New insights into the role of Mn and Fe in coloring origin of blue decorations of blue-and-white porcelains by XANES spectroscopy

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Abstract. Blue and white porcelain is one of the most valuable ancient ceramics varieties in ancient China. It is well known for its beautiful blue decorations. However, the origin of its blue color has not been very clear till now. In this research, two blue and white porcelains from Jingdezhen, Jiangxi province were selected and Mn and Fe K-edge XANES spectra were recorded from blue decorations with or without transparent glaze. Results showed that Mn K-edge XANES features were almost identical between different samples while that of iron changed. The above findings indicated the positive role of iron in the variation of blue decorations. As for manganese, although more system researches were need, its negative role on the variations of the tone of blue decorations was obtained. On the other hand, the paper also revealed the XAFS results will be affect by the glaze layer above the pigment. These findings provided us more information to understand the coloring origin of blue decorations of blue-and-white porcelain by means of XANES spectroscopy.

1. Introduction

Blue-and-white porcelain is well-known for its skillful techniques and great artistic merits all around the world. Especially in Ming and Qing dynasty, blue-and-white porcelain reached the height of its technical excellence and played an important role in the cultural exchange between the east and the west. So far, blue-and-white porcelain have been attracting more and more researchers to investigate its manufacturing techniques, the provenance of cobalt blue pigment ore, the dating and authentication, and so on. Coloring origin of the blue color in blue-and-white porcelain is one of these hot topics. Previous studies pointed out that transition elements such as cobalt, iron and manganese made the contribution to blue color And among these elements, cobalt took up the main role in blue
color while iron and manganese were responsible for the variation of the tone of blue color. Although coloring variations are usually obtained by modulating the oxidation states of transition elements, for a long time, the science study on the blue and white porcelain remained in the level of the chemical composition. And little is known about the elements’ oxidation and chemical environment which is directly correlated to its coloring origin.

X-ray absorption fine structure (XAFS) is a powerful technique, based on the development of synchrotron radiation source, to investigate the local electron and geometrical structure around an absorbed atom by analyzing the fine structure above the absorption edge. Up to date, XAFS has been applied to solve a lot of important research issues in a wide range of scientific fields, including material science, catalysts research, environment science, biology, and so on. In archaeometry and art conversation, XAFS also has its own advantages, especially in these researches on coloring mechanism of glaze and glass with amorphous phase. In our past research, Co K-edge XAFS analysis of blue decorations of blue-and-white porcelains found that Co$^{2+}$ was the main constituents coordinated with oxygen atoms situated in both octahedral and tetrahedral sites. Considering the ability in absorbing the characteristic frequencies in visible region, it was concluded that [Co$^{2+}$O$_4$]

Figure 1: Map of relationship about the glaze, pigment and body across the profile of blue-and-white porcelain

made more contribution to the blue color of blue-and-white porcelain. However, the Co K-edge spectra for all samples collected from Yuan dynasty to Ming dynasty with different tones of blue colors were almost identical. Since iron and manganese, which are also co-existed in blue decorations, are usually considered as colorant elements, it is necessary to investigate the oxidation state and local environment of iron and manganese in order to have a thorough understanding of the coloring origin of blue decorations.

However, to investigate the oxidation state of iron and manganese in blue decoration of blue and white porcelain by XAFS technique, there is a problem that should be solved firstly. Because the blue and white porcelain are under-glaze ceramics, the surface of blue pigments were covered a transparence glaze (see Figure 1). Iron and manganese contained in glaze layer will have an impact on the XAFS spectra recorded from the surface of glaze layer directly.

Thus, in this research, Mn and Fe K-edge XANES spectra of blue decoration with glaze layer above or not were obtained and compared. The primary purpose was to investigate the influence of glaze layer during the XAFS measurements nondestructively.

2. Samples and experimental

Samples analyzed in this research included two blue and white porcelains, labeled with HJ-02(Figure 2a) and JS-06 (Figure 2b). both of these were collected from Jingdezhen, Jiangxi province. The experiments were carried out as the following steps: 1) Put samples to holder and focus on one point, then collected the XANES spectra; 2) Cut off the glaze where the above point have been tested, then collected the XANES spectra again.
Mn and Fe K-edge XANES measurements were performed on beamline BL14W at Shanghai Synchrotron Radiation Facility (SSRF). The storage ring energy was operated at 3.5 GeV with a ring current of 130 mA to 210 mA. A Si (111) double-crystal monochromator was used to monochromatize the white beam. And higher harmonics were rejected with the aid of harmonic mirrors of Ni layer. At the site of sample, the flux was about $10^{12}$ photo/s and the beam size was ca. 1 (H)×1 (V) mm$^2$. All K-edge XAFS spectra of blue-and-white porcelains were recorded in fluorescence yield mode with silicon drift detector (SDD) at room temperature. The IFEFFIT package was used to analyze the raw spectra using conventional procedures\textsuperscript{4}.

3. Results and Discussion

Mn $K$-edge XANES spectra of blue decorations with or without glaze layer for HJ and JS were shown in Figure 3. As shown in Figure 3, two findings could be observed. First of all, Mn $K$-edge XANES spectra of blue color decorations with or without glaze for certain blue-and-white porcelain (sample HJ-02 and JS-06) were almost identical. This finding indicated that the oxidation state of manganese contained in blue decorations was consistent with that of glaze layers. Secondly, no significant shifts of pre-edge (peak A) and white line (peak B) between different samples were observed. Since coloring variations in porcelains are usually changed with the variations of oxidation state of transition element, the almost identical XANES features demonstrated that manganese has no direct effect on the variation of the tone of blue decorations.

![Figure 2: Photograph of the samples HJ-02 and JS-06](image)

![Figure 3: Mn $K$-edge XANES spectra of blue decorations with or without transparent glaze for HJ-02 and JS-06](image)
Fe $K$-edge XANES spectra for different blue-and-white porcelains were shown in Figure 4. Compared with XANES spectra detected directly from the glaze surface and the cut-off glaze result, two findings could be found. For HJ-02 sample, the position of absorption edge of iron in blue decorations without glaze layer shifted to lower energy compared with that of transparent glaze and Figure 4: Fe $K$-edge XANES spectra of blue decorations with or without transparent glaze for HJ-02 and JS-06
blue decorations with glaze layer. For JS-06 sample, the position of absorption edge of iron in blue decorations without glaze layer, blue decorations with glaze layer, transparent glaze were almost identical. The above results indicated that the oxidation state of iron in blue decorations and transparent glaze were different. As a result, Fe $K$-edge XANES spectra detected directly from the surface of transparent glaze of blue decorations did not reflect the real information of the oxidation state of iron contained in blue decorations. The inconsistent may be induced by two possibilities. One was influenced by manganese element since iron can be oxidized by manganese. The other possibility was about the firing atmosphere. Because previous studies pointed out that blue and white porcelain were fired at reduction atmosphere.

As a kind of under-glaze color, blue-and-white porcelain from the profile view, the location of transparent glaze layer, the pigment layer and the body. During the XANES experiments, the incident X-ray through a transparent glaze layer to reach the pigment layer, the fluorescence signal is also required to pass through the transparent glaze layer after the detector detection. During this process, the transparent glaze layer will affect the XANES measurement of blue decoration in two ways. On one hand, iron and manganese are also existing in transparent glaze (Fe: 0.8-1.92%, Mn 0.1-1.91%). In this research, it is induced that the Mn content exist in the glaze and pigments were consistent by the comparison analysis. However, the oxidation state of Fe demonstrated some shift in different part, indicating that the Fe element in glaze will have infection to the XAFS result. On the other hand, the thickness of transparent glaze layer cannot be ignored too. Under normal circumstance, structural characterization of XAFS experimental spectra contains useful information (the absorption coefficient of the oscillation part) that relative to the absorption edge height of only a few percent. Due to varying of the thickness of the transparent glaze layer in samples (thickness around 300-400μm), when the fluorescence signal of the pigment layer through the transparent glaze, the layer of glaze with what kind of impact for the fluorescence peaks, as well as how this correction is not yet clarity on past and still need more systematic research in future. Thus, results obtained here were not a conclusive
identification. If more samples were incorporated, findings we found here could be changed subsequently. Therefore, in future researches, a larger set of samples, as well as reference materials, will be considered in order to get a thorough understanding of the role of iron and manganese on the coloring mechanism of blue decorations of blue-and-white porcelains.

4. Conclusions

In this study, two blue and white porcelains from Jingdezhen, Jiangxi province were selected and the transparent glaze were polished and rubbed off at some areas with blue decorations. Mn and Fe K-edge XANES spectra recorded from blue decorations with or without transparent glaze showed that Mn K-edge XANES spectra were almost identical while the absorption edge of iron changed. These results directly ruled out the positive influence of oxidation state of Mn in the variation of the tone of blue decorations in blue-and-white porcelains. On the contrary, changes of oxidation state of iron in different samples indicated its positive role in the variation of blue decorations which should be investigated further in the future.

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References

[1] J. Li, 1998, *History of Science and Technology in China, Ceramics Volume*. (Science Press, Beijing) chapter 11.
[2] N. Wood, M. S. Tite, C. Doherty and B. Gilmore, *Archaeometry*, 2007, 49 (4), 665–84.
[3] Lihua Wang and Changsui Wang, *J. Anal. At. Spectrom*. 2011, 26, 1796-01.
[4] B. Ravel, M. Newville, *J. Synchrotron Rad*. 2005. 12, 537-42.
[5] Wu Jun, Li Jiazhi, Guo Jingkun, *Journal of Inorganic Materials*, 1999, 14(1), 143-149.