data was compared with that of imitated Longquan celadon and of Longquan celadon. The analytical results indicated that Fe, Ti and Na were the critical elements. The body of imitated GE ware which contains high Fe and Ti are the basic conditions of firing its black body, black foot and purple mouth. The glaze of imitated GE ware which contains high Na is the main condition of producing its crazing glaze. Na is the critical element which enlarges the difference in expansion coefficients between the glaze and body of imitated GE ware. Furthermore, Zijin soil was added into kaolin to make the body rich in Fe and Ti. And something which was rich in Na was used to produce crazing glaze in the manufacturing process of imitated GE ware.

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Keywords: Ancient Chinese imitated GE ware; INAA; WDXRF

1. Introduction

Imitated GE ware was a kind of special porcelain in Chinese ceramic history. Its manufacturing technology and decorating skill were copied from GE kiln. GE kiln was one of the five imperial ware kilns in Song dynasty (AD 960–1279) located in Zhejiang province of China. There are two distinctive exterior features about GE ware fired at GE kiln. One is its crazing glaze. The crazing was stained two different colors, black and yellow. This effect is called 'golden thread and iron wire', an appropriately poetic name. Another is the colors of ware's foot and its mouth. The color of GE ware's foot is black and that of mouth is purple [1]. GE ware was offered to the royal court only. The number of GE ware preserved in museums and collectors in the world is about three hundred only at present. It is so rare and precious that no one or organization is willing to provide any GE ware samples for research. Fortunately, imitated GE ware produced in Ming dynasty (AD 1368–1644) is very similar in look to GE ware. The only difference is the crazing color. The crazing colors of GE ware are black and yellow while the imitated GE ware is black only. We could infer some key conditions about firing GE ware through researching the manufacturing technology of imitated GE ware.

As we known, the contents of major, minor and trace elements in ancient porcelain body and glaze are relied on its raw material and manufacturing technology [2]. They can be used to research the provenance and the manufacturing

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technology of ancient porcelain [3–5]. In this article, we are interested in the critical elements producing the special exterior features of imitated GE ware base on the INAA and WDXRF experiments.

Instrumental neutron activation analysis (INAA) and wavelength-dispersive X-ray fluorescence (WDXRF) are methods advantage of elemental analysis. INAA is high sensitivity, blank-free and multi-elemental analysis. WDXRF systems provide the advantages of total application versatility, optimal measurement conditions programmable for each element, excellent light-element performance, very high sensitivity and low detection limits. They can be used to determine the elemental concentrations in porcelain body or glaze.

2. Samples

Imitated GE ware sherds were excavated from Maojiawan, Beijing city of China and identified clearly by archaeologists of Beijing Institute of Cultural Relics (BICR). According to the decorating patterns, archaeologists announced that they were fired in Ming dynasty (AD 1368–1644) at Hutian kiln in Jingdezhen city, Jiangxi province of China. Imitated GE ware was one of Chinese celadon, which was an important class of Chinese ceramic. In order to research the critical elements in its firing procedure, two kinds of Chinese celadon were selected as reference samples (see Table 1). Longquan celadon has been fired since Song dynasty at Longquan kiln in Zhejiang province of China. It was not only the most classical type of Chinese celadon, but also does it have a great relationship with GE ware according to the literature [6]. We can regard it as a representation of Chinese celadon produced from Zhejiang province. Imitated Longquan celadon was fired in Ming dynasty at Hutian kiln of Jingdezhen city, Jiangxi province of China. Its manufacturing technology and decorating skill were copied from Longquan kiln. The age and provenance of imitated Longquan celadon was the same as imitated GE ware. Thus, we chose Longquan celadon and imitated Longquan celadon as references.

3. Experiments

3.1. INAA measurement

One group of ware samples with 30 mm × 10 mm were cut down from the sherds. After abrading the glaze away, the pure bodies were washed in ultrasonic cleaner with tap water and deionized water, respectively, and then baked at 105 °C for 8 h. After those steps, it was ground into powder of granular diameter about 74 μm with an agate mortar. Powder sample of about 30 mg was wrapped with aluminum foil of 99.999% purity. It was simultaneously placed into the reactor of Chinese institute of atomic energy with calibration standards and quality control standard. They were irradiated under the neutron flux of 5.6×10^{13} n cm^{-2} s^{-1} for 8 h. The calibration standards are single or multi-element solutions [7]. And the quality control standard is the Chinese national certified reference material of rock (GBW07103) [8]. The sample radioactivity was twice counted. The first round was performed after being cooled for 5–7 days. The live time of measurement was 2000 s. The second round was accomplished after 18–20 days with the live time of 3000 s. The γ energy spectrum was collected by an HPGe detector connected to a multi-channel analyzer and processed with the Span 5.1 software package. Under these conditions, 21 elements of La, Sm, U, Na, K, Ce, Nd, Eu, Tb, Yb, Lu, Hf, Ta, Th, Sc, Cr, Fe, Co, Rb, Cs, and Ba were determined. The validation of the analytical method applied in these works was

Table 2
Contents of 21 elements in the certified reference material GBW07103 by INAA

Element (ppm)	Experiment value (mean ± Std.)	Reference value (mean ± Std.)
La	48 ± 2	54 ± 4
Sm	8.8 ± 0.2	9.7 ± 0.8
U	18.4 ± 0.7	18.8 ± 1.4
Na	14,400 ± 860	23,224 ± 600
K	81,300 ± 32,100	41,583 ± 700
Ce	105 ± 3	108 ± 7
Nd	50 ± 4	47 ± 4
Eu	0.84 ± 0.08	0.85 ± 0.07
Tb	1.55 ± 0.12	1.65 ± 0.09
Yb	7.9 ± 0.2	7.4 ± 0.5
Lu	1.10 ± 0.05	1.15 ± 0.09
Hf	6.5 ± 0.3	6.3 ± 0.8
Ta	6.8 ± 0.2	7.2 ± 0.7
Th	51 ± 1	54 ± 3
Sc	5.8 ± 0.1	6.1 ± 0.4
Cr	4.1 ± 2.2	3.6 ± 0.1
Fe	14,900 ± 370	14,958 ± 400
Co	2.9 ± 0.2	3.4 ± 0.7
Rb	452 ± 9	466 ± 17
Cs	34.0 ± 0.4	38.4 ± 1.2
Ba	406 ± 38	343 ± 29

Table 1
The detail information of ancient porcelain samples

Sample	Amount	Exterior characteristic	Dynasty	Provenance
Imitated GE ware	16	Crazing glaze, black body black foot, purple mouth	Ming dynasty (AD 1368–1644)	Jingdezhen city, Jiangxi province, China
Imitated Longquan celadon	15	Celadon glaze, white body	Ming dynasty (AD 1368–1644)	Jingdezhen city, Jiangxi province, China
Longquan celadon	11	Celadon glaze, white body	Song dynasty (AD 960–1279)	Longquan county, Zhejiang province, China