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The study of ancient porcelain of Hutian kiln site from Five dynasty (902–979) to Ming dynasty (1368–1644) by INAA

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Abstract Minor and trace elements of 398 pieces of ancient porcelain of Hutian kiln site from Five dynasty (AD 902–979) to Ming dynasty (AD 1368–1644) were determined by instrumental neutron activate analysis (INAA). The data of INAA and PCA show the ages of all the porcelain can be divided into Five dynasty, Northern Song dynasty, Southern Song dynasty, Early Yuan dynasty, Later Yuan dynasty and Ming dynasty according to their chemical compositions. Moreover, some archaeological questions about the ancient porcelain are discussion also.

Keywords INAA · Hutian kiln site · Greenish white porcelain · Principle factor analysis

Introduction

Jingdezhen has become to the center of ancient porcelain since Tang Dynasty (AD 800–900) in China. Hutian kiln site was one of the important kiln sites in Jingdezhen and it was famous for the greenish white porcelain in the history of Chinese ancient ceramics [1]. From the literature records and investigation of archaeologists, Hutian kiln site lasted for more than 600 years from Five dynasty (AD 902–79) to the middle of Ming dynasty (AD 1368–1644). Instrument Neutron Activate Analysis (INAA) is a traditional analysis method and it is widely used for determining the ages and provenances of archaeological objects [2–4] since Sayre's work [5]. The typical detection sensitivities of INAA are ppb level, with some elements being detected at nearly ppt levels [6]. It is close to that of ICP–MS [7]. In this paper, INAA was employed to determine the concentrations of minor and trace elements in the porcelain excavated from the Hutian kiln site, and then process the experimental data to distinguish their ages and provenances by principal component analysis (PCA) and geochemical analysis methods.

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Experimental

Samples

398 shards of ancient porcelains excavated from Hutian kiln site were selected as specimens by archaeologists. By archaeological strata, samples were divided into Five dynasty (902–979), Early Northern Song dynasty (AD 1004–1037), Later Northern Song dynasty (AD 1037–1127), Early Southern Song Dynasty (AD 1127–1200), Later Southern Song Dynasty (AD 1200–1276), Early Yuan Dynasty (AD 1279–1300) and Later Yuan Dynasty (AD 1320–1368) and Ming Dynasty (1368–1644), respectively. The decorated colors and numbers of specimen are listed in Table 1.

INAA experimental

A small sample (30 mm × 10 mm) was cut from each shard. After abrading away the glaze, the pure body was washed in an ultrasonic cleaner with tap water and then three times in deionised water, and then dried at 105 °C for 8 h. After those steps, the pure body was ground into a

Table 1 The dynasty and decorated glaze colors of 398 pieces of ancient porcelain

Dynasty	Symbol	Number of samples	Decorated colors
Five dynasty (AD 902–979)	FD	25	Celadon
Early North Song (AD 1004–1037)	EN	52	Greenish white
Later North Song (AD 1037–1127)	LN	49	Greenish white
Early South Song (AD 1127–1200)	ES	55	Greenish white
Later South Song (AD 1200–1276)	LS	61	Greenish white
Early Yuan (AD 1279–1300)	EY	37	Greenish white
Later Yuan (AD 1320–1368)	LY (BLACK)	13	Black
Later Yuan (AD 1320–1368)	LY (GW)	49	Greenish white
Ming (AD 1368–1644)	MD	49	Blue and white

powder of 74 mm size in an agate mortar. About 30 mg of each powder sample were wrapped in an aluminium foil of 99.999 % purity. The wrapped samples were placed into the reactor of the Chinese Institute of Atomic Energy simultaneously with calibration and quality control standards. They were irradiated under the neutron flux (6.9×10^{13} ncm^{-2} s^{-1}) for 8 h. The calibration standards used were single or multi-element solutions [8] and the quality control standard is the Chinese national certified reference material of rock (rock, GBW07103) [9]. The radioactivities of the samples were measured twice. The first measurement was performed after cooling for 5–7 days with a measurement live time of 2000s. The second round of measurements was carried out after 18–20 days with a measurement live time of 3000s. The γ energy spectrum was collected by an HPGe detector connected to multi-channel analyzers. Under these conditions, the contents of 18 elements were determined. The validation of the analytical method applied in this work was carried out by analysis of GBW07103. The results showed that the experimental values were well in agreement with the certified ones. The measured values and referenced values of national standard certified reference material GBW07103 was listed in Table 2. The measured values and standard deviation of the porcelain bodies in every dynasty were listed in Table 3.

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

Element (unit)	This work (mean ± SD)	Certified value (GBW07103)
Na (%)	1.98 ± 0.01	2.32 ± 0.07
Ce (μg g^{-1})	110 ± 4	108 ± 19
Nd (μg g^{-1})	51.8 ± 2.2	47 ± 5
Eu (μg g^{-1})	0.855 ± 0.025	0.85 ± 0.10
Tb (μg g^{-1})	1.61 ± 0.09	1.65 ± 0.13
Yb (μg g^{-1})	7.38 ± 0.08	7.4 ± 0.7
Lu (μg g^{-1})	1.13 ± 0.05	1.15 ± 0.12
Hf (μg g^{-1})	6.49 ± 0.33	6.3 ± 0.8
Ta (μg g^{-1})	7.32 ± 0.20	7.2 ± 0.7
Th, (μg g^{-1})	51.5 ± 0.7	54 ± 4
Sc (μg g^{-1})	5.93 ± 0.07	6.1 ± 0.6
Co (μg g^{-1})	3.24 ± 0.33	3.4 ± 1.0
Rb (μg g^{-1})	496 ± 9	466 ± 26
Sr (μg g^{-1})	122 ± 18	106 ± 9
Zr (μg g^{-1})	167 ± 9	170 ± 5
Sb (μg g^{-1})	0.21 ± 0.06	0.22 ± 0.03
Cs (μg g^{-1})	35.6 ± 0.9	38.4 ± 1.5
Ba (μg g^{-1})	443 ± 8	343 ± 45
La (μg g^{-1})	61.1 ± 2.6	54 ± 5
Sm (μg g^{-1})	11.3 ± 0.2	9.7 ± 1.2
U (μg g^{-1})	21.8 ± 0.9	18.8 ± 2.2

Principle component analysis (PCA)

All the INAA data of chemical compositions of porcelain were analyzed by PCA (IBM SPSS20 software).The scatter plots of factor 1 and factor 2, factor 1 and factor 3 are showed in Figs. 1 and 2, respectively. From Figs. 1 and 2, 398 pieces of porcelain decorated with different glazes were divided into Five dynasty, Northern Song Dynasty (including Early Northern Song Dynasty and Later Northern Song Dynasty), Southern Song (including Early Southern Song Dynasty and Later Southern Song Dynasty), Early Yuan, Later Yuan and Ming dynasty by their chemical compositions.

Discussions

The chemical compositions of porcelain body

The mainly productions of Hutian kiln site were greenish white porcelain in Song and Yuan Dynasty. Chemical compositions of 303 pieces of greenish white glaze porcelain samples fired from Early of Northern Song Dynasty (1004–1037) to Later Yuan Dynasty (AD 1320–1368) were determined by INAA. The Figs. 1 and 2 of PCA show all the greenish white glaze porcelain can be divided into

Table 3 Measured values and standard deviation of porcelain bodies

Elements	Five dynasty		Early Northern Song dynasty		Later Northern Song		Early Southern Song dynasty		Later Southern Song dynasty	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
La	54.5	3.5	9.1	2.4	8.3	1.7	12.0	5.4	12.4	8.3
Sm	7.5	0.7	3.9	0.6	3.5	0.5	3.2	0.5	3.1	0.8
U	3.9	0.2	11.6	2.3	12.8	2.0	9.4	3.0	8.7	2.7
Na_2O %	0.15	0.01	0.40	0.20	0.74	0.53	1.40	0.41	1.06	0.54
K_2O %	2.71	0.21	2.87	0.38	3.03	0.36	2.84	0.32	3.17	0.56
As	1.8	0.9	13.0	14.1	15.6	12.1	9.6	8.4	35.1	37.4
Ce	87.8	6.1	18.0	5.1	16.2	2.7	20.4	7.5	18.5	11.1
Nd	40.3	3.5	10.4	2.4	9.7	1.8	11.4	3.5	11.5	6.2
Eu	1.5	0.1	0.3	0.1	0.3	0.1	0.4	0.1	0.4	0.2
Tb	1.1	0.1	0.7	0.1	0.7	0.1	0.5	0.1	0.5	0.2
Yb	3.3	0.1	2.0	0.8	3.2	0.5	2.6	0.5	1.0	0.3
Lu	0.5	0.0	0.2	0.0	0.3	0.1	0.2	0.0	0.2	0.0
Hf	7.8	0.2	3.1	0.3	3.0	0.2	3.1	0.4	2.8	0.8
Ta	1.3	0.1	7.0	1.2	7.1	0.9	5.6	1.4	4.2	1.2
Sc	20.1	1.2	5.4	0.9	5.2	0.9	5.8	1.6	6.0	2.0
Th	15.5	0.6	1.5	0.9	1.2	0.3	2.0	1.0	1.9	1.5
Cr	103.0	5.2	4.3	6.1	3.0	1.5	5.4	4.7	3.8	8.4
Fe_2O_3 %	2.65	0.17	0.72	0.10	0.72	0.09	0.85	0.13	0.79	0.16
Co	6.5	0.8	2.2	0.9	2.0	0.8	2.2	0.7	2.6	1.4
Rb	146.0	10.5	319.0	27.5	328.9	26.8	313.3	38.9	309.3	38.2
Sr	57.4	18.4	145.1	28.8	156.1	27.2	59.4	20.9	49.9	25.4
Zr	348.0	38.2	54.3	21.6	48.7	19.4	146.6	28.0	142.9	31.9
Sb	2.4	0.2	61.1	9.9	63.4	7.6	13.1	14.3	9.9	5.4
Cs	15.1	1.3	16.2	10.8	16.6	9.5	52.5	11.8	41.7	7.3
Ba	469.3	30.9	160.1	37.2	165.7	24.9	192.3	58.3	204.2	51.3

Elements	Later Southern Song Dynasty		Early Yuan Dynasty		Later Yuan Dynasty (with black glaze)		Later Yuan Dynasty (with greenish white glaze)		Ming Dynasty (with blue and white glaze)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
La	12.4	8.3	20.7	14.7	69.6	13.8	41.2	27.8	23.3	6.9
Sm	3.1	0.8	4.2	1.5	8.2	2.1	6.3	3.0	4.6	0.8
U	8.7	2.7	9.0	4.3	4.2	0.6	6.3	2.8	8.3	2.3
Na_2O %	1.06	0.54	0.95	0.37	0.21	0.09	1.04	0.70	0.63	0.26
K_2O %	3.17	0.56	2.97	0.42	2.95	0.76	3.30	0.68	3.77	0.46
As	35.1	37.4	12.0	16.8	26.8	18.9	13.8	10.5	4.1	7.0
Ce	18.5	11.1	32.1	20.2	104.1	21.1	60.3	42.9	31.8	6.7
Nd	11.5	6.2	18.3	10.6	53.5	13.6	32.9	21.0	21.3	5.2
Eu	0.4	0.2	0.7	0.4	2.1	0.5	1.3	0.9	0.7	0.2
Tb	0.5	0.2	0.8	0.2	1.3	0.3	1.1	1.0	0.7	0.1
Yb	1.0	0.3	3.0	0.7	5.3	0.9	4.1	1.3	2.7	0.9
Lu	0.2	0.0	0.3	0.1	0.6	0.1	0.4	0.2	0.2	0.0
Hf	2.8	0.8	4.1	1.4	9.5	0.8	5.5	2.3	3.5	0.4
Ta	4.2	1.2	5.7	1.7	1.6	0.1	4.5	3.0	8.3	3.2
Sc	6.0	2.0	7.7	3.2	17.1	2.0	11.6	5.4	13.4	2.4
Th	1.9	1.5	3.8	3.1	19.4	3.2	9.5	8.1	4.6	0.9
Cr	3.8	8.4	17.1	19.1	107.2	21.3	49.4	49.4	6.8	8.5
Fe_2O_3 %	0.79	0.16	0.92	0.24	4.30	1.53	1.31	0.45	1.44	0.24

Table 3 continued

Elements	Later Southern Song Dynasty		Early Yuan Dynasty		Later Yuan Dynasty (with black glaze)		Later Yuan Dynasty (with greenish white glaze)		Ming Dynasty (with blue and white glaze)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Co	2.6	1.4	3.9	2.5	6.1	2.2	3.8	1.6	8.0	2.2
Rb	309.3	38.2	319.8	48.1	146.4	29.3	303.1	149.4	493.6	158.9
Sr	49.9	25.4	61.6	25.4	98.8	25.3	71.0	63.1	41.0	15.3
Zr	142.9	31.9	185.3	46.2	437.9	47.1	249.7	108.8	175.2	34.7
Sb	9.9	5.4	12.4	22.8	5.5	2.6	4.5	4.6	2.9	1.7
Cs	41.7	7.3	46.2	18.2	27.8	11.3	46.0	17.4	56.1	21.7
Ba	204.2	51.3	264.7	88.5	506.1	119.1	383.9	240.4	181.3	46.2

Unit, μg g^{-1}; except for the Na_2O, K_2O and Fe_2O_3 are %

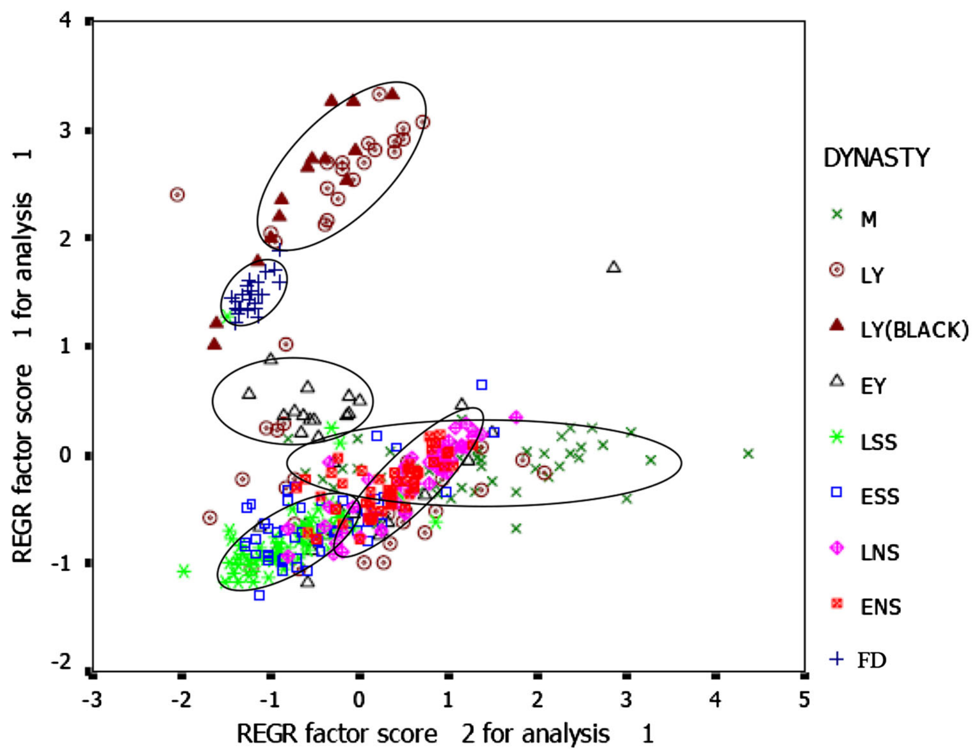
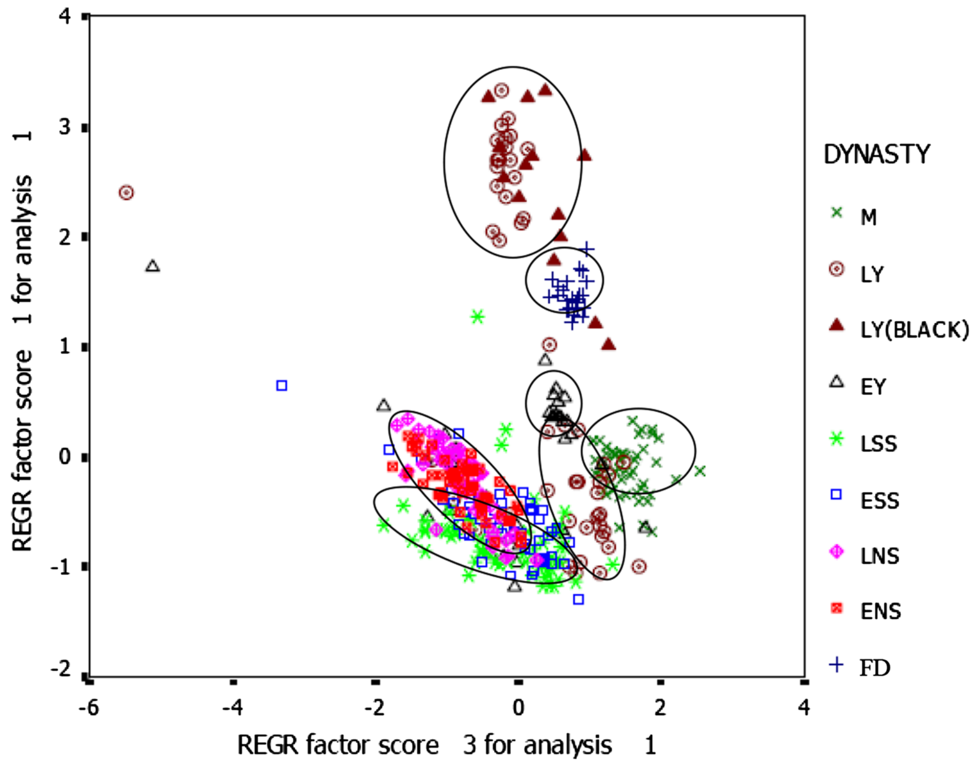


Fig. 1 The scatter plot of factor analysis

Northern Song Dynasty, Southern Song, Early Yuan Dynasty and Later Yuan Dynasty by their chemical compositions. The significant characteristic of greenish white porcelain of Hutian kiln site is that the porcelain body contains lower concentrations of minor and trace elements (Table 3), such as As, Ba, Co, Cr, Sr, etc. Most of them are lower than 100 μg g^{-1}. This conclusion is confirmed with results of PIXE analysis we previous reported [10].

Many researchers believed new technology of making porcelain by adding kaolin stone was created in Jingdezhen because the natural porcelain stone had been used up, but when it was created is still argued by some researchers [2]. Generally speaking, the concentration of Al_2O_3 of porcelain body will improve after adding kaolin. Higher concentration of Al_2O_3 can help the porcelain to be fired in higher temperature to be more hardness. The concentrations of Al_2O_3 of porcelain body is an indicator to show when the new technology to be created. The concentration of Al_2O_3 of porcelain body in Hutian kiln site [11, 13] is no more than 20 % before Early Yuan Dynasty, but it increased to nearly 21 % in the porcelain body of Later Yuan [13]. The scatter plots of PCA (Figs. 1 and 2) show the porcelain body of Later Yuan are divided into two sorts. One sort is consisted of greenish white porcelain and

Fig. 2 The scatter plot of factor 1 and factor 3



black glaze porcelain of Later Yuan. The concentrations of Al_2O_3 of them are more than 21 % [13]. Another sort of greenish white porcelain sample of Later Yuan are scattered into the groups of Song Dynasty and Early Yuan Dynasty. The concentration of Al_2O_3 of those samples is lower than 20 %. After Early Yuan Dynasty, the concentrations of Al_2O_3 of porcelain body in Jingdezhen were more than 20 % [13]. This conclusion has been confirmed by the data reported in other paper [12]. So, our conclusion is that the new technology of making porcelain by adding kaolin was created in Later Yuan Dynasty in Jingdezhen, which is agree with the results of relics investigation of archaeologists [3]. In addition, the concentration of Al_2O_3 of the porcelain body of blue and white porcelain in Ming Dynasty is lower than 20 %. Everyone knows the first empire of Ming set up the official kiln in Jingdezhen in AD 1368. The official kiln monopolized all the super quality of kaolin in Jingdezhen. Therefore, the Hutian kiln had become folk kiln since the beginning of Ming Dynasty.

The REEs pattern

Rare earth elements (REEs) can be used as indicator to show the chemical compositions differences of ancient porcelain [13]. Figure 3 shows the differences of REEs pattern of porcelain body in different Dynasty. All samples are divided into 3 groups by their REEs pattern (Fig. 3). The entire samples of Song Dynasty are in one group; samples of early Yuan Dynasty and Ming Dynasty are in one group; The celadon porcelain samples of Five dynasty, some of greenish white glaze porcelain and black glaze porcelain samples of Later Yuan are in one group. Moreover, the concentrations of light REEs (LREEs) and heavy REEs (HREEs) of porcelain body of different dynasty are different also, such as LREEs are rich in the porcelain body of Five dynasty and Later Yuan Dynasty, but HREEs are rich in porcelain body of Northern Song and Southern Song. It proved that the raw materials of porcelain body came from different strata.

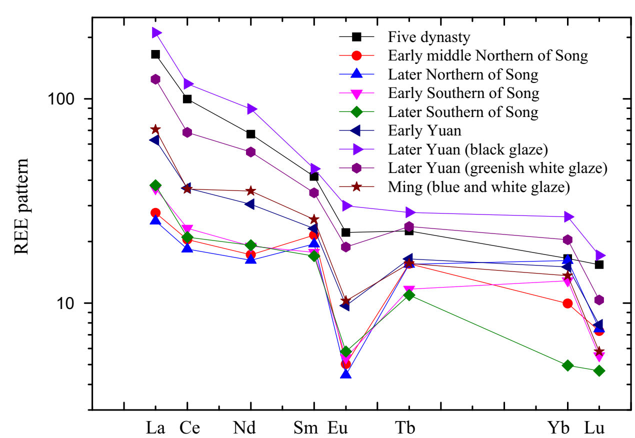


Fig. 3 The REEs pattern of porcelain body in Hutian kiln

Conclusions

According to results of PCA, we conclude that the porcelain bodies of Hutian kiln site within more than 600 years can be divided into Five dynasty, Northern Song dynasty, Southern Song dynasty, Early Yuan dynasty, Later Yuan dynasty and Ming Dynasty. Moreover, the obvious provenance characteristics of greenish white porcelain is that some trace elements are lower than 100 $\mu g\ g^{-1}$. On the other hand, we built the database of the chemical compositions of the ancient porcelain in Hutian kiln. It is very easy to identify the provenance of greenish white ancient porcelain and black glaze porcelain of Hutian kiln site.

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