PIXE study on Chinese underglaze-red porcelain made in Yuan Dynasty

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Abstract In China, the firing and glazed red techniques of producing underglaze-red porcelain began early in the Yuan Dynasty (AD1206~1368). This paper reports the results of the PIXE analysis of ancient Chinese underglaze-red porcelain produced at Kuan kiln (Jingdezhen, Jiangxi Province) in the Yuan Dynasty. In this work the elemental composition analysis of the obtained samples was carried out using the PIXE facility of a 3 MeV tandem accelerator at Fudan University. The major, minor and trace elements of the clay body, white and red glazes were determined, and details of the results are presented. The obtained data can be used for identification of precious Chinese Yuan underglaze-red porcelain.

Keywords Underglaze-red porcelain, PIXE, Composition, Trace elements

CLC numbers O571.33, O657.34, K876.3

1 Introduction

As is well known, underglaze-red is one of the most important traditional underglaze colors for porcelain in ancient China, and the underglaze-red porcelain is a famous sort of ancient Chinese porcelain among the high-temperature glazed pottery.[1] Early attempt to produce the underglaze-red porcelain began in the Yuan Dynasty in Jingdezhen, southern China. Since the proper red color transmutation involved rigorous technological processes, only a limited amount of underglaze-red porcelain was successfully produced, and very few specimens could be preserved up to now. In fact, it is very difficult to collect even their potsherds used as samples for scientific investigation. Hence the work for studying the Yuan Dynasty underglaze-red porcelain has been scarcely done. Using ICP method, Zhang F K and Zhang P S[1] measured the chemical compositions of several underglaze-red potsherds, but gave no report on the potsherds produced in the Yuan Dynasty. In this work, we used the PIXE method for non-destructive analysis of the Yuan Dynasty's underglaze-red potsherds, and determined the chemical composition and trace elements of the body and glaze materials for white and red colors. Our attention is focused on the variation of trace elements in the glaze materials. The present investigation is of particular interest, since the underglaze-red porcelain made in the Yuan Dynasty was investigated for the first time by using the modern PIXE technique. Our results will give very useful information in the characterization of precious ancient Chinese underglaze-red porcelain.

2 Experimental

A collection of underglaze-red potsherds, excavated from the ruins of ancient Kuan klin located in geological stratum of the Yuan Dynasty, was obtained over years from Jingdezhen. Six specimens were selected for the present investigation, including five underglaze-red potsherds of irregular shape and one monochrome-red glazed bowl with long legs glazed in white color. In addition, two underglaze-red potsherds of the Ming Dynasty (AD1368~1644) and more than ten modern underglaze-red porcelain were also included in this study.

Experiments were performed at the Institute of Modern Physics, Fudan University, Shanghai. Exter-

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nal-beam PIXE was carried out for all samples using the 9SDH-2 beamline of the 3.0 MeV tandem accelerator. Samples were placed at 10 mm outside the beam exit window (7.5 μm Kapton). After passing through the Kapton film and air, 2.8 MeV protons with beam current of 0.05~0.5 nA hit the sample with a small spot of 1 mm in diameter. The induced X-rays were detected by an ORTEC Si(Li) detector with an energy resolution of 165eV (FWHM) at 5.9 keV. For measurements of trace elements (Z>23), an Al absorber (0.125 mm thick) was placed in front of the detector in order to suppress the low energy X-rays, and high beam current (0.5 nA) was used to increase the X-ray emission. The obtained PIXE spectra were recorded and analyzed with conventional electronics followed by a multi-channel analyzer. Details of the experimental method and PIXE setup have been given elsewhere.[2-4]

3 Results and discussions

Figs.1 and 2 show the PIXE spectra measured from the glaze for chemical composition and trace elements, respectively. The data analysis was performed using GUPIX-96 program.[5] Table 1 lists the results for the chemical composition of clay and glaze of six samples obtained from the analysis. For the samples studied here, we have found that the clay minerals contain mainly SiO_2 (73.0%~76.0%) and Al_2O_3 (18.3%~20.7%) with small content of K_2O (2.35%~3.03%), Fe_2O_3 (0.81%~1.33%) and CaO (0.14%~0.32%). As for the glazes, we have found lower contents of Al_2O_3 and SiO_2 and higher contents of K_2O and CaO; the obtained contents of K_2O lies 2.2%~4.0%, and the obtained content of CaO amounts to 5.6%~7.8% for the white glaze and is higher (9%~10%) for the red glaze. The result indicates that the glazes used in the Yuan Dynasty belong to the Al_2O_3-SiO_2 system with rich Ca, and the main chemical compositions of clay and white glaze are similar to the underglaze-blue porcelain made in the Yuan Dynasty.[6]

Red is the key color for underglaze-red porcelain. Traditionally the red colorant used by ancient potters in the Jingdezhen region was known as copper bloom, in Chinese term as "tong hua", which is the main material generally adopted for firing underglaze-red porcelain. The "tong hua" is a kind of copper oxide layers, which is made by firing a Cu bar at high temperature. With adding some kinds of clay material the mixture was ground in a grinder to become fine powder and was then used as colorant to paint in an underglaze-red. The development of making copper red glaze in Jingdezhen is not clear. For the samples analyzed, we found that in the red color area there was considerable amount of CuO content with a variable degree of red color from sample to sample. As given in Table 1, for samples Nos.1, 2, 3 and 5, the red glaze shows the CuO content in the range 0.23%~5.97%. The CuO content is less for light red color and amounts up to 4%~6% for dark color of samples Nos.2 and 3. And the glazed surface of their dark areas showing somewhat rough and slightly sunken, does not appear as smooth even as compared with the other glazed areas in vivid red color. Sample No.4 is believed to be the typical one of failure in firing, for part of the colorful pattern has been turned to brown

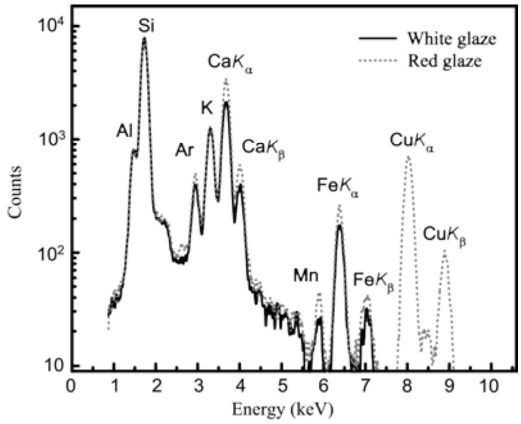

Fig.1 PIXE spectra of an underglaze-red potsherd (Yuan Dynasty). Measurements were made on the red and white colored areas of the glazed surface for chemical compositions analysis.

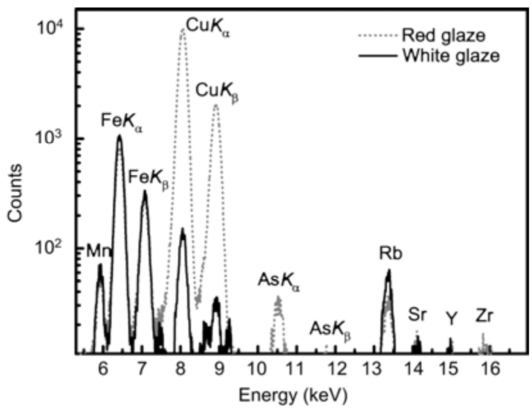

Fig.2 PIXE spectra of an underglaze-red potsherd (Yuan Dynasty). Measurements were made on the red and white col-

ored areas of the glazed surface for trace elements analysis.

Table 1 Chemical composition of body, glaze (white and red) measured from underglaze-red porcelain made in Yuan Dynasty (wt.%)

Sample No.		Al_2O_3	SiO_2	S	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	Remark
1	Body	18.29	75.64	0.25	2.78	0.32	0.072	0.037	1.07	——	
	White	13.26	72.56	0.27	3.33	7.52	0.022	0.086	1.32	0.100	
	Red	13.38	72.09	0.13	3.58	7.11	0.022	0.135	1.80	0.229	
2	Body	18.54	75.46	0.17	2.87	0.19	0.071	0.06	1.11	——	
	White	13.52	73.93	0.20	3.28	6.39	0.022	0.085	1.02	0.033	
	Red	13.54	72.01	0.16	3.19	7.59	0.021	0.098	1.10	0.774	
	Red	12.79	66.72	0.36	2.84	8.48	——	0.130	1.15	5.97	Black
3	Body	18.83	76.03	0.077	2.35	0.17	0.051	0.066	0.809	0.077	
	White	12.75	74.10	0.24	2.79	7.02	0.047	0.144	1.18	0.209	
	Red	12.69	72.85	0.26	2.48	7.77	——	0.134	1.34	0.928	
	Red	12.71	68.77	0.12	2.25	9.10	——	0.138	1.09	4.315	Black
4	Body	19.48	74.46	0.068	2.63	0.14	0.103	0.062	1.23	0.017	
	White	13.76	74.37	0.069	3.33	5.88	0.023	0.089	0.879	0.098	
	Red	13.46	74.52	0.013	3.62	5.75	0.036	0.090	0.970	0.047	
5	Body	20.71	73.36	0.03	2.64	0.27	0.081	0.073	1.33	0.008	
	White	13.77	73.48	0.034	3.68	5.61	0.050	0.138	1.71	0.021	
	Red	14.10	73.94	——	4.00	4.46	0.079	0.152	2.35	0.246	
6	Body	20.60	73.00	0.19	3.03	0.26	0.083	0.080	1.22	0.015	Monochrome red porcelain
	White	12.52	73.98	0.19	3.47	6.79	0.043	0.155	1.29	0.010	
	Red	12.28	70.87	0.24	2.78	10.86	0.011	0.069	1.16	0.208	

color. In the cutting edge of this potsherd, we can see a certain amount of CuO material used for the glaze was still in its clay layer, not completely diffused into its glaze surface where the content of CuO was not noticeably observed. In the white glaze part of some samples, it is possible to observe, with help of a magnifier, certain groups of red spots in different density, arising from the diffusion of CuO grains into the white glaze surface during the firing process. It is seen that a small amount of CuO content (0.1%~0.2%) showed up in the white glaze for samples Nos.1 and 3. Sample No.6 is a monochrome–red bowl with long legs. The red color in the glaze surface is uniform and vivid. An amount of 0.208% for the CuO content was found in the red glaze. From the appearance of samples Nos.2, 3 and 4, we believe that the underglaze-red industry in the period of Yuan Dynasty was still in a primitive stage.

Table 2 lists contents of seven trace elements (Ni, Zn, Ga, As, Rb, Sr and Zr) determined for the clay and glaze of the Yuan underglaze-red potsherds obtained from the external-beam PIXE measurement. There is a significant difference between the obtained constituent of the white and red glazes. According to Tables 1 and

2, for the red glaze, the Cu content appears to be considerably high and the element As is present for all six

Table 2 Some trace elements of body, glaze (white and red) measured from underglaze-red porcelain made in Yuan Dynasty (μg/g)

Sample No.		Ni	Zn	Ga	As	Rb	Sr	Zr	Remark
1	Body	20	128	47	19	297	69	86	
	White	50	97	65	12	327	160	29	
	Red	88	120	89	240	373	195	36	
2	Body	22	97	40	9.3	434	39	31	
	White	62	62	69	6.0	476	121	31	
	Red	——	150	86	151	453	121	23	
	Red	——	207	108	286	460	159	——	Black
3	Red	33	294	194	177	438	298	45	
	Red	——	285	126	357	349	231	46	Black
4	Red	37	124	65	——	454	148	32	Color not diffuse to surface
	Red	104	83	45	160	371	128	26	Translucent glaze removed
5	Body	181	40	71	——	484	109	24	
	Red	64	89	77	184	547	142	84	
6	White	109	107	70	——	511	123	——	Monochrome red porcelain
	Red	179	56	66	37	327	263	20	

samples. Their corresponding X-ray peaks were clearly observed in the measured PIXE spectra (Fig.2). For the white glaze of samples No.1~3, the Cu content was much lower and only a very small amount of As was found (but not found in samples 4~6). Variation of the As was found for the red glaze lies in the range 150~360 μg/g. It is interesting to note that after a thin layer of translucent glaze on the outer surface of sample No.4 was removed, the amount of As content in the red colored area inside was found to be increasing. Apparently As originated from the red pigment used for the Yuan Dynasty underglaze-red porcelain. It is reported[7, 8] that there are two kinds of As ore (FeAsS and $CuAsS_3$) used in ancient China, and many famous bronze artifacts excavated are found to have As admixture. Its appearance in the Cu red pigment is likely from the Cu ore, although the provenance of Cu ore used in Jingdezhen during the Yuan Dynasty needs further investigation. For comparison, we examined two underglaze-red potsherds of Ming Dynasty with appreciable amount of As, even higher than 2000 μg/g in some areas (see Fig.3). Fig.4 is the PIXE spectrum obtained for the glaze of a modern underglaze-red porcelain. It shows clearly that no As peak appears there, as the firing and glazed color techniques have been modified in the modern age.

4 Conclusion

We have determined the clay body and glaze composition of six samples selected for the investigation of ancient Chinese underglaze-red porcelain made in the Yuan Dynasty. We found that the potsherds studied here were characterized by high purity ceramics, and main chemical compositions of the clay body and white glaze used for underglaze-red porcelain are basically consistent with the underglaze-blue porcelain. Copper was found as an underglaze-red pigment from the red colored area on the glazed surface. The obtained CuO content in the red glaze lies in the range 0.2%~6.0% varying with the degree of red color. For monochrome red porcelain as sample No.6, the CuO content in the glaze is low, the measured value of 0.2%(wt) is equivalent to the lowest value obtained for the underglaze-red samples.

Our PIXE analysis confirmed that the copper red pigment was used for making underglaze-red porcelain in the period of Yuan Dynasty. The element As was found as an admixture in the CuO pigment. For the six samples analyzed, the As content in the range 150~350 μg/g was obtained. However, no As content was found in the modern underglaze-red porcelain for the sample studied. Since amount of major and trace elements may reflect the firing and glazed color techniques of making ancient porcelain, the obtained variation of elemental concentrations will be useful for us to explore the ages of production of the Chinese underglaze-red porcelain and to distinguish the products between the true one produced in the Yuan Dynasty and the faked one made with modern technique. However, our results were obtained from the limited samples collected, further PIXE analysis of a larger number of samples from the Yuan Dynasty underglaze-red porcelains for a detailed study is necessary.

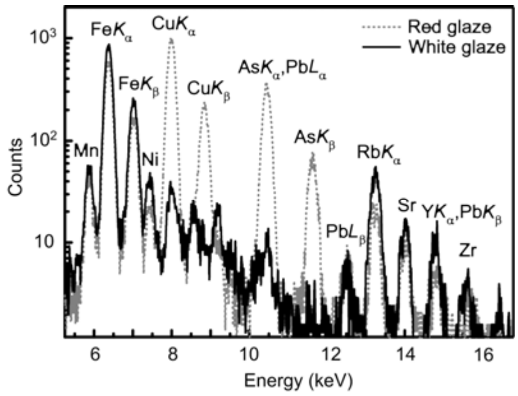

Fig.3 PIXE spectra of a Ming Dynasty underglaze-red potsherd. Measurements were made on the red and white colored areas of the glazed surface for trace elements analysis.

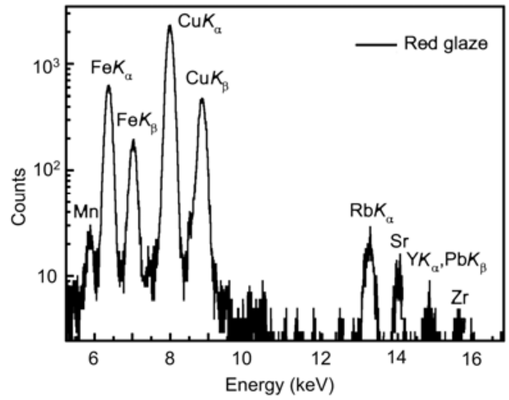

Fig.4 PIXE spectrum of a modern underglaze-red potsherd. Measurements were made on the red areas of the glazed surface for trace elements analysis.

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