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The white porcelains from Dehua kiln site of China: Part I. Chemical compositions and the evolution regularity

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Abstract

Dehua county in Fujian province of China has a long history of white porcelain production from the Song to Qing Dynasties. The development and flourish of Dehua porcelain has always been closely related to the export trade. In this part of the study, white porcelain samples of the Song to Qing Dynasties excavated from Wanpinglun, Qudougong, Zulonggong, Jiabeishan and Xingjiao kiln sites were analyzed to investigate chemical compositions of body and glaze and the evolution regularity in the course of time. The study demonstrates that the composition of Dehua body has similar evolution regularity through the Song to Qing Dynasties with Dehua glaze, and the samples of the Ming Dynasty have extraordinary high K_2O both in bodies and glazes.

Keywords: Dehua kiln; White porcelain; Chemical composition; Evolution regularity

1. Introduction

Dehua county is located in central Fujian Province on the southeast coast of China. Dehua is surrounded by mountain and water, rich in porcelain stones, has a convenient transportation, and has been a famous ceramics making area in south China. As far back as the Neolithic Period, people in Dehua already knew how to make hard pottery. Porcelain making in Dehua started in the Tang Dynasty (618–907 A.D.), a book named "*Tao Ye Fa*" on porcelain making technology was handed down. Dehua porcelains began to be exported abroad in large quantities in the Song Dynasty (960–1279 A.D.) and Yuan Dynasty (1279–1368 A.D.) to Southeast Asia and the Middle East along the Marine Silk Road. Dehua white porcelain production reached its climax in the Ming Dynasty (1368–1644 A.D.), when large varieties of Dehua white wares were exported to Europe, called blanc de chine by French. Blanc de chine is the masterpiece of Dehua white ware with an ivory white tone, a translucent body and superb shaping and sculpture workmanship, thus often called as "lard white" or "ivory white". In the Qing Dynasty (1644–1911 A.D.), blue and white wares became the main export item of Dehua kiln, thus the output and quality of white porcelains declined dramatically.

The production of Dehua porcelain always catered to the demand of overseas market, accordingly the development and flourish of Dehua porcelain has always been closely related to the export trade.

Over 200 kiln sites from the Song to Qing Dynasties have been discovered within the scope of Dehua county. Archaeological excavations were carried out on five Dehua kiln sites, listed in Table 1.

Wanpinglun kiln site started producing porcelains in the Northern Song Dynasty (960–1126 A.D.) and continued up to the Southern Song Dynasty (1127–1279 A.D.). The excavated porcelains are mainly domestic wares including various shapes such as bowl, plate, dish, jar and ewer. Large quantities of white porcelains were excavated from the late Northern Song stratum, a lot of green, black and brown-glazed porcelains were discovered from the Southern Song stratum [1].

Qudougong kiln site was listed as National Key Cultural Relics Conservation Unit in 1988 and was rated as one of the ten

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Table 1
Excavated Dehua kiln sites.

Kiln site	Time	Location	Date of excavation
Wanpinglun	Song	Gaide village, Gaide township	1976
Qudougong	Yuan	Baomei village, Longxun town	1976
Zulonggong	Yuan, Ming	Baomei village, Longxun town	2004
Jiabeishan	Yuan, Ming	Baomei village, Longxun town	2001
Xingjiao	Qing	County town	2004

major archeological findings of Fujian province for the 50th Anniversary of the Founding of the People's Republic of China. A chamber dragon kiln more than 57 m long and 1.4–2.95 m wide was excavated in 1976, usually called ‘‘chicken-cage’’ kiln by local people. Over 6000 white porcelain wares were discovered, which are mainly domestic wares such as bowl, plate, dish, ewer, jar, vase, Xi, cup, box and stem cup. Stamping, carving, applique and relief carving techniques were used for decoration [1].

Zulonggong kiln site is just next to Qudougong kiln site. Yuan and Ming remains were excavated in 2004.

Jiabeishan kiln site is located within the conservation scope of National Key Cultural Relics Conservation Unit-Qudougong kiln site. The excavated white porcelains have various vessel shapes such as bowl, plate, dish, cup, Xi, ewer, vase, jar, spoon, lamp, box, inkslab, pitcher, receptacle, water-jet, moulage, sculptured figures and animals, showing white, ivory-white, greenish white or yellowish white tones. The ivory-white wares account for over 70% of the Ming porcelains from Jiabeishan kiln site, representing the highest technological level of white porcelain production of Dehua kiln [2].

Xingjiao is a kiln site of the Qing Dynasty. One step kiln, blue and white porcelains, white porcelains and a few colored-glazed porcelains were excavated in 2004 [3].

In this part of the study, white porcelain samples excavated from Wanpinglun, Qudougong, Zulonggong, Jiabeishan and Xingjiao kiln sites were analyzed to investigate chemical compositions of body and glaze and the evolution regularity in the course of time.

2. Experimental

Glaze and body compositions were examined by energy-dispersive X-ray fluorescence (EDAX Eagle-III μProbe, USA). The body test was performed on a polished fracture surface, and the glaze test was performed on a natural external surface. Four measurements were carried out and the average was adopted for each test.

3. Results and discussion

3.1. Dehua white porcelain samples

Visual appearances of the samples are presented in Table 2.

3.2. Chemical compositions and the evolution regularity

3.2.1. Body

Fig. 1 shows the factor loading diagram of the body compositions. Figs. 2–5 compare the oxide contents of Fe_2O_3, K_2O, Al_2O_3 and SiO_2 in the bodies.

From the Song to Ming Dynasties, Fe_2O_3 content became gradually less and reached the lowest in the Ming Dynasty, whereas Fe_2O_3 content rose up in the Qing Dynasty. K_2O content was on the increase through the Song to Ming Dynasties and reached the top in the Ming Dynasty, but fell off in the Qing Dynasty. SiO_2 and Al_2O_3 contents fluctuated slightly during the Song, Yuan and Ming Dynasties, while

Table 2
Appearance description of the samples.

Time	Kiln site	Vessel shape	Glaze	Body
Song	Wanpinglun	Pitcher, bowl, box, vase	Bright surface, translucent or transparent, pale greenish-white	Pale gray or white, well-sintered
Yuan	Qudougong	Vase, Xi, stem cup, Junchi, plate, bowl, dish	Bright surface, translucent or transparent, white or pale greenish-white	Pale gray or white, well-sintered
Yuan	Zulonggong	Plate, Xi, bowl	Bright surface, translucent or transparent, white or pale greenish-white	White, well-sintered
Yuan	Jiabeishan	Bowl, plate, Xi	Bright surface, translucent or transparent, white or pale greenish white	White, well-sintered
Ming	Zulonggong	Ewer, cup, lid, plate, jar	Mainly ivory-white, translucent, smooth and mild as frozen fat, a few pale yellowish-white	White, well-sintered with gloss at cross-section, translucent (except for a few thick bodies)
Ming	Jiabeishan	Bowl, dish, plate, sculpture, jar, spoon, cup	Mainly ivory-white, translucent, smooth and mild as frozen fat, a few pale greenish-white or pale yellowish white	White, well-sintered with gloss at cross-section, translucent (except for a few thick bodies)
Qing	Xingjiao	Cup, spoon, bowl, plate	Bright surface, translucent or transparent, pale grayish-white	Pale gray or white, well-sintered

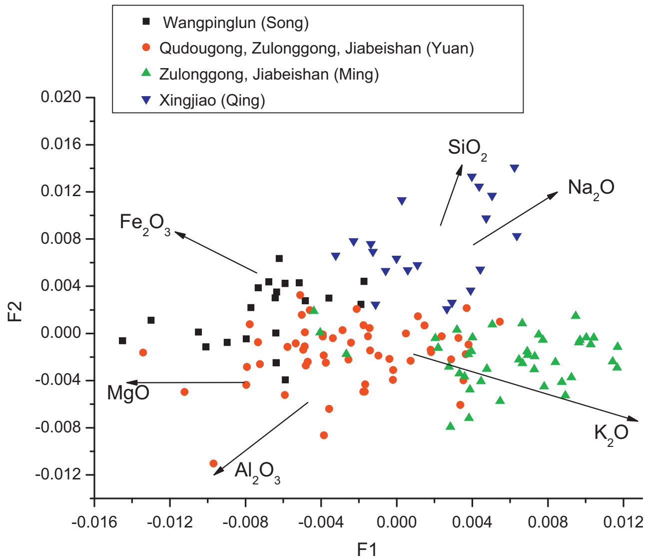

Fig. 1. Factor loading diagram of the major and minor chemical compositions of the bodies (factor contribution rate 72.3%).

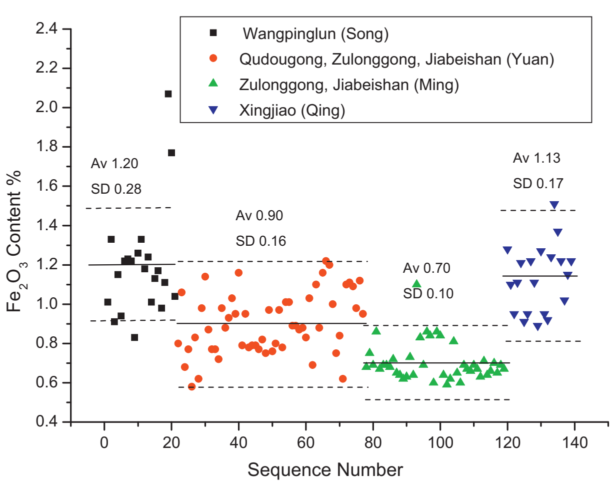

Fig. 2. Fe_2O_3 contents of the bodies.

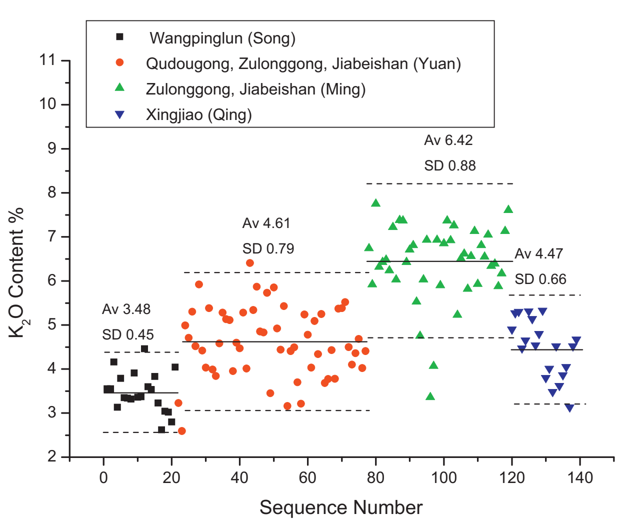

Fig. 3. K_2O contents of the bodies.

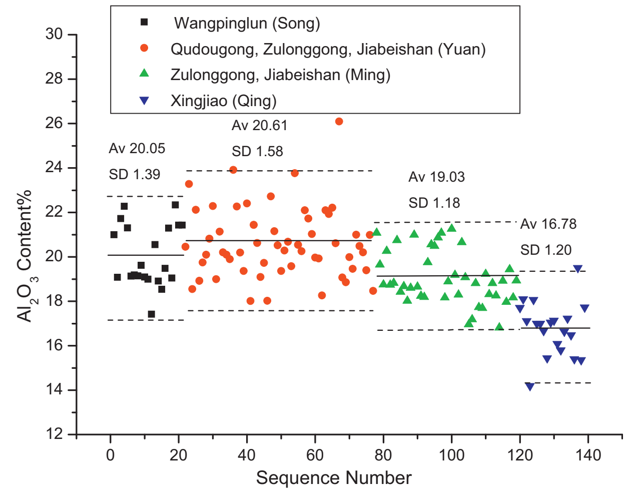

Fig. 4. Al_2O_3 contents of the bodies.

Dehua body in the Qing Dynasty had the lowest Al_2O_3 content and the highest SiO_2 content.

The Ming Dynasty is a period of great prosperity of white porcelain production of Dehua kiln. The lowest Fe_2O_3 content of body creates the high body whiteness. The highest K_2O content of body results in more amount of glass phase in body, thus increasing the translucency of body and forming the special features of "ivory-white".

Dehua county is mountainous and abundant in high-quality porcelain stones, laying a good foundation of raw material for the rise and development of porcelain production in Dehua. According to the literature [4], the formation of Dehua porcelain stone came from the weathering of the feldspar-rich rocks such as quartz porphyry. The porcelain stone heavily weathered near the earth's surface can serve as the material for bodies, while the lightly weathered porcelain stone under the earth deeply which is rich in feldspar is suitable for preparing glazes. The body of Dehua white porcelain is prepared using the local porcelain stone without adding other materials, called "Unitary Formula".

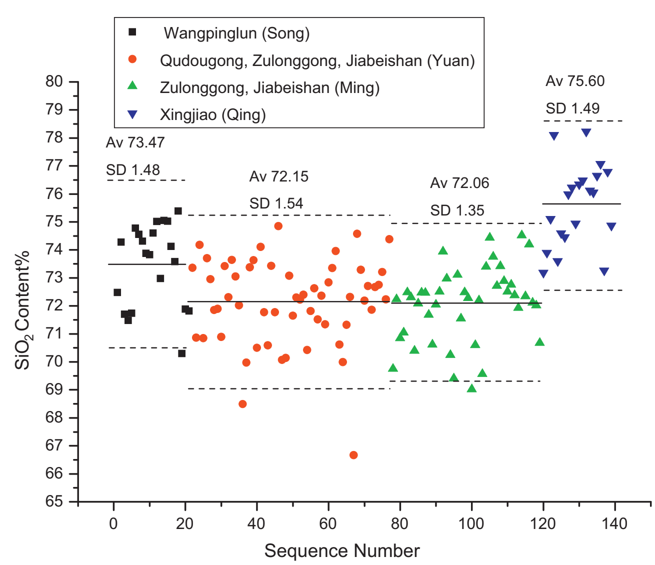

Fig. 5. SiO_2 contents of the bodies.

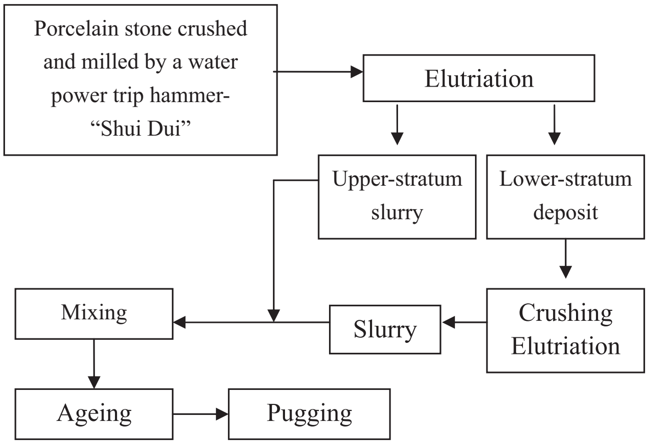

Fig. 6. The treatment process of the body material for Dehua white porcelain.

The treatment process of the body material for Dehua white porcelain is shown in Fig. 6 [5].

Adopting experimental archaeological method, we simulated the elutriation process of Dehua porcelain stone, to investigate the influence of elutriation on chemical composition. Three kinds of Dehua porcelain stones used for bodies at present were collected from Shangyong town, Sanban town and Gaide township, respectively. Shangyong porcelain stone (number 1) is white clod, Sanban porcelain stone (number 2) is pale gray clod, and Gaide porcelain stone (number 3) is loose sand-like beige powder, all the three belong to soft porcelain stone minerals near the earth's surface. Three suspensions were prepared by dipping three porcelain stones in water, respectively, grinding number 1 and 2 clods, then fully stirring the slurry. After natural sedimentation for 4 h, the upper-stratum slurries numbered 1-1, 2-1, 3-1 and the lower-stratum deposits numbered 1-2, 2-2, 3-2 were obtained for analysis. The XRF and XRD results are given in Tables 3 and 4.

According to Tables 3 and 4, porcelain stones from Shangyong and Sanban were heavily weathered, and consist mainly of quartz, sericite and kaolinite. Sericite provides the source of K_2O. Partial quartz particles precipitated. Sericite and kaolinite belong to layered silicate clay minerals which can be dispersed by water, so most of sericite and kaolinite were dispersed by water and entered the upper-stratum slurry. Compared with the original porcelain stones, the upper-stratum slurry is poorer in SiO_2 and richer in Al_2O_3 and K_2O. Fe_2O_3 content in the upper-stratum slurry is slightly higher than in the lower-stratum deposit, suggesting that Fe_2O_3 exists both in the crystal lattice of clay minerals and in the form of iron-contained mineral particles. The iron-contained mineral particles precipitated together with quartz particles to the lower-stratum deposits. In general, for the heavily weathered porcelain stone, elutriation process can increase Al_2O_3 and K_2O and reduce SiO_2 contents in the upper-stratum slurry, thus achieving the objective of controlling chemical composition by adjusting the mixture proportion of the upper-stratum slurry

Table 3
Chemical compositions of Dehua porcelain stones for bodies (wt%).

Source	Number	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
Shangyong town	1	0.07	0.13	23.17	70.26	4.24	0.08	0.04	1.01
	1-1	0.07	0.11	26.53	66.83	4.27	0.11	0.08	1.01
	1-2	0.24	0.12	22.73	71.36	3.48	0.08	0.08	0.90
Sanban town	2	0.48	0.06	25.19	67.43	3.78	0.08	0.06	1.94
	2-1	0.49	0.11	27.34	64.90	3.89	0.12	0.06	2.08
	2-2	0.49	0.18	22.65	70.54	3.29	0.08	0.03	1.74
Gaide towship	3	0.47	0.20	27.83	63.78	5.76	0.10	0.06	0.80
	3-1	0.31	0.24	36.90	58.16	2.32	0.10	0.07	0.88
	3-2	0.16	0.12	20.98	71.97	4.83	0.12	0.07	0.74
	3-3	0.23	0.30	32.17	61.07	4.11	0.11	0.08	0.92
	3-4	0.28	0.00	16.24	76.02	5.63	0.11	0.02	0.70

Table 4
Crystal phase attributes of Dehua porcelain stones for bodies (wt%).

Source	Number	Crystal phase
Shangyong town	1	Quartz, sericite, kaolinite
	1-1	Quartz, sericite, kaolinite
	1-2	Quartz, small amount of kaolinite and sericite
Sanban town	2	Quartz, sericite, kaolinite
	2-1	Quartz, sericite, kaolinite
	2-2	Quartz, small amount of sericite and kaolinite
Gaide towship	3	Quartz, potassium feldspar, kaolinite, sericite, small amount of white mica
	3-1	Kaolinite, sericite, quartz, small amount of potassium feldspar
	3-2	Quartz, potassium feldspar, sericite, small amount of kaolinite and white mica
	3-3	Quartz, sericite, potassium feldspar, kaolinite, small amount of white mica
	3-4	Quartz, sericite, potassium feldspar, small amount of kaolinite and white mica

and lower-stratum deposit. Elutriation process has little effect on Fe_2O_3 content. The simulation experiment demonstrates that elutriation technique is a key procedure of body composition control.

The sand-like Gaide porcelain stone has relatively high amount of potassium feldspar, suggesting that it was weathered lightly. Potassium feldspar and sericite are the source of K_2O. K_2O content in the upper-stratum slurry (3-1) is much higher than in the lower-stratum deposit (3-2), which resulted from the precipitation of most potassium feldspar particles. So in order to avoid losing the K_2O-rich potassium feldspar, milling is necessary before elutriation. We did another elutriation experiment for the finely ground Gaide porcelain stone, the upper-stratum slurry and the lower-stratum deposit are numbered as 3-3 and 3-4, respectively. K_2O content of 3-3 was markedly enhanced compared with 3-1. Therefore, the crushing and milling before elutriation is quite important, which determines the particle size distribution of the porcelain stone, directly influencing the effect of the subsequent elutriation process. In ancient times, potters used an original but effective water power trip hammer named ‘‘Shui Dui’’ for crushing and milling of porcelain stone.

The chemical composition difference among Dehua ware bodies of the Song, Yuan and Ming Dynasties comes from the chemical composition difference among the porcelain stones of the three dynasties, mainly reflected in the variation of Fe_2O_3 and K_2O contents. The porcelain stone employed in the Ming Dynasty is of the best quality, corresponding to the best quality of white wares. There should not be much difference in chemical composition between the porcelain stone used in the Qing Dynasty and the Ming Dynasty. But the body composition of the Qing Dynasty has lower K_2O and Al_2O_3 contents and higher SiO_2 content than that of the Ming Dynasty, possibly resulting from the relatively rough elutriation technique or the higher proportion of the ‘‘Sand Head’’ of the Qing Dynasty. Therefore both the selection of porcelain stone and the processing technique influence the body compositions of different times.

3.2.2. Glaze

Fig. 7 shows the factor loading diagram of the glaze compositions. Figs. 8–13 compare the oxide contents of Fe_2O_3, K_2O, CaO, Al_2O_3, SiO_2, MnO and P_2O_5 in the glazes.

Similar to the body, Dehua glaze of the Ming Dynasty also has the lowest Fe_2O_3 and the highest K_2O contents. From the Song to Ming Dynasties, Fe_2O_3 content became gradually less and reached the lowest in the Ming Dynasty, whereas Fe_2O_3 content rose up in the Qing Dynasty. K_2O content was on the increase through the Song to Ming Dynasties and reached the top in the Ming Dynasty, but fell off in the Qing Dynasties. CaO content was running down through the Yuan to Qing Dynasties, CaO content in the Song Dynasty lied between that of the Yuan and Ming Dynasties. Dehua glaze belongs to ash glaze since it contains MnO and P_2O_5 which progressively increased from the Song to Ming Dynasties but dramatically dropped to the lowest in the Qing Dynasty. Dehua glaze was confected by mixing porcelain stone and glaze ash, the preparation process of the glaze

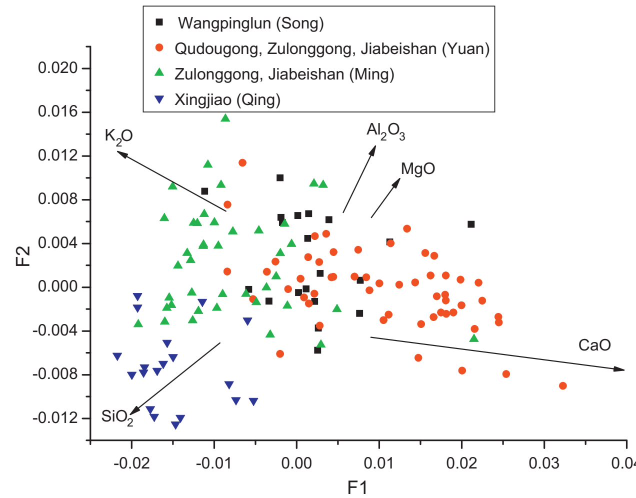

Fig. 7. Factor loading diagram of the major and minor chemical compositions of the glazes (factor contribution rate 80.3%).

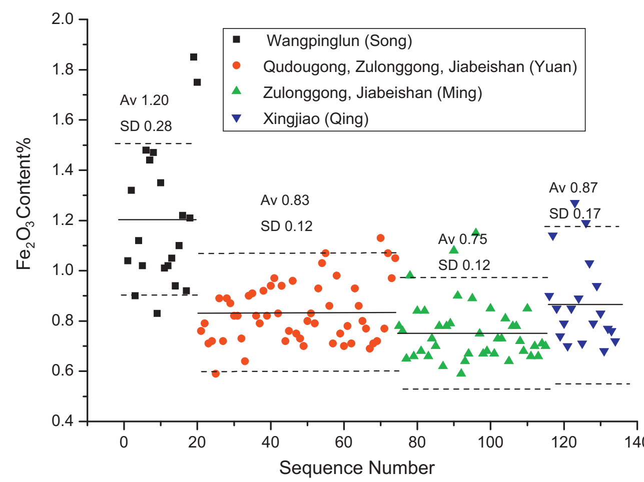

Fig. 8. Fe_2O_3 contents of the glazes.

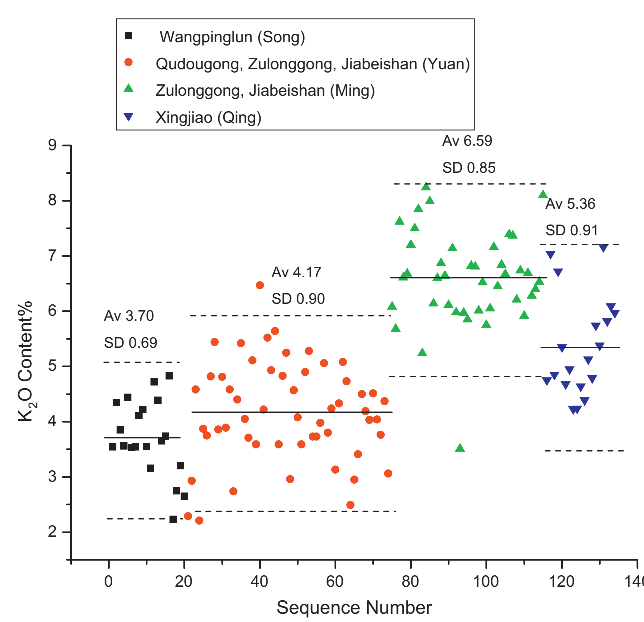

Fig. 9. K_2O contents of the glazes.

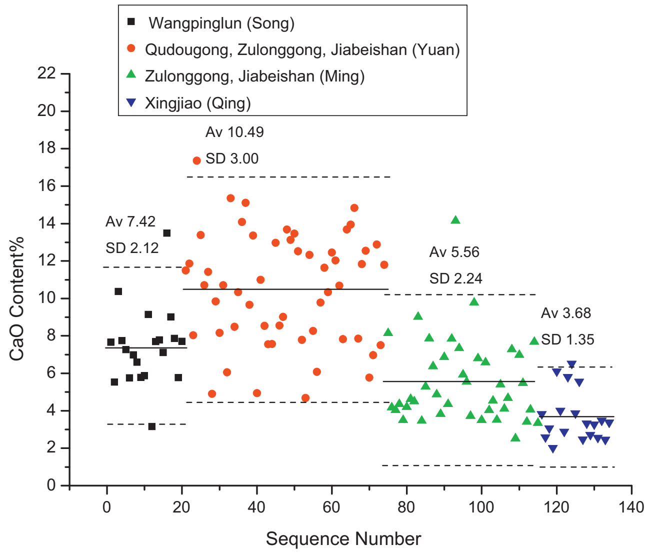

Fig. 10. CaO contents of the glazes.

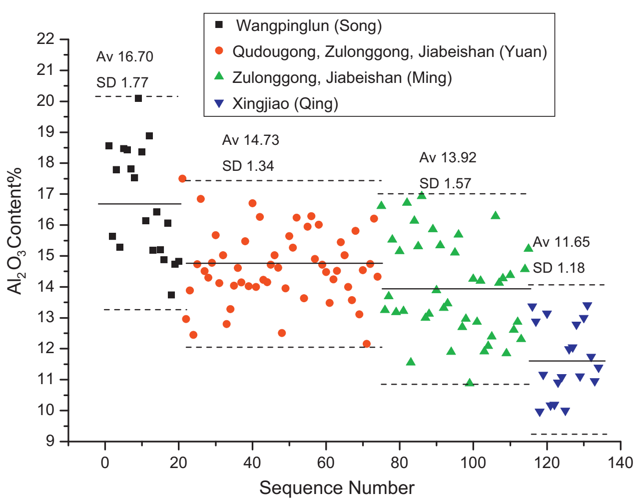

Fig. 11. Al_2O_3 contents of the glazes.

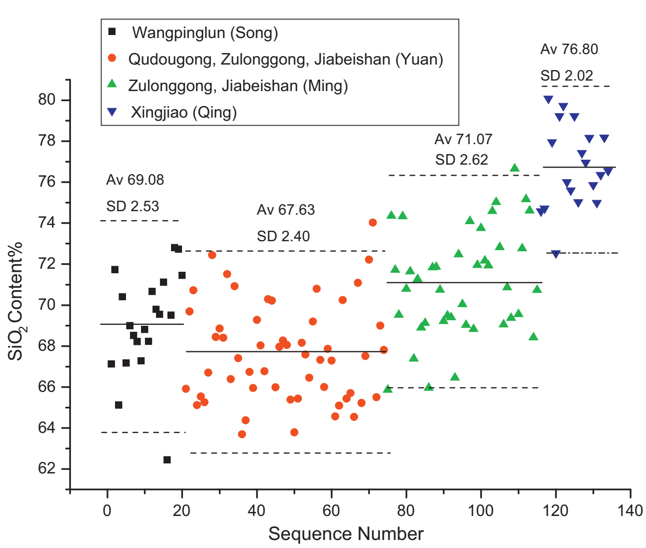

Fig. 12. SiO_2 contents of the glazes.

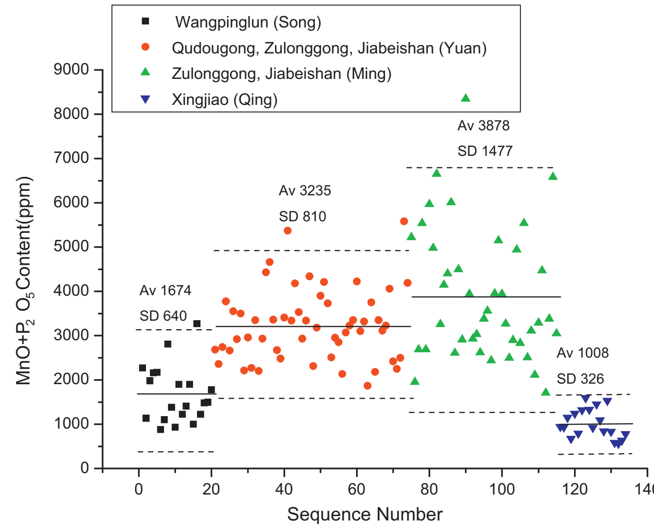

Fig. 13. MnO and P_2O_5 contents of the glazes.

for Dehua white porcelain is shown in Fig. 14 [5]. The lowest Al_2O_3 contents in the Qing Dynasty suggest that the least amount of glaze ash and the most amount of porcelain stone were used for preparation of the glazes in the Qing Dynasty.

Similar to the body, the glaze of the Qing Dynasty has the lowest Al_2O_3 content and the highest SiO_2 content, which is due to the rough elutriation technique resulting in high amount of dissociative quartz.

The porcelain stone used for body is deeply weathered with a lot of sericite, while the porcelain stone used for glaze is lightly weathered with high amount of potassium feldspar. From the chemical composition, the glazes of the Song and Yuan Dynasties belong to calcium–potassium glazes, while the glazes of the Ming and Qing Dynasty are potassium–calcium glazes. In the Ming Dynasty, the glaze formula had a dramatic change, deliberately cutting down the dosage of glaze ash to about a half of that of the Yuan Dynasty. The high K_2O content of over 6% can abate the trend of viscosity decrease at the high temperature, making the glaze a very viscous glass at temperatures above 1250 °C, which is beneficial to the prevention of glaze flow and the enhancement of the mildness of glaze surface. High K_2O content of glaze is a key element ensuring the formation of "ivory-white".

3.3. Elements affecting the visual appearance of Dehua white porcelain

The elements affecting the visual appearance of Dehua white porcelain include two aspects, body and glaze compositions and

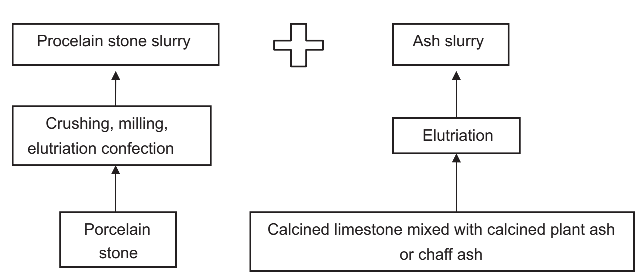

Fig. 14. The glaze preparation process for Dehua white porcelain.

firing technique. Body and glaze compositions are the basis, which are decided by some factors such as the selection of porcelain stones suitable for body making or glaze preparation, the degree of elutriation processing of the porcelain stones, the ratio of upper – stratum slurry to lower – stratum deposit for body material confection, the ratio of porcelain stone to ash for glaze slurry preparation. Firing technique refers to temperature schedule and atmosphere of firing process.

From the Song to Qing Dynasties, the kiln shape and structure evolved in accordance with certain regularity. The Wanpinglun kiln of the Song Dynasty is a dragon kiln shaped like a narrow tunnel built up a low slope [1]. Dragon kiln has a straight flame and free flow of gas. The firing of dragon kiln is usually uneven with a fluctuation of temperature and atmosphere. Up to the Yuan and Ming Dynasties, a kind of chamber dragon kiln with separate chambers was put into use. Both the Qudougong kiln of the Yuan Dynasty and the Jiabeishan kiln of the Ming Dynasty belong to chamber kilns [1,2]. Every chamber has a partition wall with some blowholes at the lower part of the wall. Each chamber can be regarded as a semi-reverse flame kiln. Compared with dragon kiln, the temperature and atmosphere control of chamber dragon kiln is better. In the Qing Dynasty, step kiln became mature. The Xingjiao kiln of the Qing Dynasty is a typical step kiln with separate stepped chambers [3]. The wideness of each chamber is bigger than the depth. Every chamber has an independent firing box. Obviously, the control of step kiln should be better than dragon kiln and chamber dragon kiln. According to visual appearance, Dehua white porcelains of the Song and Qing Dynasties mainly appear to be pale greenish-white or pale grayish-white, probably fired in weakly reducing atmosphere. Dehua white porcelains of the Yuan Dynasty turn out to be white or pale greenish-white, possibly fired in neutral or weakly reducing atmosphere. Dehua white porcelains of the Ming Dynasty are of the best quality, mainly showing ivory-white and a few showing pale yellowish-white, suggesting that the porcelains were fired in oxidation atmosphere.

Analysis results show that the compositions of Dehua body and glaze have similar evolution regularity through the Song to Qing Dynasties. The Ming Dynasty keeps Fe_2O_3 content at the lowest level and K_2O content at the highest level both in body and glaze, indicating that the quality of the porcelain stone is the best at that time. High whiteness of Dehua ware is achieved due to the fairly low content of the coloring element in both body and glaze. The high K_2O content results in the generation of large amounts of glass phase in body and the concomitant decrease in porosity of body, realizing the body translucency. And also the high K_2O content ensures the good mildness of glaze. The oxidation atmosphere and appropriate heating, soaking and cooling schedules guarantee the formation of ‘‘ivory-white’’ porcelain with a translucent body covered by a layer of mild and frozen fat-like glaze in the Ming Dynasty.

4. Conclusion

The body of Dehua white porcelain was prepared using the local porcelain stone without adding other materials, called ‘‘Unitary Formula’’. Elutriation technique is a key procedure of body composition control. The porcelain stone used for body is deeply weathered with a lot of sericite, while the porcelain stone used for glaze is lightly weathered with high amount of potassium feldspar.

The composition of Dehua body has similar evolution regularity through the Song to Qing Dynasties with Dehua glaze. From the Song to Ming Dynasties, Fe_2O_3 content became gradually less and reached the lowest in the Ming Dynasty, whereas rose up in the Qing Dynasty. K_2O content was on the increase through the Song to Ming Dynasties and reached the top in the Ming Dynasty, but fell off in the Qing Dynasties.

The Ming Dynasty is a period of great prosperity of white porcelain production for Dehua kiln. High whiteness of Dehua ware is achieved due to the fairly low content of the coloring element in both body and glaze. The high K_2O content is the key to ensure the body translucency and also the good mildness of glaze. The oxidation atmosphere and appropriate heating, soaking and cooling schedules guarantee the formation of ‘‘ivory-white’’ porcelain with a translucent body covered by a layer of mild and frozen fat-like glaze.

Both body and glaze of the Qing Dynasty have the lowest Al_2O_3 content and the highest SiO_2 content compared with the Song, Yuan and Ming Dynasties, possibly resulting from the relatively rough elutriation technique. The least amount of glaze ash and the most amount of porcelain stone were used for preparation of the glazes in the Qing Dynasty.

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