

Study of arsenic in *Famille rose* porcelain from the Imperial Palace of Qing Dynasty, Beijing, China



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ABSTRACT

Famille rose porcelain from the imperial workshop was one of the symbols of the highest level of manufacturing techniques in ancient China. It was very precious and only owned by the royals at the early stage. The major feature of *famille rose* is the use of opaque white pigment. Considered to originate in Europe, this technique was a witness of technological exchanges between China and European countries in the 17th–18th centuries. However, limited by its preciousness, most of the previous studies focused on the chemical composition of *famille rose* relics via nondestructive analysis methods. In this work, selected samples excavated at the Forbidden City of China were analysed by microscopy observation, Laser Ablation Inductive Coupled Plasma-Atomic Emission Spectrometry (LA-ICP-AES), synchrotron radiation X-ray Absorption Near-Edge Spectroscopy (XANES) and micro X-ray Diffraction (μ XRD). The results revealed that two painting methods which related to Chinese and European techniques were applied. Chemical composition indicate that opaque white is a kind of arsenic-lead white. Moreover, the synchrotron radiation results show that As^{5+} is the major state in opaque white and exists mostly probably as AsO_4^{3-} ion.

1. Introduction

Ceramics manufacture in China shows a continuous development which can trace back to 20000 years ago [1]. It was one of the most significant forms of Chinese art and global ceramics. Among this extraordinarily rich cultural heritage, wares made in an imperial factory (official workshop) only used by the royal household, represent the top level of firing techniques and aesthetic notions in ancient China.

Famille rose porcelain was one of the symbols of the imperial wares which were made in the imperial factory in the Qing Dynasty (A.D. 1636–1912). It was also called *fen-cai* (powdered colours) or *ruan-cai* (soft colours) in Chinese. It was created in the last years of the Emperor Kangxi's reign (A.D. 1662–1722) [2,3]. In order to make a *famille rose* porcelain, white porcelain was fired at Jingdezhen Imperial Kiln (in Jiangxi Province) firstly, then craftsmen painted the pigments on the glaze and fired the porcelain again. At last, the finished products were

sent to the royal family for appreciation in the Forbidden City in Beijing [2]. Most of the Chinese traditional overglaze enamel recipes were based on the $\text{SiO-K}_2\text{O-PbO}$ system which was considered as water-colour style. But *famille rose* shows oil-based colour style using a different production technique [4]. The appearance transformed from transparency to opaque or semi-opaque was a revolution in ceramics making and greatly extended the content of ancient Chinese ceramics [4]. In essence, this revolution was due to the arsenic opalization in enamel and related to a new overglaze enamel colour in China: opaque white (*bo li bai* in Chinese) [5]. Hence, the character of *famille rose* is that opaque white is painted as the base of colouring areas. Other colours are brushed on top of it or mixed with it to get variations in tone.

Arsenic is the major difference between opaque white and other Chinese traditional enamel ingredient. However, using arsenic to make opaque effect was not traditional Chinese porcelain manufacturing

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technology. The dominant view is that arsenic technology was spread from Europe to China [3,4]. According to the literature, in the early Qing Dynasty, lots of European missionaries came to China. In order to perform missionary work smoothly, the missionaries taught Chinese imperial artisans how to make enamel and glass in return, including introduced arsenic as opalifer into silicate technology [6,7]. Soon Chinese craftsmen applied this technique to make *famille rose* porcelain. It was a witness of cultural and technological exchanges between China and Europe during the eighteenth-century.

It is well known that study on arsenic in opaque white colour is very significant for us to understand firing techniques of *famille rose*. But only a few scientific analyses had been applied on this object. Preliminary experiments revealed that arsenic was commonly used as the opalifer in *famille rose* [4,8–10]. Besides, some researchers attempted to detect arsenic chemical forms in opaque white with non-destructive methods. Kerr thought that crystal of PbAs_2O_4 was the origin of opaque white [4]. On the basis of Raman spectroscopy measurements, Miao considered that $\text{As}_m\text{O}_{2m+1}^{m-2}$ -ion which mainly relates to As^{3+} , existed in opaque white [11], but only one related peak could be found. After then, Van Pevenage confirmed that AsO_4^{3-} -ion could be distinguished by Raman, and she also stated that a lead arsenate similar to mimetite ($\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$) could be identified using Raman spectroscopic analysis [12]. So far, due to the lack of other scientific evidence, the physico-chemical status of the arsenic as an opalifer agent is still puzzling for scientists.

There were two major reasons for the limitation of the *famille rose* research. One is the result of the imperial factory privacy, especially royal wares from the Forbidden City. Literature fails to reveal how the ancient craftsmen made arsenic opaque white in details. The other one is that *famille rose* wares are very rare and precious. The pigment on *famille rose* wares is flaky. Most of them were classified as cultural heritage relics which limited the possibilities to apply traditional analytical techniques. Therefore, only a few scientific investigations involved this kind of valuable products, especially about the opaque white colour.

Recently, spectacular synchrotron experiments were performed in the field of ancient and historical materials with a strong increase over the past ten years [13–15]. The special advantages of nondestructive, element-selective, micro-scale analysis and the flexible sample support system could fulfil needs for relatively size-constrained experiments while keeping intact precious artefact samples [13,16]. Thus, in this work, we analysed selected porcelain shards which were excavated at the Forbidden City by using various scientific methods including advanced synchrotron radiation techniques to obtain a deep understanding about arsenic opaque white and *famille rose*. Firstly, microscopy observation was used on samples to clarify the painting methods of opaque white. Next, the chemical composition was determined by Laser Ablation Inductive Coupled Plasma Atomic Emission Spectrometry (LA-ICP-AES). Based on that basic information, synchrotron radiation X-ray absorption near-edge spectroscopy (XANES) and micro X-ray diffraction (μ -XRD) were applied to identify the species and status of arsenic contained in pigments. The results may give us more understanding of arsenic technology in *famille rose*, and it can provide some references for revealing the ingredients or manufacturing process of the arsenic opaque white.

2. Experimental

2.1. Material

Samples were provided by the Palace Museum, Beijing, China (Shown in Fig. 1). They were excavated at *Nan Da Ku* in the Forbidden City during 2014. In Chinese, *Nan Da Ku* means the storeroom located at the south. It is located at the south-west inside the Forbidden City. The samples were found in a pit site where the royals used to bury broken porcelain together. Archaeologists thought that ceramic shards

of the periods from the Emperor *Hongwu's* reign (A.D. 1368–1398) in Ming Dynasty to the Emperor *Guangxu's* reign (A.D. 1875–1908) in Qing Dynasty were buried in this pit during the Emperor *Guangxu* to Emperor *Xuantong's* reign of the Late Qing Dynasty (A.D. 1875–1911) [17]. Selected samples were named as X1 and C2. X1 was painted with lotus and C2 was painted with peony. Lotus and peony are both common pattern on ancient Chinese porcelain.

2.2. Methods

The surfaces of shards were examined under a Nikon SMZ1000 stereomicroscope, and the cross-sections were examined and photographed with a KEYENCE VH-Z20R stereomicroscope. The results are shown in Figs. 2 and 3.

Chemical compositions of the samples' glaze and pigments were analysed by using LA-ICP-AES. A LEEMAN-Prodigy ICP-AES with a NEW-WAVE laser ablation system was used to perform the analysis. Al, Fe, Mg, Ca, Na, K, Mn, P, Ti, Sb, Cu, Pb, As, Co, Ba, Sn, Sr, B, V, Ni, Zr and Ag elements were collected. Corning B and NIST 610 glass standards were used as the standard reference materials to obtain quantitative results [18]. The average results for three repeat analyses of standards are listed in Table 1. The published values of NIST 610 and Corning B were from Pearce et al. [19] and Brill [20,21], respectively. The results are shown in Table 2. Each colour was tested twice, and the results were similar.

The XANES spectra at arsenic *K*-edge were collected at the beamline station 1W1B, Beijing Synchrotron Radiation Facility (BSRF), China. The electron energy of the storage ring was 2.5 GeV, and during the measurements, the electron current dropped from 250 to 150 mA. The XANES spectra were collected in fluorescence yield mode using Silicon Drift Detector. The Si (111) double crystal monochromator was employed to scan over the *K*-edge of arsenic at 11,867 eV. Results of the samples are illustrated in Fig. 4 along with standard references.

The μ -XRD patterns were collected on beamline station 15U of the Shanghai Synchrotron Radiation Facilities (SSRF, Shanghai, China) by angle-resolved measurements with a wavelength of 0.6199 Å. The monochromatic X-ray beam was produced by using double crystals (silicon 111) and was focused to a beam size of 3.9 (vertical) \times 4 (horizontal) μm^2 full width at half maximum by a pair of Kirkpatrick–Baez mirrors. The diffraction patterns were recorded by using a rayonix SX165 CCD detector. The CeO_2 powder was used to calibrate the distance and orientation of the detector. The collected images were integrated into one-dimensional diffractions patterns by the software of FIT2D [22]. The result is shown in Fig. 5.

3. Results and discussion

3.1. Microscopy observation

Two painting methods were observed under stereomicroscopes. One is a layered painting. It means that opaque white was painted on glaze first and then other colours were painted on top. The other way is to paint directly, which means that other colours were mixed with opaque white before painting them on the glaze.

Fig. 2 is the microscopy results of X1. Fig. 2a and b have partially enlarged details of X1's surface. The pink area corresponds to Fig. 2c. Blue area corresponds to Fig. 2d. It can be clearly seen that a white layer exists between the glaze layer and the coloured layer in Fig. 2c and Fig. 2d. In X1, layered painting method was used. Moreover, it can be seen that the pink and blue colours on the surface are uneven. They both have dark areas and light areas, which display transition effects.

Fig. 3 is the microscopy results of C2. Fig. 3a and b have partially enlarged details of C2's surface. The cross-section in Fig. 3c corresponds to Fig. 3a. The cross-section in Fig. 3d corresponds to the red area of Fig. 3b. It can be clearly seen that glaze layer and the coloured layer are next to each other. Observation on the surface (Fig. 3a) shows that the

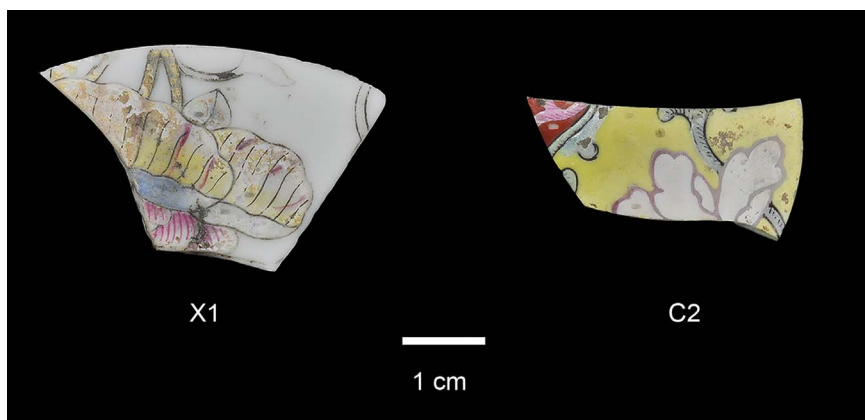


Fig. 1. Photographs of samples. Scale bar: 1 cm.

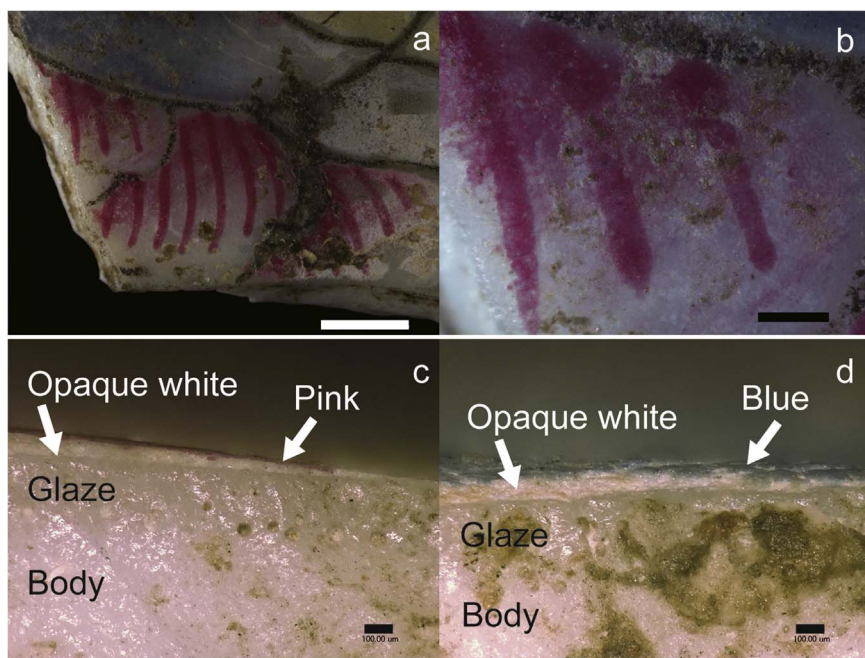


Fig. 2. Microscopy observation of X1 (a: Surface of X1, scale bar: 500 μm ; b: Surface of X1, scale bar: 100 μm ; c: Cross-section of pink area of X1, scale bar: 100 μm ; d: Cross-section of blue area of X1, scale bar: 100 μm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

pink and yellow colours of C2 are uniform. Therefore, it is reasonable to conclude that opaque white and other colours were painted on glaze directly on C2 at one time.

In the Qing Dynasty, two typical painting methods were used on porcelain [23,24]. The first one is called *Ping-tu* in Chinese, which means that the pattern was painted with monochrome without variation. This technique was classical in Chinese traditional technique and was the only methods used in Chinese ceramics painting before the Qing Dynasty. This method corresponds to C2. The second one is the layered painting, which was the method used in X1. It was introduced to China from European technique, enamelling on metal. To enamel on metal, white colour needs to be brushed first to cover the body's original colour. Then other colours were painted layer by layer. *Ping-tu* method and layered painting method are based on Chinese technique and European technique respectively. Combined with the microscopy observation of X1 and C2, it is considered that Chinese technique and European technique were both used at that time. Hence, it is reasonable to say that *famille rose* porcelain was the product of Chinese and European technique's combination.

3.2. Chemical composition

After confirming the painting methods of opaque white pigment, we wonder whether different painting methods are corresponding to

different formulas of opaque white or not. Therefore, we used LA-ICP-AES to get their chemical composition. The results are shown in Table 2.

The chemical results demonstrate that the major flux in pigments is PbO. Iron is the primary colourant in red pigment of C2, while cobalt is the main colourant in blue pigment. Green pigment is led by copper. Yellow areas on samples are lead stannate yellow. Arsenic is widely distributed in coloured areas except in red areas. Previous studies pointed that iron-generated red pigment do not use together with opaque white pigment [8] and our results also proved it. In X1, the content of the arsenic compound in coloured areas is much lower than that in the white area. It corresponds to its painting method. Since the coloured pigments covered the opaque white, it may influence the collection of arsenic signals. In C2, because the pink colour was mixed with opaque white to paint at one time, the content of the arsenic in the pink area was similar to that in the white area of X1. The content of major elements between the white area of X1 and the pink area of C2 is similar. It is considered that different painting methods have a little influence on the formula of opaque white.

Moreover, in Table 2, it can be found that arsenic is the major colour-generating element in the white area of X1. According to its chemical composition, opaque white is a kind of lead-based arsenic white essentially. Si, Pb and As are the major elements of opaque white. According to common raw materials used in ancient Chinese

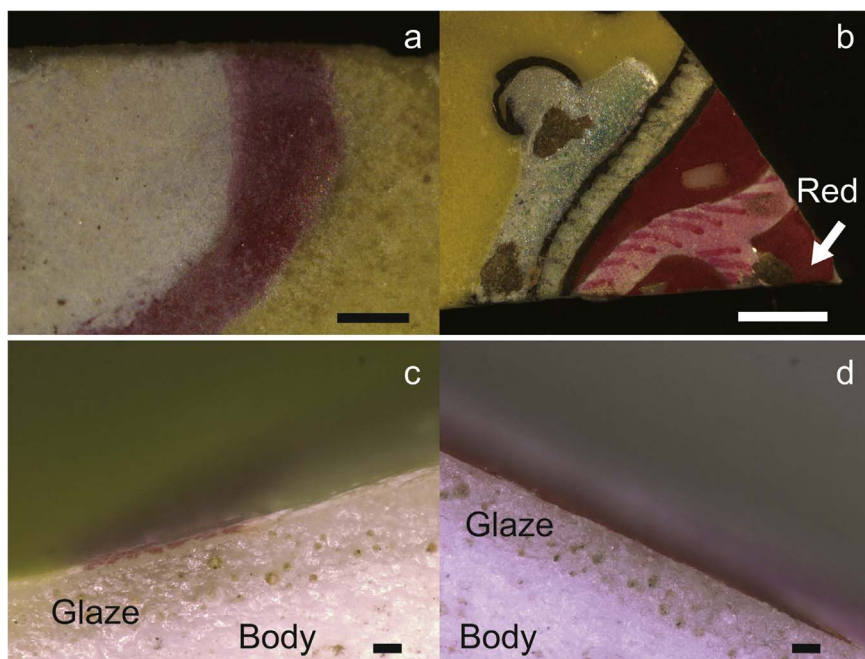


Fig. 3. Microscopy observation of C2 (a: Surface of C2, scale bar: 100 μm ; b: Surface of C2, scale bar: 500 μm ; c: Cross-section of pink and yellow area of C2, scale bar: 100 μm ; d: Cross-section of red area of C2, scale bar: 100 μm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

handicrafts [2,8,9], we considered that original opaque white might consist of quartz, cerussite (or linarite), saltpetre and white arsenic (arsenic trioxide).

The formula of ancient opaque white was not recorded in literature, so some of the scholars have summarised the current formula of opaque white used in Jingdezhen. Zhang had written a modern formula [8]. The raw material of opaque white consisted of K_2O 10%, SiO_2 38%, As_2O_3 3.4% and PbO 49% [8]. The arsenic to lead ratio is about 1/14. However, in ancient samples, the arsenic to lead ratio is about 1/9 in opaque arsenic. According to previous studies, the arsenic oxide will sublime over 600 $^\circ\text{C}$. So, it is reasonable to believe that the proportion of arsenic is higher than 1/9 in the raw material of ancient opaque white. It means that the proportion of arsenic in ancient opaque white is much higher than that in modern times. It is meaningful for us to rebuild the making technology of ancient *famille rose* in the future.

3.3. Synchrotron radiation (SR)-based analytical techniques

On purpose of giving more details on how arsenic existed in pigments, we first applied the SR-XANES technic on samples. The XANES technology is sensitive to the local environment around the arsenic ion. Therefore, it can be used to distinguish the chemical species of arsenic [25–28]. Before the experiment, spectra of sodium arsenite (Na_2HAsO_4) and arsenic trioxide (As_2O_3) were collected to calibrate peak position as standard sample references. In this experiment, X-ray beam was applied to measure the cleaned surface, and the XANES spectra were obtained in the fluorescence yield mode. Samples were analysed by XANES spectroscopy at the As K -edge. XANES spectra of model compounds are

displayed in Fig. 4, together with the XANES spectra of samples.

It is known that the larger oxidation state the ion is at, the larger attraction force between a nucleus and an electron will be. So, with the increasing oxidation state of arsenic, the absorption of edge shifts to a higher energy. For this reason, the XANES peak position is suitable to be used to distinguish between As^{3+} and As^{5+} [26]. It is seen that the white line of As^{5+} is located at 11,875 eV, and the white line of As^{3+} is located at 11,871 eV. In all XANES spectra of samples, the white line is located at 11,875 eV, which indicates that arsenic mainly occurs as As^{5+} . And there is no distinct difference between different colours. Compared with previous Raman results [11,12], XANES spectra could be able to offer a strong and direct evidence of valence state of arsenic in enamel.

In ancient Chinese literature, orpiment, realgar, arsenopyrite, and arsenolite are the most commonly seen arsenic-bearing minerals in handicraft industry [29]. But all of these four kinds of the mineral are not As^{5+} . Hence, there is a high possibility that As^{5+} is the product of firing process.

Besides, we performed μ -XRD to give further information on the arsenic form which exists in opaque white. The spectrum is shown in Fig. 5. We searched for the peaks in the JCPDS (Joint Committee on Powder Diffraction Standards) database and found that the peaks with cross marks are possibly related to arsenate-lead compounds especially with AsO_4^{3-} -ion. In previous works, Miao and Van Pevénage had also considered that AsO_4^{3-} -ion exists in opaque white by Raman spectroscopy [11,12]. But in Raman, some of the spectra of lead arsenate compounds are similar [30,31]. The μ -XRD spectrum shows more information than the past studies, but more analyses are required to

Table 1

The results of some major and minor elements of NIST 610 and Corning B glass standards, by LA-ICP-AES (in wt% for Na_2O , MgO , Al_2O_3 , K_2O , CaO , Fe_2O_3 , and in ppm for others).

	Na_2O	MgO	Al_2O_3	K_2O	CaO	Fe_2O_3	CoO	CuO	PbO	SnO_2
NIST610										
average	13.10	0.09	2.21	–	11.83	0.09	530	620	560	–
Published value	14.00	0.08	2.00	0.04	12.00	0.07	515	538	445	505
Relative error (%)	6	13	11	–	1	28	3	15	26	–
Corning B										
average	16.14	1.06	4.61	0.95	9.01	0.39	430	28,000	4790	450
Published value	17.00	1.03	4.36	1.00	8.56	0.34	460	26,600	6100	400
Relative error (%)	5	3	6	5	5	14	6	5	21	12

Table 2
Chemical compositions of major and minor elements of two samples (wt%).

Sample		Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	As ₂ O ₃	PbO	SnO ₂	CoO	CuO
X1	Glaze	12.05	0.74	3.81	5.82	–	1.35	0.02	–	0.07
	White	1.18	0.54	2.12	1.62	6.13	56.87	0.08	–	0.06
	Blue	0.61	0.19	0.83	3.61	2.69	56.21	0.07	0.98	0.08
	Yellow	0.91	0.44	0.87	1.28	3.16	60.52	3.80	–	0.07
	Pink	0.95	0.28	0.81	1.73	2.27	58.42	0.06	–	0.04
C2	Yellow	1.14	0.65	0.41	1.67	0.12	64.92	3.30	–	0.12
	Dark Pink	2.49	0.45	1.05	1.83	2.89	43.61	0.29	0.01	0.11
	Light Pink	0.78	0.16	0.79	2.26	6.89	57.78	0.04	–	0.09
	Green	4.49	0.74	1.63	1.17	0.12	48.32	0.25	0.04	1.45
	Red	6.46	11.35	2.33	1.34	–	45.34	0.03	–	0.15

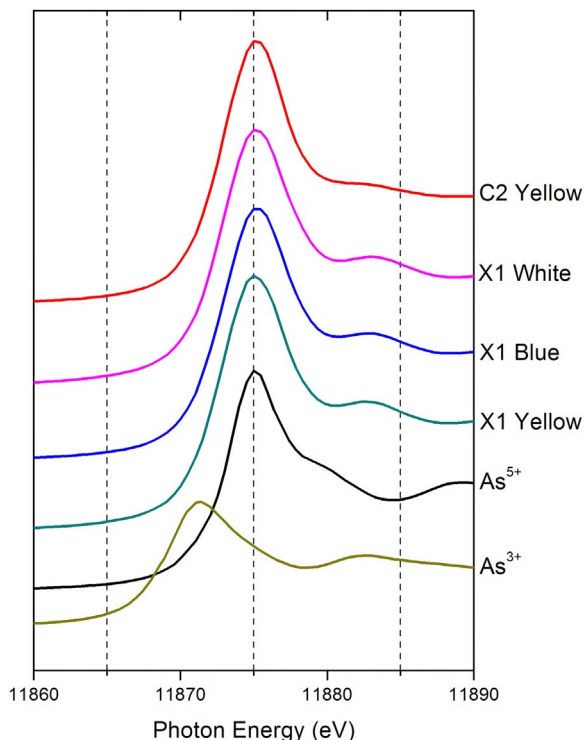


Fig. 4. As K-edge XANES spectra for samples.

confirm the arsenic compounds which exist in opaque white. It will help us to understand the firing techniques of arsenic in ancient Chinese porcelain.

4. Conclusion

Based on experimental results, we can provide three main conclusions.

Firstly, microscopy observation shows that the two samples have different ways of using opaque white. These two methods represent Chinese and European painting techniques. Secondly, LA-ICP-AES results prove that arsenic plays an important role in *famille rose*. It is widely distributed in pigments. Quartz, cerussite (or linarite), saltpetre and white arsenic may be the raw materials of opaque white. The proportion of arsenic in ancient opaque white is much higher than that in modern times. Different painting methods have little influence on the formula of opaque white. Red pigment area which was due to iron does not use opaque white. Thirdly, by using the XANES, the arsenic valence was considered as 5+. And compared to μ XRD result, it showed a high probability that AsO_4^{3-} ion exists in opaque white.

These analyses provide us with some basic information about arsenic technology in *famille rose* porcelain. It could also offer references to further researches on *famille rose* and the spread of arsenic technology in porcelain production.

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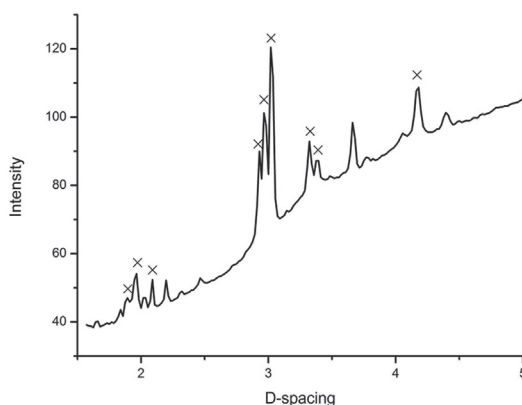


Fig. 5. μ XRD of opaque white on X1.

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