SCIENCE CHINA
Technological Sciences

January 2011 Vol.54 No.1: 99–104
doi: 10.1007/s11431-010-4195-x

Study on the diversification of origins and primary development of Chinese porcelain glazes

WU Juan[1], ZHANG MaoLin[1], WU JunMing[1*], LI QiJiang[1], LI JiaZhi[2], DENG ZeQun[2] & JIANG Xia[1]

[1] *Institute of Ancient Ceramic, Jingdezhen Ceramics Institute, Jingdezhen 333001, China;*
[2] *Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*

Received June 28, 2010; accepted October 15, 2010

With the support of the Origin Exploring of Chinese Civilization Projects (II) and National Natural Science Foundation of China, the close relationship among “pottery coat”, “kiln sweat” and Chinese proto-porcelain glaze were studied, the characteristics and the key foundation of the origin of porcelain glaze were also discussed based on the relevant research results by Shanghai Institute of Ceramics, Chinese Academy of Sciences and Jingdezhen Ceramics Institute.

proto-porcelain glaze, “pottery coat”, “kiln sweat”

Citation: Wu J, Zhang M L, Wu J M, et al. Study on the diversification of origins and primary development of Chinese porcelain glazes. Sci China Tech Sci, 2011, 54: 99–104, doi: 10.1007/s11431-010-4195-x

1 Introduction

China is the only country with more than ten-thousand-years continuous development history of ceramic, which implicates abundant scientific and artistic information. The invention of glaze was an important technical breakthrough in the process from pottery to porcelain. The water-tightness of glaze endows porcelain some functions that pottery doesn’t have. The glaze also enhances mechanical strength, aesthetic properties and duration of ceramic ware. With the emergence of celadon artifact, it gradually took the role of bronze ware in daily life because of the impermeability of glaze. In fact, glaze is a glassiness layer adhered on ceramic body, and makes no essential difference in material micro-structure, physical or chemical properties to glass. So the invention of glaze can also be considered as the invention of glass. Generally, the preparing process of glaze includes: 1) raw materials are first made into glaze slip; 2) glaze slip is deposited on the body of pottery or porcelain; 3) glaze slip is finally fired and melted into glaze.

The invention of porcelain glaze is a noticeable research topic for its close relationship with some significant problems in the development history of Chinese ceramic, such as the origin of proto-porcelain, the invention of porcelain, and so on. In fact, there are different viewpoints on the origin of glaze: 1) low refractoriness raw material used in the kiln wall was melt while firing; 2) the surface of pottery body made from low melting point raw material was melt in high firing temperature; 3) the evolution of coating used for the decoration of pottery [1]; 4) inspiration derived from the forming of kiln sweat or the thin glass layer on the ware in the firing process [2]. Among these viewpoints, the third and fourth are widely accepted. But which is the real original manner of Chinese ceramic glaze? That is to say, the problem of the origin of Chinese ceramic glaze hasn’t been authentically resolved because of insufficient specimens and restrictions of analytical methods. Recently, archaeological

*Corresponding author (email: woshiwxb@126.com)

excavations have constantly increased along with the rapid development of social economy, and new related archaeological materials and specimens have been continuously discovered. Meanwhile, more modern testing techniques have been widely and deeply applied in the scientific study on ancient ceramic. All these have provided powerful support to further study on the origin of Chinese ceramic glaze. Therefore, on the basis of former studies on the ancient pottery, proto-porcelain and early porcelain by Jingdezhen Ceramics Institute and Shanghai Institute of Ceramics, Chinese Academy of Sciences [3 – 6], the origin and early development of Chinese ceramic glaze are further studied in this paper.

2 Origin of Chinese ceramic glaze

As mentioned above, the third and fourth viewpoints on the origin of Chinese ceramic glaze are widely accepted, therefore, in this paper the relationships of the raw material recipe and manufacture technology between "pottery coat" and "kiln sweat" with proto-porcelain glaze are discussed.

2.1 Chemical composition characteristics of "pottery coat" and "kiln sweat"

The relevant archaeological excavations (such as the excavation of Nanzhuangtou site in Xushui, Hebei province, the excavation of Xianrendong site in Wannian, Jiangxi province, etc.) indicate that pottery began to be manufactured about ten thousand years ago [7]. Ancient potters had accumulated a wealth of experiences in treatment of raw materials, process of forming and firing for a long time. As we know, primitive pottery with rough surface had high water absorption, and was easy to be made dirty. To improve this situation, "pottery coat" was invented as a kind of decorating layer on the surface of pottery body (see Figure 1). "Pottery coat" is generally red or black. Sometimes ancient potteries were even directly painted with "pottery coat" to have better decorative effect. Relevant research showed that the raw materials used for the preparation of "pottery coat" can be divided into two kinds: the first kind is obviously different from the raw materials used for the preparation of pottery body, the other kind is similar to raw materials used for the preparation of pottery body, but being further processed (smaller particle size and higher plasticity). Generally, compared with pottery body, the chemical composition of "pottery coat" has higher concentration of Fe_2O_3 and lower concentrations of K_2O, Na_2O, CaO and MgO due to the selection or treatment of raw materials (see Table 1). Some of them are very similar to that of proto-porcelain glaze. Both glaze and "pottery coat" were used to improve the appearance and properties of artifact as a thin layer covered on the body. But it must be emphasized that "pottery coat" can not be melt into glassy state in a low firing temperature (~800°C, or even lower [7, 8]).

It's not difficult to find that "pottery coat", as a thin decorative layer covered on body, is very similar to ceramic glaze in the preparing method. They played a common role in improving the appearance effect and practical function.

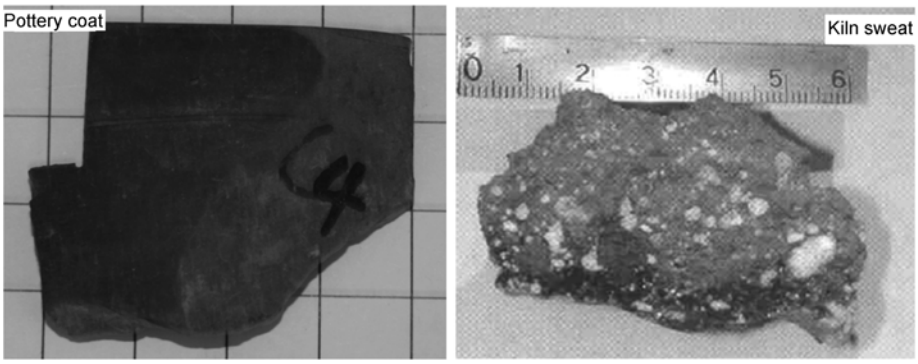

Figure 1 Chinese ancient "pottery coat" [9] and "kiln sweat"[10].

Table 1 Chemical composition of "pottery coat" and "kiln sweat" samples from Hubei, Jiangxi, Zhejiang province, etc.

	Number		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	MnO	P_2O_5
"Pottery coat"	14	Mean (wt%)	0.48	0.95	17.99	69.84	1.82	0.92	0.72	7.08	0.10	0.19
		S.D.	0.33	0.42	1.13	2.34	0.77	0.47	0.57	2.73	0.12	0.07
Slip glaze	9	Mean (wt%)	0.87	1.44	21.47	59.67	4.36	1.73	1.32	6.66	0.09	0.08
		S.D.	0.28	0.83	4.37	7.75	0.29	1.49	0.23	3.08	0.06	0.16
"Kiln sweat"	5	Mean (wt%)	0.28	3.05	13.13	65.88	5.35	6.24	0.75	3.35	1.32	0.91
		S.D.	0.10	1.45	2.43	9.31	1.40	4.95	0.33	0.96	1.12	0.63

"Kiln sweat" is produced in the firing process of ceramics. When ash of burning firewood float down on the ceramic body or kiln wall, it is possible to react and melt into a thin glassy layer in the enough high temperature, which is visually named "kiln sweat" (see Figure 1). Besides with high contents of flux elements, the contents of MnO_2 and P_2O_5 are also relatively high in "kiln sweat" (see Table 1)[2]. Undoubtedly, the emergence of "kiln sweat" was first benefited from the development of firing technique. Relevant researches [7] showed that most pottery artifacts were directly fired on the ground or in primitive kiln before Shang dynasty in China. The primitive kiln was a horizontally through-draught cave, and had gradually developed into the vertically through-draught cave. But the highest firing temperature in primitive kiln was still lower than 1000°C. Therefore, "kiln sweat" was almost impossible to come into existence at that time. Up to Shang dynasty, more effective up-draught kiln on the ground began to be built and used, and the kiln chamber was also enlarged. Then the highest firing temperature could reach up to 1200°C, which made the emergence of "kiln sweat" possible.

Most of the "pottery coat" and "kiln sweat" samples mentioned above had a possibility of melting into glaze in a certain temperature (> 1200°C) due to the high contents of flux elements. And "pottery coat" was similar to ceramic glaze in the main preparing method (thin layer covered on body, fine raw materials processing techniques, etc.). Meanwhile, "kiln sweat" also provided a direct to the glassy material. In this situation, the combination of the preparing method of "pottery coat" and the glassy state effect of "kiln sweat" finally provided the whole technological processes and laid down a solid foundation for the invention of ceramics glaze in China.

2.2 Chemical composition and technological conditions of proto-porcelain glaze in China

The relevant archaeological excavation indicated that proto-porcelain was invented in the Shang Dynasty (16th century B.C.–11th century B.C.). On the one hand, the modeling and firing techniques of proto-porcelain basically inherited that of impressed-stoneware produced in a large scale during Shang Dynasty. Sometimes proto-porcelain and impressed-stoneware were even fired in the same kiln, and the sintering temperature was up to 1200°C[11]. On the other hand, compared with impressed-stoneware, one of the most important features of proto-porcelain was a thin layer of transparent glaze on the surface of the body. The glazing technique was quite primitive at that time, mainly including two methods: brushing or dipping. And most of the glaze layers of proto-porcelain were rather thin and easy to be stripped from body [12] (see Figure 2). The means and standard deviations of chemical composition of early proto-porcelain glazes are listed in Table 2 for further studies.

Generally, the glaze of the early proto-porcelain excavated in China belonged to the high firing temperature glaze (~1200°C). And the proto-porcelain glaze unearthed from Jiangxi and Zhejiang provinces could be divided into two

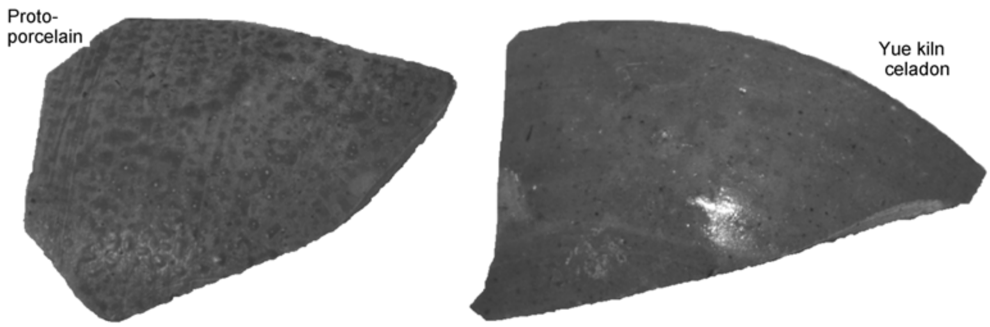

Figure 2 Specimen of proto-porcelain in Shang Dynasty and Yue celadon in Eastern Han Dynasty.

Table 2 Means and standard deviations of major and minor elements of proto-porcelain samples excavated from different sites

Site	Number		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	MnO	P_2O_5
Deqing, Zhejiang	43	Mean (wt%)	0.78	2.83	11.97	64.68	2.11	14.56	0.41	1.67	0.25	0.47
		S.D.	0.44	0.74	1.06	3.27	0.67	4.67	0.08	0.48	0.11	0.16
Xiaoshan, Zhejiang	17	Mean (wt%)	1.24	1.72	14.11	70.76	4.19	4.66	0.40	1.93	0.09	0.19
		S.D.	0.37	0.40	1.10	2.31	2.03	2.70	0.05	0.45	0.05	0.08
Yingtan, Jiangxi	8	Mean (wt%)	0.48	1.76	17.32	61.68	5.91	4.87	1.38	6.12	0.12	0.26
		S.D.	0.15	0.09	0.47	0.13	1.41	3.41	0.49	3.57	0.08	0.06
Qingjiang, Jiangxi	9	Mean (wt%)	0.68	2.01	14.70	64.05	5.12	6.50	1.16	5.21	0.34	0.29
		S.D.	0.36	0.90	4.17	6.24	2.25	5.11	0.55	2.67	0.31	0.24

kinds (see Figure 3). The division was related to the main kinds of the flux elements used in glaze. The first kind (Most of the samples) had a relatively high content of CaO (>10%) and low contents of Fe_2O_3 and K_2O (<2%). There were more Fe_2O_3 and K_2O (>5%) contents in the second glaze (<5%). Undoubtedly, the obvious differences between chemical compositions indicated that the different raw materials were selected.

Why did early proto-porcelain glaze have two different types of raw material recipes in China? It is an inevitable question for the studies of the origin of porcelain glaze in China. The specific origin of glaze should be closely related to the local natural resources (raw materials, fuel, etc.). According to the chemical composition of some proto-porcelain glaze samples (see Table 2), the contents of MnO and P_2O_5 in the first type of proto-porcelain glaze which took CaO as main flux were relatively high (generally >0.4%). Although limestone with high content of CaO is one kind of the raw material usually used for the preparation of porcelain glaze, the use of limestone would not increase the contents of MnO and P_2O_5 (generally <0.1%) in glaze. However, as we know, firewood was the main fuel used for the ceramics production in southern China, and plant ash which also had high content of CaO would be easy to be obtained. It was possible for ancient potters to derive inspiration from the forming of “kiln sweat”. Thus plant ash which also has relatively high contents of MnO and P_2O_5 was taken as the main raw materials for the preparation of the first type of proto-porcelain glaze [2]. In spite of having a certain concentration of CaO, the second type of proto-porcelain glaze also had relatively high contents of Fe_2O_3 and K_2O. Meanwhile, the contents of MnO and P_2O_5 were much lower than those of the first type of proto-porcelain glaze. So the high concentration of CaO in the second type of proto-porcelain glaze was nearly impossible to be provided by plant ash as the first one. It was not difficult to find that the chemical composition of the second type of proto-porcelain glaze was very similar to that of some “pottery coat” (see Figure 4).

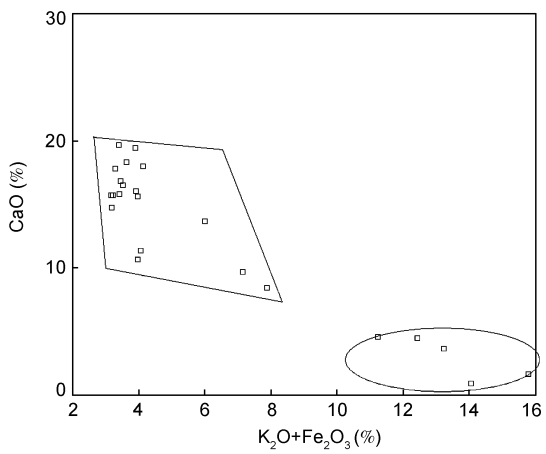

Figure 3 Scattering diagram of the concentrations of CaO and $K_2O+Fe_2O_3$ in proto-porcelain glazes from Zhejiang and Jiangxi provinces.

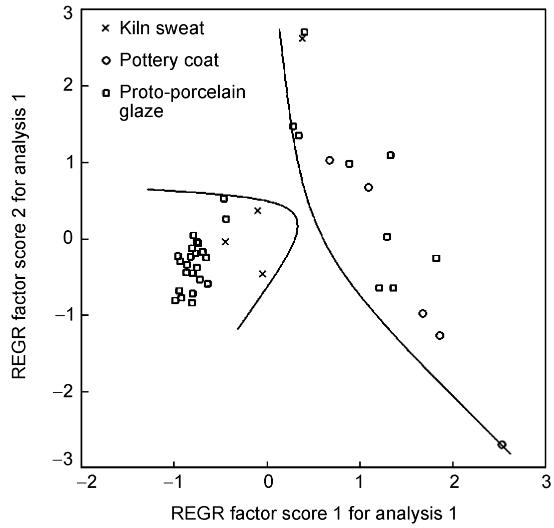

Figure 4 Scattering diagram of factor analysis on the chemical compositions of proto-porcelain glaze, “pottery coat” and “kiln sweat” .

Such high degree of similarity suggested that the invention of the second type of proto-porcelain glaze was closely related to the preparation of “pottery coat”.

Furthermore, the decoration effects of the two types of proto-porcelain glazes were quite different. The high calcium content glaze (the first one) was relatively more transparent, while the glaze with a high iron content (the second one) had darker color and higher covering power. Actually, the co-existence of different preparing methods of glaze just indicated that the invention of glaze was closely related to local resources (raw materials, fuel, etc.).

The invention of proto-porcelain glaze was benefited from the improvement of firing technique besides the raw material recipe of glaze. Actually, the gradual improvement of firing technique was considered as one of the three major technological breakthroughs in the development history of Chinese ceramic. The first took place in the Shang Dynasty. The highest firing temperature of impressed-stoneware reached up to 1200°C, which was nearly 200°C higher than that of early pottery production [11]. It made the invention of glaze possible. For example, the so-called "slipware” excavated from the tombs of Shang Dynasty in Jiangshan, Zhejiang province had a layer of black, rough, lackluster and permeable “pottery coat” on the body, which had a high content of Fe_2O_3 (see Table 1). The sintering temperature of the samples was proved to be about 1100°C. When these “pottery coat” samples were further heated up to 1200°C, “pottery coat” began to be melted into a layer of smooth, black or brown glassy glaze [13]. Obviously, plant ash or “pottery coat” could be melted into glassy state only in an enough high firing temperature. After long-term observation and contact, ancient potters gradually realized that the glassy surface of ceramic not only had decoration effect but also could enhance the abrasion resistance. Above all, it had gradually taken the role of bronze ware in daily life because of the impermeability of glaze. Undoubtedly, the breakthrough of firing technique was a crucial condition for the invention of glaze.

3 Emergence of mature porcelain glaze in China

The preparing technology of proto-porcelain took a great leap during the Eastern Han Dynasty (25–220AD), and mature porcelain—Yue celadon, was finally invented in the Yue kiln site of Zhejiang province. Compared with proto-porcelain, one of the essential characteristics of mature porcelain was that the quality of glaze and matching of body and glaze were greatly improved.

Relative studies indicated that Yue celadon glaze was similar to the first type of proto-porcelain glaze in chemical composition, which also took CaO as the main flux. The content of CaO in the celadon glaze was about 14%–16%, some even up to 20% (see Table 3). Obviously, celadon glaze still belonged to the high temperature glaze of $CaO(MgO)-K_2O(Na_2O)-Al_2O_3-SiO_2$ series. But the highest sintering temperature of Yue celadon already reached up to 1300°C[14] . Little rudimental quartz or other crystals existed in the transparent and uniform celadon glaze. The thickness of celadon glaze was generally between 0.1 and 0.3 mm. In addition, as mentioned above, proto-porcelain glaze was easy to be stripped from body, but the body and glaze of Yue celadon matched well (see Figure 5). Most of the celadon glazes presented daffodil yellow, bluish gray or cyan (see Figure 6) due to 2% content of Fe_2O_3, a certain content of TiO_2 (generally less than 1%) and different firing atmospheres. From then on, the development of Chinese porcelain entered a new stage.

Table 3 Means and standard deviations of major and minor chemical compositions of Yue celadon glaze samples [14]

Site	Number		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	MnO	P_2O_5
Shaoxing	8	Mean (wt%)	0.90	2.34	13.69	62.06	1.87	14.56	0.76	2.30	0.32	0.77
		S.D.	0.07	0.63	0.70	3.18	0.11	2.49	0.02	0.23	0.11	0.14
Shangyu	9	Mean (wt%)	0.54	2.19	13.33	60.03	1.92	17.65	0.47	2.05	0.32	0.59
		S.D.	0.13	0.57	0.66	2.37	0.11	2.41	0.43	0.59	0.28	0.51
Shanglinhu	5	Mean (wt%)	0.82	3.86	13.33	59.08	1.58	14.84	0.71	3.14	0.58	1.46
		S.D.	0.03	2.05	0.38	2.48	0.27	0.68	0.06	1.55	0.20	0.66

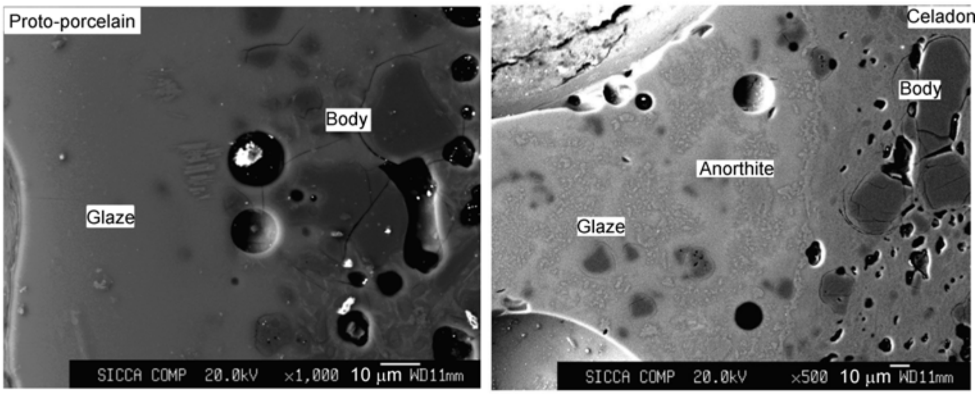

Figure 5 Microstructure of typical proto-porcelain and Yue kiln celadon samples in China [3].

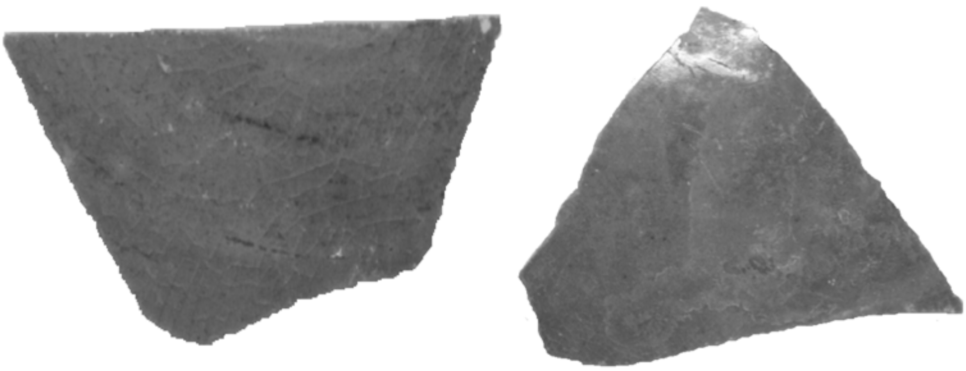

Figure 6 Early Yue celadon samples.

4 Conclusions

1) It was possible for most of "pottery coat" and "kiln sweat" samples to be melted into glaze in a certain high temperature (>1200°C) due to the high content of flux. And "pottery coat" was similar to ceramic glaze in the main preparing method (thin layer covered on body, fine raw materials processing techniques, etc.). Meanwhile, "kiln sweat" also provided a direct reference to glassy material. In this situation, the combination of the preparing method of "pottery coat" and the glassy state effect of "kiln sweat" finally provided the whole technological processes and laid down a solid foundation for the invention of ceramics glaze in China.

2) The proto-porcelain glazes can be divided into two kinds. The division is related to the main kinds of the flux elements used (CaO, Fe_2O_3, K_2O, etc.) in glaze. Undoubtedly, the obvious differences of chemical compositions indicate that the different raw materials were selected. The decoration effects of the two types of proto-porcelain glazes were quite different. The high calcium content glaze (the first one) was relatively more transparent, while glaze of high iron content (the second one) had darker color and higher covering power. Actually, the co-existence of different preparing methods of glaze just indicated that the invention of glaze was closely related to local resources (raw materials, fuel, etc.).

3) The invention of proto-porcelain glaze was benefited from the improvement of firing technique besides the raw material recipe of glaze. The breakthrough of firing technique was a crucial condition for the invention of glaze.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 50762006, 50962008), the Jiangxi Provincical Department of Eduction (Grant No. LS0908) and the Natural Science Foundation of Jiangxi Province (Grant No. 2009GQW0014).

1 Li J Z. Formation and development of the green glaze in Zhejiang Province (in Chinese). J Chin Cer Soc, 1983, 11: 118
2 Zhang F K. Shanghai Institute of Ceramics, Chinese Academy of Sciences. The Research on China Ancient Ceramics - The Origin of Chinese Traditional High-Temperature Glazes (in Chinese). Beijing: Science Press, 1987. 41–46
3 Wu J, Li J Z, Wu J M, et al. Property and provenance study of fancy proto-porcelain unearthed from the elite burials of the Yue state at Hongshan. Sci China Tech Sci, 2010, 53: 369–374
4 Wu J, Luo H J, Li Q J, et al. Composition model and microstructure characteristic of Yue ware, Longquan ware and Southern-Song Guan ware (in Chinese). J Chin Cer Soc, 2009, 37: 1408–1414
5 Wu J, Wu J M, Li Q J, et al. Scientific studies on pottery and pro-porcelain from group of graves in Henglingshan, Guangdong province (in Chinese). Sci China Ser E-Tech Sci, 2009, 39: 1074–1080
6 Wu J, Wang H S, Li J Z, et al. The technical research on the huge glazed brick from the relic of Nanyue Kingdom Palace. Sci China Ser E-Tech Sci, 2007, 37: 1140–1147
7 Li J Z. The History of China Science and Technology (Ceramics) (in Chinese). Beijing: Science Press, 1998. 10–20
8 Wang C S. Primary study on early pottery (in Chinese). China Cultural Relic News, 2005-11-11
9 Institute of Archaeology, China Academy of Social Sciences. Trial excavation bulletin of Maiping and Majiashan sites in Hanyuan county, Sichuan province (in Chinese). Sichuan Culture Relics, 2006, (2): 3–19
10 Feng M, Li G N, Ling X, et al. Preliminary research on the bluish-white porcelain in Fanchang Kiln (in Chinese). Sci Conserv Archaeol, 2004,16: 29–32
11 Li J Z. The History of China Science and Technology (Ceramics) (in Chinese). Beijing: Science Press, 1998. 104–106
12 Luo H J, Li J Z, Gao L M, et al. Chemical composition and microstructure study on proto-porcelain glaze (in Chinese). ISAC 92, 1992. 72–77
13 Li J Z, Deng Z Q, Zhang Z G, et al. Study on the Black Slipware and Proto-porcelain from Jiangshan, Zhejiang province, the Research on China Ancient Ceramics (in Chinese). Beijing: Science Press, 1987. 56–63
14 Li J Z. The History of China Science and Technology (Ceramics) (in Chinese). Beijing: Science Press, 1998. 127–129