Study on Coloration Mechanism of Chinese Ancient Ceramics by X-ray Absorption Near-edge Structure

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Abstract. The Fe K-edge X-ray absorption near-edge structure (XANES) spectra of a series of ceramic shards were measured by fluorescence mode to reveal the color-generating techniques of Chinese porcelain. The analysis disclosed relationships among the chemical form of the iron, the firing conditions and the colors of the ceramics. The results indicate that the coloration for different ceramics depend on the valence states of iron as the main color element in glaze and the proportion of Fe$^{2+}$ and Fe$^{3+}$ was attributed to the baking technology. The findings provide important information for archaeologist on the coloration researches.

1. Introduction

The invention of porcelain was China’s great contribution to the world civilization [1]. With the increase of production, the prosperity of the government porcelain kilns greatly promoted the porcelain baking technology. To reveal the information about the production technology, numerous researches have been focused on the color-generating elements in ancient ceramics glaze among which chemical structure analyses of the transition elements is most popular [2-5]. Therefore, amounts of advanced scientific techniques are used to investigate the archaeological materials.

Proton induced x-ray emission (PIXE) technique was performed to revealed that the glaze of ancient Ru porcelain has very high iron content [6-7]. X-ray photoelectron spectroscopy (XPS) was applied to the moon-white glaze on ancient Ru ceramics in order to investigate the origins of the colour [8]. Mössbauer spectroscopy and Neutron activation analysis (NAA) reveal that the different coloration on the glaze is originated from the conditions of production processes [9-10]. Also, synchrotron radiation technologies, such as SRXRF and XANES, have been applied in porcelain structure analysis [5,11-12]. However, the production of porcelain involved roughly the raw materials, a delicate refinement procedure, and a developed firing technology, so there is no uniform interpretation on the color-generating mechanism for different typical porcelain. It is a debate problem in the archaeology and ancient ceramics research. To clarify the principle of the coloration for Fe as the color element, four different ancient ceramics were selected as prototypes.

In the present paper, fluorescence x-ray absorption fine structure was used to investigate the Fe chemical form and atomic structure in glaze for four ancient ceramics. With the advantage of the sensitivity of the XANES spectroscopy to the local structure around Fe atoms, in conjunction with linear combination fitting (LCF) method, we aim to reveal the production techniques of different ancient ceramics. Our findings indicate that the coloration mechanism depends on the firing conditions.
2. Experimental

Four classical ancient porcelain shards were studied by XANES. Ru and Cyan porcelain were from Ru kilns in Henan province and Jingdezheng in Jiangxi province, respectively. Xin’an ceramic was produced in Anhui Province and Qionglai sample was from Sichuan Province. They were marked by RC-1, RC-2, RC-3, CC, XA and QL, respectively. Reference samples used as standards for iron in various oxidations states included iron metal, FeO, Fe2O3 and Fe3O4.

The Fe K-edge XANES spectra were recorded in the fluorescence mode at the U7C beamline in the National Synchrotron Radiation Laboratory (NSRL) and at the BL14W1 beamline in the Shanghai Synchrotron Radiation Facility (SSRF). The energy of storage ring of NSRL is 800 MeV and the average current is 200 mA, and that of SSRF is 3.5 GeV and 300 mA, respectively. The resolution of double crystal monochromater Si (111) is about 1~2 eV at Fe K-edge. The seven-element Ge solid state detector (SSD) calibration and the solid angle determination were performed using a set of appropriate approach. Through all experiments, no damage caused by x-ray could be observed in the samples.

3. Results and discussion

According to the XRF results, the content of iron is the most condensed of transition element among Mn, Cu, Ni and Zn, with the ratio of more than two magnitudes. It is a well known fact that iron is one of most important elements for coloration and the colors of porcelain are closely related to the chemical states of iron [6]. To obtain basic information on various oxidation states of iron, the reference compounds were measured. Figure 1(a) displayed the Fe K-edge XANES spectra of metallic iron, Fe3O4, Fe2O3 and FeO. It is understood that the absorption edge shifts to a higher energy as the valence state of the absorber atom in sample increases [11]. It was found that the absorption edge energy of metallic iron is located at the lowest energy level among samples. The pre-edge peak and the absorption edge energy of magnetite (Fe2+, Fe3+) are located at lower position than those in compounds containing trivalent iron. Compared with metallic iron, iron oxides exhibit a small pre-edge peak on the lower-energy side of the absorption edge, corresponding to transitions from 1s to 3d levels. The pre-edge peak also shifts to a higher energy with an increase in the valence state of the absorber atom [6,11]. Thus, it is found that each iron compound has its own characteristic XANES spectrum.

![Figure 1](image_url)

**Figure 1** Fe K-edge XANES spectra of iron reference oxidations (a) and ancient ceramics samples (b) and the pre-edge peak of reference and samples (inset).

The valence states of transition elements in ancient ceramics maybe influenced by many factors, such as the geological processes, the decoration procedure and the production courses. In order to exclude the interference of a number of factors, we firstly chose the series of RC ceramics to study since they used the same clay and the same decoration techniques. Fe K-edge of XANES spectra of three ancient RC ceramics shards were shown in Figure 1(b). It was found that the spectra of ancient RC ceramics are characterized by fine structures with a pre-edge peak at 7112 eV and the absorption at 7121 eV. The oxidation states of iron in these ceramics were determined to be divalent and trivalent,
since the energies of the pre-edge peak and the absorption edge are close to magnetite. It is also observed that the intensities of the pre-edge peaks of ancient RC ceramics are weak (see Fig 1(b). inset), which also reflected the low chemical states of iron in ancient RC samples. Therefore, it is expected that the main chemical form of iron is Fe$^{2+}$ and Fe$^{3+}$ in ancient RC ceramics, which is consistent with the previous report [8,12].

It was found that the differences between the XANES spectra measured on three ancient RC samples could not be characterized by their pre-edge peak and absorption edge. But the glaze colors of them are distinct with each other, which are moon-white (light yellow), gray-green and bean-green for RC-1, RC-2 and RC-3, respectively. To reveal the origins of the coloration mechanism, the XANES spectra of three samples were studied by linear combination fitting (LCF) method with fitting results shown in Figure 2. As seen from Fig. 2(a-c), Fe$_3$O$_4$ is the main component for all RC samples, in good agreement with the results of the previous report [8]. According to the results, the relationships of the proportions of Fe$^{2+}$ and Fe$^{3+}$ and the main wavelength were summarized in Table I. It was seen that the proportion of Fe$^{2+}$/Fe$^{3+}$ is greater than 1.0 in all RC samples glaze which reflected more divalent iron in chemical form for ancient RC ceramics. As is well known, the color-generating mechanism is closely related to the valence states of iron. The proportion of divalent and trivalent irons reflected the firing conditions during the production processes. The greater Fe$^{2+}$/Fe$^{3+}$ revealed that the ancient RC ceramics were produced under reducing conditions. The larger proportion of Fe$^{2+}$/Fe$^{3+}$ in glaze is, the closer green colors of the ancient RC ceramics are. The smaller proportion of Fe$^{2+}$/Fe$^{3+}$ in glaze is, the closer yellow colors of RC porcelain are.

### Table I
Colors, proportion of Fe$^{2+}$ and Fe$^{3+}$ and main wavelengths for the ancient ceramics.

| Samples | Color       | Proportion Fe$^{2+}$/Fe$^{3+}$ | Main wavelength |
|---------|-------------|-------------------------------|-----------------|
| RC-1    | Gray-green  | 1.39                          | 535             |
| RC-2    | Moon-yellow | 1.22                          | 560             |
| RC-3    | Light-Cyan  | 1.16                          | 585             |
| CC      | Light-Cyan  | 0.90                          | 598             |
| XA      | Dark-Gray   | 0.42                          | 633             |
| QL      | Dark-Brown  | 0.27                          | 645             |

Excepted for the ancient Ru kiln, there are many other kilns using Fe as the coloring agent. To confirm the universality of color-generating mechanism for all porcelain that the Fe is the main color element, other three typical samples were subsumed. Fe K-edge XANES spectra of three samples were also shown in Figure 1(b). It was found that the differences between the XANES spectra measured on each ceramics shards could be characterized easily by their absorption edge energy and the pre-edge...
peak. The absorption edge of CC from Jingdezhen is located at 7124 eV and the pre-edge is at 7114 eV. The pre-edge peak and the absorption edge of ancient XA and QL located at 7114 eV and 7126 eV, respectively. The oxidation states of iron in these ceramics were determined to be entirely trivalent, since the energies of the pre-edge peak and the absorption edge are close to hematite. It is also observed that the intensities of the pre-edge peaks of ancient XA, QL, and CC ceramics are stronger than those of RC samples (see Fig 1b. inset). As a conclusion, the observed increase in the intensity of the pre-edge peak for XA, QL and CC porcelains suggests that these ceramics had been fired under the oxidation conditions since the chemical form of iron is mainly trivalent iron in their glaze.

Ancient CC, XA and QL porcelains are also fitted by the linear combination fitting method and the results were displayed in Fig. 2 (d-f) and Table I. It is instructive to clarify that ancient CC, XA and QL ceramics are also the same coloration principle for different kilns. The main form of iron for CC is magnetite and the proportion of Fe$^{2+}$ and Fe$^{3+}$ close to 1.0. The color of glaze was shown light cyan due to the interaction of divalent and trivalent iron under firing processes. For ancient XA and QL samples, the color element is also iron with the form of Fe$_2$O$_3$, so these samples show dark brown. According to discussion above, we can conclude that the color-generating element of ancient RC, CC, XA and QL ceramics is iron and the color-generating mechanism depends on the valence states of transition element which were caused by the firing conditions. However, the relationship of the transition elements and coloration techniques is very complex. Whether the coloration mechanism is related with interaction of all transition elements, there is not a clear interpretation. To reveal the origins of the questions, further research and precise approach are needed.

4. Conclusions
In this report, four typical ancient famous ceramics were studied by using fluorescence XANES. The results revealed that the color-generating mechanism of ancient ceramics is depended on the chemical states of the transition elements (the main color element) in the glaze. It is suggested that the colors of ancient RC samples vary with the proportion of Fe$^{3+}$ and Fe$^{2+}$ that change from cyan through bean green to yellow with the increase of trivalent oxidation state of iron. The ancient XA and QL ceramics show dark brown because of the chemical form of trivalent iron in glaze. The Cyan ceramics is light green due to the interaction of the divalent and trivalent iron.

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References
[1] Li J Z History of Science and Technology of China:Ceramics Volume.SciencePress 1998, Beijing
[2] Yu K N and Miao J M 1999 Appl. Radiat. Isot. 51 279
[3] Wu J, Leung P L, Li J Z, Stokes M J and Li M T W 2000 X-Ray Spectrom. 29 239
[4] Matsunaga M and Nakai I 2004 Archaeometry. 46 103
[5] Padovani S, Borgia I, Brunetti B, Sgamellotti A, Giulivi A, D’Acapito F, Mazzoldi P, Sada C and Battaglin G 2004 Appl. Phys. A 79 229
[6] Matsunaga M and Nakai I 2004 Archaeometry. 46 103
[7] Zhu D, Cheng H S and Lin J W 2006 Nucl. Instrum. Methods Phys. Res., Sect. B 249 633
[8] Wang J, Z H, Li W and Li G 1995 Chin. Ceramic. 31 27
[9] Zhang B, Z W, Li G, Xie J and Gao Z 1999 J. Zhengzhou Univer. 31 1
[10] Chevalier R, Coey J M D and Bouchez R 1976 J. Phys. (Paris), Colloques 37 861
[11] Calas G, Manceau A and Petiau J 1998 in Synchrotron radiation applications in mineralogy and petrology (ed. A. Barto-Kyriakidis)Theophrastus Publications, Athens, Greece. 77-96
[12] Zhang M, Wang C, Jin P, Wei S, Xu W, Chen D and Wu Z 2008 Nucl. Tech. 31 648