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# CHINA NUCLEAR SCIENCE AND TECHNOLOGY REPORT

## Mössbauer效应对几种古代名瓷的应用研究

## APPLIED INVESTIGATION OF MÖSSBAUER EFFECT FOR THE FAMOUS ANCIENT CHINESE PORCELAINS

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## 摘　　要

分析了宋代和元代著名的汝瓷、钧瓷和官瓷样品，比较了古瓷和仿古瓷的穆斯堡尔参数，讨论了这些古瓷的烧制技术、着色机理和微观结构，得到了以下结果：(1) 汝瓷釉中含有结构铁$Fe^{2+}$，$Fe^{3+}$和磁性成分$Fe_3O_4$。推断宋代和元代汝瓷原始烧成温度约为1250℃。它们的烧制气氛为还原气氛。汝瓷的釉色与铁的化学状态有关。(2) 钧瓷釉中含有铁矿物（$Fe_2O_3$，$Fe_3O_4$）和已进入粘土晶格的结构铁（$Fe^{2+}$，$Fe^{3+}$）。推断宋代钧瓷（$SJ_2$）的原始烧制温度高于1200℃，元代钧瓷（$YJ_3$）的原始烧成温度略高于1250℃。宋代天蓝钧瓷在重还原气氛中烧成。宋代天青钧瓷和仿古蓝钧瓷在中等还原气氛中烧成。元代钧瓷（$YJ_3$）在弱还原气氛中烧成。推断古钧瓷的$Fe^{2+}$和$Fe^{3+}$的配位数均为4。钧瓷的着色机理非常复杂。铁的化学状态是影响钧瓷釉色的因素之一。(3) 南宋官瓷粉青釉与灰青釉中结构铁较多。米黄釉中氧化铁较多。粉青釉和灰青釉的烧制气氛为重还原气氛，烧制温度较高。米黄釉为轻还原气氛，烧成温度较低。

# Applied Investigation of Mössbauer Effect for the Famous Ancient Chinese Porcelains

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## ABSTRACT

The famous Ru porcelain, Jun porcelain and Guan porcelain of Song Dynasty and Yuan Dynasty are analyzed. The Mössbauer parameters of the ancient porcelains and the imitative ancient porcelains are compared. The firing techniques, coloring mechanism and microstructures of the ancient Chinese porcelains have been discussed. The results are shown as follows: (1) The Ru porcelain glaze contain structure iron ($Fe^{2+}$, $Fe^{3+}$) and magnetic component $Fe_3O_4$. The original firing temperatures of Ru porcelain of Yuan Dynasty and Song Dynasty are inferred to be 1250℃. The original firing atmospheres are determined to be reductive. The glaze color of the Ru porcelain is related to the chemical state of iron. (2) The ancient Jun porcelain glazes contain iron minerals ($Fe_2O_3$, $Fe_3O_4$) and structural iron ($Fe^{2+}$, $Fe^{3+}$) entered clay mineral lattice. The original firing temperature of Jun porcelain ($SJ_2$) of Song Dynasty is determined to be above 1200 ℃, the original firing temperature of Jun porcelain ($YJ_3$) of Yuan Dynasty is a little higher than 1250℃. The firing atmosphere of sky-blue Jun porcelain of Song Dynasty is strongly reductive atmosphere. The firing atmosphere of sky-green Jun porcelain of Song Dynasty and the imitative ancient blue Jun porcelain is modestly reductive atmosphere. The firing atmosphere of moon-white Jun porcelain of Yuan Dynasty is weak reductive atmosphere. The coordination numbers of both $Fe^{2+}$ and $Fe^{3+}$ are 4. The coloring mechanism of Jun porcelain is very complex. Iron is only one of the major colorant in Jun porcelain. The chemical state of iron is only one of factors that influence the glaze color of Jun porcelain. (3) The glaze color of Southern Song Guan porcelain is related to the chemical state of iron. The more structure iron content is contained in powder-green glaze as well as greyish-green glaze. The more ferric oxide content is contained in cream-yellow glaze. The firing atmosphere of powder-green glaze and greyish-green glaze is strongly reductive atmosphere, the cream-yellow glaze is to be weak reductive atmosphere. The firing temperature of the former is higher than the later.

## INTRODUCTION

Some valuable results [1~6] have been obtained in the studies of ancient potteries by Mössbauer spectroscopy in the world. However, there are few applications in the study of ancient porcelain. In comparison with potteries, the porcelain glaze components are complex, the firing technique is hard and the artistic value is high. Some famous ancient porcelains are studied by Mössbauer effect. The iron mineral components of the ancient porcelain are analyzed, the original fired temperature and firing atmosphere are inferred, the microstructure of the glaze is studied and the colouring mechanism of the glaze is discussed.

China's ceramics have been reputably known by all the world. China's ceramics have produced a tremendous and everlasting social effect. It has made a great contribution to the world civilization. China's ceramic has become a treasure which has been enjoied in common by all human. Ru, Jun and Guan porcelain studied in this paper are three kinds of the five famous porcelains (Ru, Jun, Guan, Ge and Ding porcelain) in Song Dynasty (A.D. 960 ~ 1279) and Yuan Dynasty (A.D. 1206~1368) of China. The artistic value of the three porcelains are extremely great. There were employed by the emperors in the palace.

Celadon was the major porcelain of Chinese ancient times. It has a very important position in the history of Chinese ceramics. Ru porcelain belongs to celadon. It was mentioned in " Tan Zhai Bi Heng" of the Southern Song Dynasty (1126~1279) that " Ru Kiln is in the number One" [7]. It has a very high artistic value. They have the glaze colors of sky-green, sky-blue, bean-green, moon-white, etc. The sky-green and sky-blue are especially precious. In 1987, the actual kiln site of Ru kiln that fired the Ru porcelain specially for royal court was found in qingliangsi in the Baofeng county, Henan province. This is an important discovery in archaeology. The discovery has created favorable conditions for investigation of science and technique and imitation of ancient Ru porcelain.

The Jun porcelain is unique in Chinese porcelain history because of its gorgeous glaze color. It is stated as "one color in, a thousand colors out (of the kiln)". Different glaze color can result from firing with the same material in the same kiln, even the different position on the same that porcelain can assume different color. The glaze color gives the feeling of deep, sobriety and rosy clouds. The glaze color fired is random. The unique style of Jun porcelain has led interesting of many archaeologists and scientists. Chen Xianqiu et al. have extensively investigated the scientific and technological aspects of ancient Jun and Ru porcelain by means of chemical analysis, X-ray diffraction and electron microscopy [8~10].

Southern Song Guan kiln has always been the focus of the world attention. The ruins of Wuguishan Guan kiln has been generally acknowledged to be "Jiaotanxia Guan kiln" in the history. The porcelains fired in that kiln were especially employed by the emperor in the Southern Song palace. The characteristics of Guan porcelain were thin body with thick glaze and glazed many times with" a purple mouth rim and a iron foot base". There are sky-green, powder-green, greyish-green, dark-green, cream-yellow and so on. Chen Xianqiu, Ye Hongming et al. have deeply investigated about Southern Song Guan porcclain [11~14].

## 1 SPECIMEN CONDITIONS

The specimen conditions are listed in Table 1.

**Table 1 Specimen Conditions of Ancient Porcelains**

| Serial No. | Name | Years | Kiln site | Glaze | Body |
|---|---|---|---|---|---|
| $SR_1$ | Ru porcelain shard | North Song Dynasty (A. D. 960~1127) | Qingliangsi in Baofeng County, Henan, China | sky-green, with craze, 0. 2 mm thick | dark gray. delicate |
| $SR_2$ | Ru porcelain shard | North Song Dynasty | Qingliangsi in Baofeng County, Henan, China | sky-green, with craze, 0. 2 mm thick | greenish gray. slightly coarse |
| $SR_3$ | Ru porcelain shard | North Song Dynasty | Qingliangsi in Baofeng County, Henan, China | beans-green, with craze, 0. 2 mm thick | greenish gray, hard, delicate |
| $SR_4$ | Ru porcelain shard | North Song Dynasty | Qingliangsi in Baofeng County, Henan, China | beans-green, with craze, 0. 2 mm thick | greenish gray, coarse |
| $YR_5$ | Ru porcelain shard | Yuan Dynasty (A. D. 1279~1386) | Longwang in Ruzhou, Henan, China | moon-white 1 mm thick | dark gray. hard |
| $YR_6$ | Ru porcelain shard | Yuan Dyansty (A. D. 1279~1386) | Donggou Ruzhou Henan, China | beans-green | with red and yellow spot, coarse |
| $C_2$ | Clay | 1987 | Qingliangsi | | |
| $SJ_1$ | Jun porcelain shard | Song Dynasty | Yanhedian, Yuzhou, Henan, China | sky-green, gas hole, 1~1. 5 mm thick | dark gray, 4~5 mm thick |
| $SJ_2$ | Jun porcelain shard | North Song Dynasty | Daijian, Yuzhou, Henan, China | sky-blue, gas hole, 1~2 mm thick | light gray, delicate |

| Serial No. | Name | Years | Kiln site | Glaze | Body |
|---|---|---|---|---|---|
| $YJ_3$ | Jun porcelain shard | Yuan Dynasty | Yuzhou, Henan, China | outer surface: moon-white, with opalescence, gas bubbles, 1.2~1.5 mm thick<br>inner surface: olive-green, 0.5 mm thick | light gray, hard, 9 mm thick |
| $YJ_4$ | Jun porcelain glaze | Yuan Dynasty | Yuzhou, Henan, China | sky-blue, with craze gas bubbles, 1~1.5 mm thick | gray delicate, 3~5 mm thick |
| $G_{31g}$ | Guan porcelain glaze | Southern Song (A.D. 1127~1279) | Wuguishan, Hangzhou, China | powder-green, with craze, 1 mm thick | gray |
| $G_{39g}$ | Guan porcelain glaze | Southern Song (A.D. 1127~1279) | Wuguishan, Hangzhou, China | powder-green, with craze, 1 mm thick | gray |
| $G_{32g}$ | Guan porcelain glaze | Southern Song (A.D. 1127~1279) | Wuguishan, Hangzhou, China | greyish-green with big craze, 1 mm thick | grak gas bubbles. |
| $G_{40g}$ | Guan porcelain glaze | Southern Song (A.D. 1127~1279) | Wuguishan, Hangzhou, China | greyish-green with big craze. 1 mm thick | |
| $G_{34g}$ | Guan porcelain glaze | Southern Song (A.D. 1127~1279) | Wuguishan, Hangzhou, China | cream-yellow with craze 0.4 mm thick | cream-yellow |
| $G_{41g}$ | Guan porcelain glaze | Southern Song (A.D. 1127~1279) | Wuguishan, Hangzhou, China | cream-yellow with craze 0.4 mm thick | cream-yellow |

## 2 EXPERIMENTAL METHODS

The ancient Ru porcelains $SR_3$, $SR_4$, $YR_5$, $YR_6$ and the ancient Jun porcelains $SJ_1$, $SJ_2$, $YJ_3$, $YJ_4$ were re-fired in a nitrogen atmosphere in an electrical furnace, re-fired temperature is 200~1200℃. The temperature was kept constant at each temperature point for 8 h and then cooled naturally. The glaze and body were separated carefully. The radiation source is $^{57}Co(Pd)$. Room temperature transmission spectra of every specimen were measured. The spectra obtained were computer-fitted to a least-squares Lorentzian function. α-Fe was used for speed of calibration. The isomeric shift (IS) was with respect to α-Fe.

## 3 EXPERIMENTAL RESULTS

### 3.1 Mössbauer study of the ancient Ru porcelain

### 3.1.1 Chemical states of iron in Ru porcelain glaze

Fig. 1 shows the Mössbauer spectrum from the moon-white Ru porcelain ($YR_5$) glaze found at the Longwang kiln site of the Yuan Dynasty. The spectrum indicates the existence of three iron components: (1) $Fe^{2+}$; (2) $Fe^{3+}$; (3) magnetic component. The paramagnetic peak of ferrous iron has the highest intensity $Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.60$. Ferric iron and the magnetic component have relatively weak intensities. This indicates that large amounts of ferrous iron $Fe^{2+}$ are present in the Ru porcelain glaze of the Yuan Dynasty. When the glaze is fired in a reductive atmosphere, the glaze undergoes vitrification (900～1000℃) and recrystallization (>1000℃). Some of the iron ions of the iron mineral originally existing in the clay disengage themselves from the mineral and enter the newly formed clay mineral lattice. These iron ions ($Fe^{2+}$ and $Fe^{3+}$) are called structural iron. The superfine internal magnetic field of the magnetic component has an intensity ($H$) of 40 MA/m (501 kOe), with quadrupole splitting ($QS$) $= -0.284$ mm/s and isomeric shift ($IS$) $=0.147$ mm/s. These magnetic components may be $Fe_3O_4$. Chemical analysis generally shows only $Fe_2O_3$. This is obviously inaccurate.

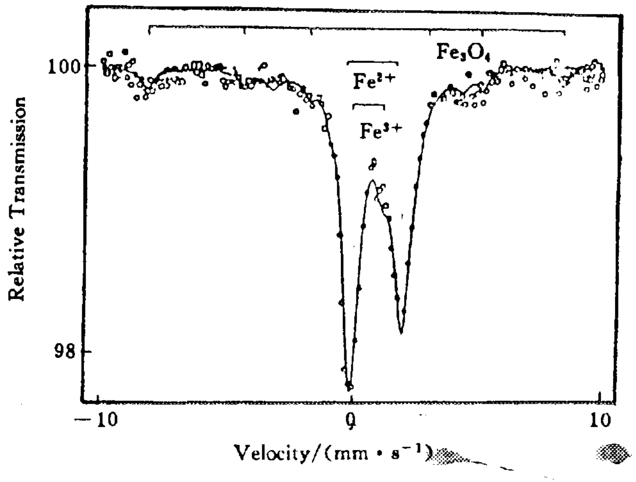

Fig. 1 Room temperature Mössbauer spectrum of the glaze of Chinese Yuan Dynasty Ru porcelain ($YR_5$)

### 3.1.2 The original firing condition

The experiments proved that the phase of ancient porcelain does not change as

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1 Oe≙(1000/4π)A/m.

long as the re-firing temperature does not exceed the original firing temperature. Fig. 2(a) shows that the $Fe^{2+}$ *QS* of the paramagnetic peak of Yuan Dynasty Ru porcelain ($YR_5$) glaze does not change with re-firing temperature. Above 900℃, curve (b) gradually approaches curve (a) as the firing temperature increases. Curves (a) and (b) intercept at about 1250℃. This indicates that the original firing temperature of Yuan Dynasty Ru porcelain ($YR_5$) was probably about 1250℃.

Fig. 3 (a) shows that the $Fe^{2+}$ relative intensity $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of the paramagnetic peak of Yuan Dynasty Ru porcelain ($YR_5$) glaze does not change with re-firing temperature, while Fig. 3(b) shows the severe change of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of the imitative ancient Ru porcelain sky-green glaze with firing temperature. Curve (b) gradually approaches curve (a) as the temperature increases. The two curves intercept at about 1250℃. These results also indicate that the original firing temperature of Yuan Dynasty Ru porcelain was probably about 1250℃.

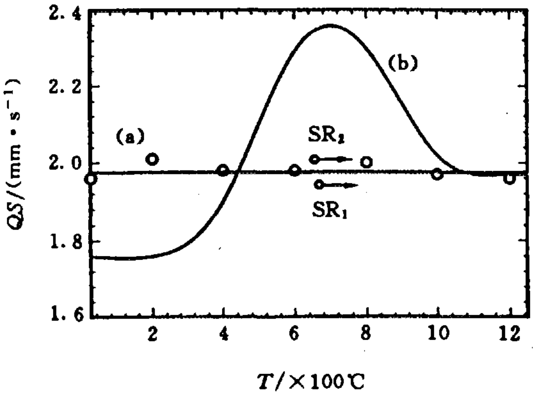

Fig. 2 (a) The relationship between $Fe^{2+}$ *QS* of the glaze of sample $YR_5$ and re-firing temperature. (b) The relationship between $Fe^{2+}$ *QS* of the glaze of the imitative ancient Ru porcelain and firing temperature

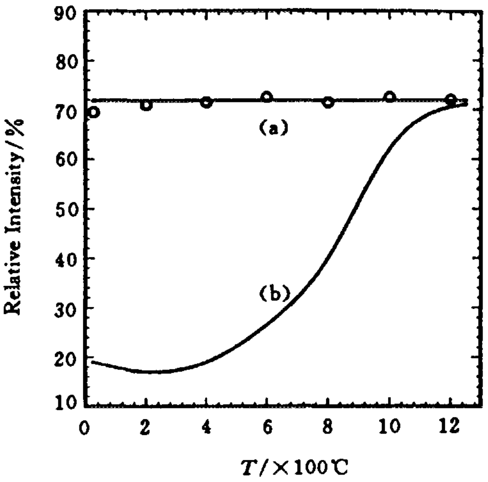

Fig. 3 (a) The relationship between $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of the paramagnetic peak of the glaze of specimen $YR_5$ and re-firing temperature. (b) The relationship between $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of the glaze of the imitative ancient Ru porcelain and firing temperature

The $Fe^{2+}$ relative intensity $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of paramagnetic peaks of Yuan Dynasty Ru porcelain glaze is about 77%. The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of paramagnetic peaks of unfired imitative ancient Ru porcelain sky-green glaze and unfired clay are about 30%[15]. These indicate that the firing atmosphere of Yuan Dynasty Ru porcelain was strongly reductive. It is one of the unique advantages of Mössbauer spectroscopy to use the $Fe^{2+}$ relative intensity of the paramagnetic peak to determine the original firing atmosphere of ancient porcelain.

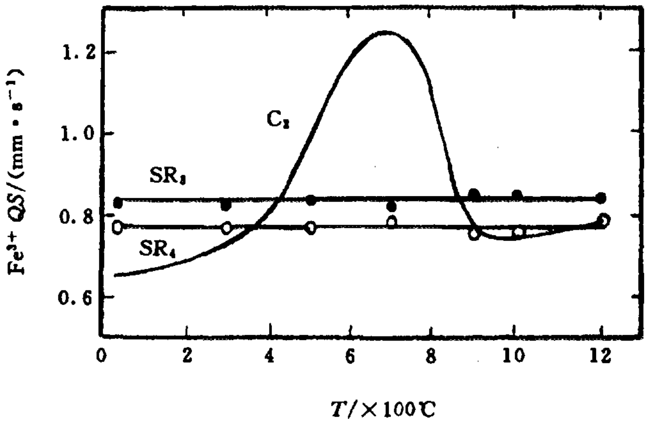

Fig. 4 $C_2$ shows the relationship between the $Fe^{3+}$ *QS* of the clay from Qingliangsi site and firing temperature. $SR_3$ and $SR_4$ shows the relationship between $Fe^{3+}$ *QS* of the bodies of Qinliangsi Ru porcelain of Song Dynasty and refiring temperature

The $Fe^{2+}$ *QS* of Song Dynasty Ru porcelain glaze $SR_1$ and $SR_2$ are also marked separately in Fig. 2. These can be used to determine the original fired temperature and atmosphere of the Song Dynasty Ru porcelain. Fig. 4 $C_2$ shows the relationship between the $Fe^{3+}$ *QS* of the clay from Qingliangsi site of Song Dynasty Ru porcelain and the firing temperature. Fig. 4 $SR_3$ and $SR_4$ show the relationship between the $Fe^{3+}$ *QS* of Song Dynasty Ru porcelain bodies from Qingliangsi and re-firing temperature. Fig. 4 shows that the $Fe^{3+}$ *QS* does not change with re-firing temperature. These indicate that the original fired temperature of $SR_3$ and $SR_4$ were above 1200℃. The $SR_3$, $SR_4$ and $C_2$ intercept at about 1200℃. These also indicate that original fired temperature of Song Dynasty Ru porcelain was probably about 1250℃.

### 3.1.3 The coloring mechanism

Ru porcelain is classified as celadon, and iron is the major colorant of celadon [16]. The glaze color of celadon is related to the chemical states of iron. The concentrations of $Fe^{2+}$ and $Fe^{3+}$ affect the glaze color directly. When $Fe^{2+}$ and $Fe^{3+}$ co-exist, the glaze color is blue. When $Fe^{2+}$ concentration is low, the glaze color is green. Conversely, when $Fe^{2+}$ concentration is high, the glaze color becomes yellow.

The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of Song Dynasty sky-green Ru porcelain ($SR_1$) glaze is 0.82. The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of Yuan Dynasty moon-white ($YR_5$) glaze is 0.77. The $Fe^{2+}$ concentrations of these specimens match the colors they actually show.

The glaze color of Ru porcelain is also related to the oxides of iron in the glaze material. At high temperature, the oxide particles distribute in the glass state material ($SiO_2$). The glass state material appears light blue. This establishes the base tone of light blue for Ru porcelain.

### 3.2 Mössbauer study of the ancient Jun porcelain glaze

#### 3.2.1 Iron minerals in ancient Jun glaze

The Mössbauer spectra of the ancient Jun glaze show that there is a small amount of $Fe_2O_3$ and $Fe_3O_4$ iron minerals in the glaze. In the center of the spectrum there is a relatively strong paramagnetic doublet formed by the structural iron. The structural iron is referred to the $Fe^{2+}$ and $Fe^{3+}$ in the lattice of clay minerals.

#### 3.2.2 The original firing temperature

Figs. 5(a') and 5(b') show the relationship between the quadrupole splitting (*QS*) of $Fe^{2+}$ and $Fe^{3+}$ of the paramagnetic peak of Yuan Jun glaze ($YJ_3$) and re-firing temperature, respectively. The *QS* basically does not change with re-firing temperature. Figs. 5(a) and 5(b) show the relationships of the *QS* of $Fe^{2+}$ and $Fe^{3+}$ of the modern imitative ancient sky-blue Jun porcelain (IJ) glaze and firing temperature, respectively. At 1200～1250℃, the corresponding curves (a') and (a), (b') and (b) have the tendencies of interception, but they do not actually intercept. This situation indicates that the original firing temperature of ancient Jun kilns was a little higher than 1250℃. The experiments prove that if the re-firing atmosphere is the same as the original firing atmosphere and the temperature in the re-firing process does not surpass the original firing temperature, the Mössbauer parameters of the shard do not change. This es-

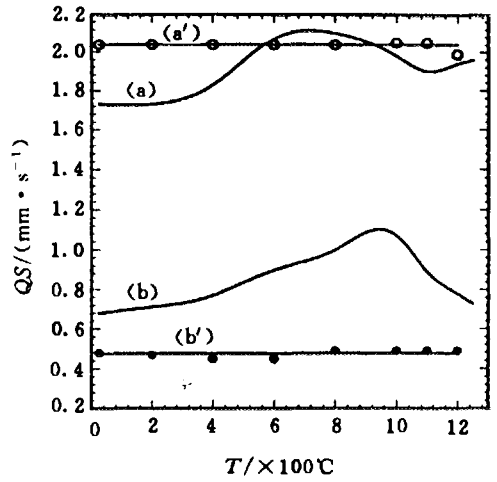

Fig. 5 The relationship between the quadrupole splitting (*QS*) of Yuan Dynasty Jun porcelain glaze ($YJ_3$) and re-firing temperature, and between the *QS* of the imitative ancient Jun porcelain glaze (IJ) and firing temperature. (a') The $Fe^{2+}$ *QS* of $YJ_3$; (a) the $Fe^{2+}$ *QS* of IJ. (b') The $Fe^{3+}$ *QS* of $YJ_3$; (b) the $Fe^{3+}$ *QS* of IJ.

tablishes the basis for comparing the Mössbauer parameters of ancient and imitative ancient Jun porcelain. The two curves in Fig. 6 show relationship between the $Fe^{2+}$ $QS$ of the body and the $Fe^{3+}$ $QS$ of the glaze of the sky-blue Jun porcelain ($SJ_2$) with re-firing temperature. In the re-firing temperature range 1200℃, the Mössbauer parameters basically do not change. These indicate that the original fired temperature of the Jun poacelain of Song Dynasty was a little higher than 1200℃.

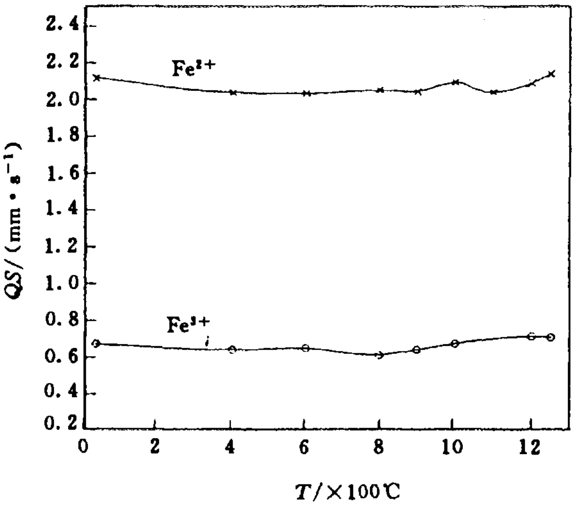

Fig. 6 The relationship between the $Fe^{2+}$ $QS$ of body, $Fe^{3+}$ $QS$ of glaze of Yuan Dynasty Jun porcelain ($SJ_2$) and refiring temperature

### 3.2.3 The original firing atmosphere

Fig. 7(a') shows the relationship between the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of the paramagnetic peak of Yuan Dynasty Jun($YJ_3$) glaze and re-firing temperature. Curve (a) shows the relationship between the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of the modern imitative ancient blue Jun glaze ($IJ_1$) and firing temperature. Curve (b') shows the relationship between the magnetic ratio ($M_1+M_2$) of $Fe_2O_3$($M_1$) and $Fe_3O_4$($M_2$) in the glaze of ($YJ_3$) with re-firing temperature. Curve (b) shows the relationship between the magnetic ratio ($M_1+M_2$) in the glaze of ($IJ_4$) and firing temperature. The $Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.68$ for the Yuan Dynasty Jun glaze, whereas the $Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.3$ for the unfired clay minerals. These indicate the firing atmosphere of Yuan Dynasty Jun porcelain was reductive. At 1250℃, the $Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.76$ for the imitative ancient blue Jun glaze. Thus, it can be seen that the reductive atmosphere of Yuan Dynasty Jun porcelain is weaker than that of the imitative ancient blue Jun porcelain, and it is weak reductive. The $Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.75$ for the Song Dynasty sky-green Jun porcelain ($SJ_1$) glaze and the $Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.82$ for the Song Dynasty sky-blue Jun porcelain ($SJ_2$) glaze. It shows that the firing atmosphere of the sky-green Jun porcelain was modestly reductive, the sky-blue Jun porcelain was fired in the strongly reductive.

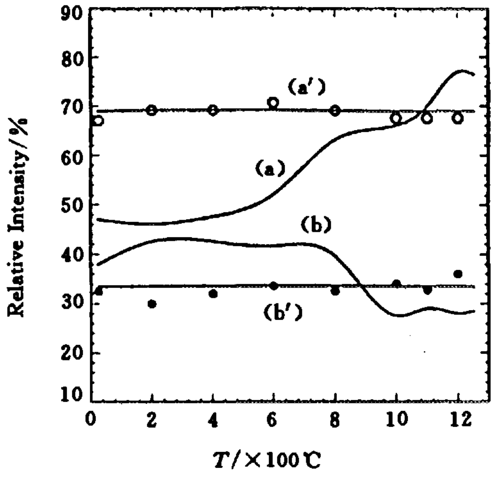

Fig. 7 The relationships between $Fe^{2+}/(Fe^{2+}+Fe^{3+})$, $(M_1+M_2)$ of the glaze of Yuan Dynasty Jun porcelain ($YJ_3$) and re-firing temperature, and between $Fe^{2+}/(Fe^{2+}+Fe^{3+})$, $(M_1+M_2)$ of the glaze of the imitative ancient Jun porcelain (IJ) and firing temperature. (a') The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of $YJ_3$; (a) the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of IJ. (b') The $(M_1+M_2)$ of $YJ_3$; (b) the $(M_1+M_2)$ of IJ.

**3.2.4** The coordination number of the iron ions in Yuan Dynasty Jun glaze

The *IS* and *QS* of iron atoms in silicate minerals are related not only to the valence of the iron atoms, but also to the coordination number (*CN*) of the iron atoms. The relationships between *IS*, *QS* and *CN* were discussed in Ref. [17]. From the values of *IS* and *QS*, the *CN* of an unknown mineral can be determined. For $Fe^{2+}$ in Yuan Dynasty Jun glaze. $IS=1.06$ mm/s. $QS=2.03$ mm/s; and for $Fe^{3+}$, $IS=0.44$ mm/s. $QS=0.47$ mm/s. Both $CN_s$ of $Fe^{2+}$ and $Fe^{3+}$ in Yuan Dynasty Jun glaze are inferred to be 4.

**3.2.5** The coloring of the Jun Porcelain

Iron is one of the major coloring agent of Jun porcelain. The glaze color is related to the chemical state of iron. The fired temperature and firing atmosphere are important conditions for the coloring of Jun porcelain. The concentrations of $Fe^{2+}$ and $Fe^{3+}$ affect the variation of glaze color. Table 2 lists the relationship between $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of some ancient Jun glazes and the glaze colors. For the sake of comparison conveniently, $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of imitative ancient sky-blue Jun porcelain glaze and the average value of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of some clays have been listed. The firing atmospheres to be inferred are also listed.

**Table 2 The relationship between $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of some ancient Jun glazes and the glaze colors. The firing atmospheres to be inferred are also listed**

| Serial No. | Name | $[Fe^{2+}/(Fe^{2+}+Fe^{3+})]/\%$ | Glaze color | Firing atmosphere |
|---|---|---|---|---|
| IJ | Imitative ancient Jun porcelain | 76 | sky-blue | moderately reductive atmosphere |
| $YJ_3$ | Yuan Dynasty Jun porcelain | 68 | moon-white | weak reductive atmosphere |
| $SJ_1$ | Song Dynasty Jun porcelain | 75 | sky-green | moderately reductive atmosphere |
| $SJ_2$ | Song dynasty Jun porcelain | 82 | sky-blue | strongly reductive atmosphere |
|  | Clays | 30 (average value) |  |  |

The Mössbauer spectra show that the glaze contains $Fe_2O_3$ and $Fe_3O_4$ abundantly. The variations of the relative intensity of $Fe^{2+}$ and magnetic ratio with firing temperature can be seen in Figs. 7(a) and 7(b). The $Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.68$ of Yuan Dynasty Jun porcelain ($YJ_3$), the glaze color is moon-white. The $Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.75$ of Song Dynasty Jun porcelain ($SJ_1$), the glaze color is sky-green. The $Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.82$ of Song Dynasty Jun porcelain ($SJ_2$), the glaze color is sky-blue. It is inferred that three specimens were succesively fired in a weak reductive, modestly reductive and strongly reductive atmosphere. The $Fe^{2+}/(Fe^{2+}+Fe^{3+})=0.76$ for the imitative ancient blue Jun glaze (when firing at the temperature of 1250℃), the firing atmosphere is a modestly reductive atmosphere. The part of $Fe_2O_3$ and $Fe_3O_4$ in the glaze become FeO or Fe ions in reductive atmosphere. The iron mineral particles distribute in the glass state material. This renders the glaze to be blue. The color tone is related to the concentrations of the particles.

### 3.3 The coloring mechanism and firing technology of Southern Song Guan porcelain

Southern Song Guan porcelain belongs to celadon. It's coloring agent is iron. There are three major glaze colors of Guan porcelain: powder-green, greyish-green, cream-yellow. The iron contents of the different glaze color specimens by neutron activation analysis are shown in Table 3. The average value of iron contents of the powder-green glazes is equal to $6.42\times10^{-3}$, the greyish-green glaze is equal to $6.42\times10^{-3}$, the cream-yellow glazes is equal to $6.34\times10^{-3}$. There are not obviously difference of iron contents for different color glazes.

The iron content of each chemical state for different color Guan porcelain glaze is shown in Table 4. The Mössbauer spectra show that there are two sextets in the magnetic spectra and two doublet spectra in the paramagnetic spectra. The glazes contain magnetic components of $Fe_2O_3$, $Fe_3O_4$ and paramagnetic components structure iron ($Fe^{2+}$, $Fe^{3+}$). The structure iron content ($Fe^{2+}+Fe^{3+}$) contained in powder-green glaze, as well as greyish-green glaze, is equal to 71~81%. The ferric oxide content of cream-yellow glaze is equal to 37.2%~53.0%. The powder-green glaze and greyish-green glaze contain more structure iron, and less ferric oxide. The cream-yellow glaze contains more ferric oxide, and less structure iron.

The average value of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ for powder-green glaze is equal to 70.7%. For greyish-green glaze is 73.0% and for cream-yellow glaze is 55.5%. The original firing atmosphere of powder-green and greyish-green glaze are thus determined to be strongly reductive atmosphere, the cream-yellow glaze to be weak reductive atmosphere or first reductive late oxidation. The original firing temperature of powder-green and greyish-green glaze is higher than cream-yellow glaze.

**Table 3 The iron content of Southern Song Guan porcelain glaze by neutron activation analysis** ($\times 10^{-6}$)

| Serial No. | Glaze color | Iron content | Average value for each glaze color | Average value for all glaze color |
|---|---|---|---|---|
| $G_{1go}$ | powder-green | 6.81E+3 | 6.42E+3 | 6.41E+3 |
| $G_{2go}$ | powder-green | 6.21E+3 | | |
| $G_{3g}$ | powder-green | 6.69E+3 | | |
| $G_{4g}$ | powder-green | 5.69E+3 | | |
| $G_{23g}$ | powder-green | 7.19E+3 | | |
| $G_{25go}$ | powder-green | 6.55E+3 | | |
| $G_{25gi}$ | powder-green | 6.11E+3 | | |
| $G_{26g}$ | powder-green | 6.42E+3 | | |
| $G_{27g}$ | powder-green | 6.17E+3 | | |
| $G_{31g}$ | powder-green | 6.36E+3 | | |
| $G_{5g}$ | greyish-green | 6.53E+3 | 6.42E+3 | |
| $G_{6g}$ | greyish-green | 6.40E+3 | | |
| $G_{7g}$ | greyish-green | 7.47E+3 | | |
| $G_{8go}$ | greyish-green | 5.53E+3 | | |
| $G_{8gi}$ | greyish-green | 5.97E+3 | | |
| $G_{9g}$ | greyish-green | 6.91E+3 | | |
| $G_{30g}$ | greyish-green | 6.04E+3 | | |
| $G_{32g}$ | greyish-green | 6.57E+3 | | |
| $G_{15g}$ | cream-yellew | 6.49E+3 | 6.34E+3 | |
| $G_{24g}$ | cream-yellew | 6.19E+3 | | |

NOTE: 6.42E+3=$6.42\times10^{-3}$.

**Table 4 The iron content of different chemical state in every color Guan glaze by Mössbauer spectroscopy**

| Serial No. | Glaze color | Magnetic component | paramagnetic component | | |
|---|---|---|---|---|---|
| | | $(Fe_2O_3+Fe_3O_4)/\%$ | $Fe^{2+}/\%$ | $Fe^{3+}/\%$ | $[Fe^{2+}/(Fe^{2+}+Fe^{3+})]/\%$ |
| $G_{31g}$ | powder-green | 29.0 | 50.0 | 21.0 | 70.4 |
| $G_{39g}$ | powder-green | 18.8 | 57.8 | 23.5 | 71.0 |
| $G_{32g}$ | greyish-green | 20.0 | 54.0 | 26.0 | 67.5 |
| $G_{40g}$ | greyish-green | 23.5 | 60.2 | 16.3 | 78.6 |
| $G_{34g}$ | cream-yellow | 53.0 | 25.0 | 22.0 | 53.2 |
| $G_{41g}$ | cream-yellow | 37.2 | 36.3 | 26.5 | 57.8 |

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