SCIENCE CHINA
Technological Sciences

February 2010 Vol.53 No.2: 369–374
doi: 10.1007/s11431-010-0013-8

Property and provenance study of fancy celadon samples excavated from the Noble Burials of the Yue State at Hongshan, China

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Received July 30, 2009; accepted October 27, 2009

The Noble Burials of the Yue State at Hongshan in Wuxi City with many fancy burial objects were excavated by Archaeology Institute of Jiangsu Province and Xishan District Committee for Administration of Cultural Relics of China. It was appraised as one of the ten major archaeological excavations in 2004. Some precious ceramic samples excavated from this site are very important for studying the development history of Chinese ceramics, especially for studying the origin of porcelain. With the cooperation of Archaeology Institute of Nanjing Museum, the ceramic samples excavated from the Noble Burials of the Yue State at Hongshan were collected and systematically analyzed. Compared with the celadon samples produced in Yue-kiln site during later Eastern Han Dynasty (25–220 A.D.), some important topics such as the provenance and properties of the ceramic samples excavated from the Noble Burials of the Yue State at Hongshan were deeply studied.

Noble Burials of the Yue State at Hongshan, multivariate statistical analysis method, origin of porcelain, celadon

Citation: Wu J, Wu J M, Li Q J, et al. Property and provenance study of fancy celadon samples excavated from the Noble Burials of the Yue State at Hongshan, China. Sci China Tech Sci, 2010, 53: 369–374, doi: 10.1007/s11431-010-0013-8

The Noble Burials of the Yue State is located in the Xishan urban area, Wuxi City, Jiangsu Province, China which is adjacent to the Huangdai Town, Xiangcheng District of Suzhou City. Seven noble tombs of the Yue State during the Warring States Period (475–221 B.C.) were excavated by Archaeology Institute of Jiangsu Province and Xishan District Committee for Administration of Cultural Relics in the development zone of Hongshan from March 2003 to June 2005. It is the first time that so many noble tombs of the Yue State were discovered in the Taihu Lake Basin [1]. It is of an extremely important value for the study of the history and culture of the Yue State during the Warring States Period. A large number of relics and remains were unearthed in this excavation. For example, only in Qiuchengdun site 1098 burial artifacts such as celadon, pottery, jade and colored glaze were unearthed. The number and size of the excavated artifacts exceeded any archaeological findings of noble burials of the Yue State in Jiangsu and Zhejiang provinces before. And some of the excavated 581 ceramic samples feature beautiful patterns and excellent manufacturing (see Figure 1). The precious artifacts have received considerable attention due to their academic research value: (1) Should these ceramic artifacts belong to proto-porcelain or porcelain series? The conclusion might change the development history of ceramics and bring forward the time of porcelain invention by several hundred years. In fact, some local media had already used the title of paper such as "the invention time of Chinese porcelain had been brought forward by 500 years" [2]. (2) Where was the production site of the ceramic artifacts?

With the cooperation of Archaeology Institute of Jiangsu Province and Institute of Cultural Relics Protection in

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Figure 1 Some ceramic samples unearthed from the noble burials of the Yue State at Hongshan.

Deqing County, Zhejiang Province, more than 50 ceramic samples unearthed from Qiuchengdun, Laohudun and Wanjiafen noble burials of the Yue State at Hongshan were collected and systematically analyzed so as to resolve the above two problems. The manufacture technology, physical properties and production site of these ceramic samples were deeply studied compared with the celadon samples unearthed from Deqing, Xiaoshan, Shangyu, Shaoxing, and Cixi in Zhejiang Province.

1 Experiment

1.1 Chemical composition analysis

More than 50 ceramic samples unearthed from the Noble Burials of the Yue State at Hongshan and produced in Fengjiashan, Tingziqiao Yue-kiln site in Deqing County, Zhejiang Province were analyzed by EAGLE-III energy dispersion X-ray fluorescence spectrometer of EDAX company. Tables 1–4 list the results.

Table 1 Major element compositions of the sample bodies from the Noble Burials of the Yue State at Hongshan and Yue-kiln site of Deqing County (wt%)

Site	Name		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	Si/Al (mol)
Qiuchengdun Tomb	celadon	mean	0.62	0.84	18.02	73.58	2.00	0.34	0.70	2.92	0.42
		S.D.	0.21	0.09	0.78	1.21	0.15	0.15	0.05	0.28	
Wanjiafen Tomb	impressed stoneware	mean	1.02	1.18	18.24	71.31	2.18	0.59	0.63	3.84	0.43
		S.D.	0.46	0.20	0.94	1.95	0.40	0.54	0.04	0.92	
Laohudun Tomb	celadon	mean	0.52	0.59	17.50	74.59	1.67	0.32	0.68	3.13	0.40
		S.D.	0.15	0.14	1.20	1.02	0.20	0.11	0.04	0.12	
Fengjiashan Kiln site	celadon	mean	0.79	0.72	17.61	73.90	1.84	0.49	0.73	2.92	0.41
		S.D.	0.35	0.17	0.73	0.95	0.23	0.29	0.07	0.21	
Tingziqiao Kiln site	celadon	mean	1.04	0.83	16.69	74.94	1.74	0.58	0.66	2.52	0.38
		S.D.	0.36	0.12	0.11	0.76	0.06	0.31	0.04	0.12	

Table 2 Major element compositions of glazes and slip coatings of the samples from the Noble Burials of the Yue State at Hongshan and Yue-kiln site of Deqing County (wt%)

Site	Name		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	Si/Al (mol)
Qiuchengdun Tomb	glaze	mean	0.45	3.25	12.63	62.53	1.85	15.76	0.40	2.13	0.34
		S.D.	0.38	0.39	0.77	2.21	0.63	3.31	0.05	0.34	
Qiuchengdun Tomb	slip coating	mean	0.83	1.54	17.85	70.05	3.685	1.505	0.7	2.84	0.43
		S.D.	0.13	0.38	1.82	2.33	0.755	0.765	0.01	0.01	
Wanjiafen Tomb	slip coating	mean	1.44	1.30	13.93	70.95	5.22	1.69	0.72	3.77	0.33
		S.D.	0.46	0.64	1.85	3.06	1.76	1.00	0.30	1.38	
Laohudun Tomb	glaze	mean	0.53	3.10	12.62	64.34	1.98	13.70	0.44	2.30	0.33
		S.D.	0.28	0.60	0.99	3.24	0.41	4.60	0.10	0.36	
Fengjiashan Kiln site	glaze	mean	0.50	3.32	13.35	65.23	2.52	11.15	0.48	2.45	0.35
		S.D.	0.44	1.27	1.54	3.69	0.70	4.90	0.09	0.33	
Tingziqiao Kiln site	glaze	mean	0.80	2.95	12.46	64.37	2.05	13.98	0.43	1.98	0.33
		S.D.	0.23	0.55	0.65	2.59	0.71	3.57	0.07	0.16	

Table 3 Trace element compositions of the sample bodies from the Noble Burials of the Yue State at Hongshan and Yue-kiln site of Deqing County (μg/g)

Site	Name		MnO	CuO	ZnO	PbO_2	Rb_2O	SrO	Y_2O_3	ZrO_2	P_2O_5
Qiuchengdun Tomb	celadon	mean	260	100	130	40	160	70	50	350	260
		S.D.	40	20	60	20	20	10	10	40	150
Laohudun Tomb	celadon	mean	270	90	120	40	140	70	50	400	60
		S.D.	30	30	20	30	10	20	10	50	80
Fengjiashan Kiln site	celadon	mean	250	80	130	40	150	80	50	390	180
		S.D.	60	20	30	20	20	20	10	50	100
Tingziqiao Kiln site	celadon	mean	230	90	130	50	160	80	40	460	200
		S.D.	30	20	20	20	20	20	10	60	80

Table 4 Trace element compositions of the sample glazes from the Noble Burials of the Yue State at Hongshan and Yue-kiln site of Deqing County (μg/g)

Site	Name		MnO	CuO	ZnO	PbO_2	Rb_2O	SrO	Y_2O_3	ZrO_2	P_2O_5
Qiuchengdun Tomb	celadon	mean	3100	130	160	60	130	340	40	290	5340
		S.D.	1060	20	40	60	30	130	10	40	1050
Laohudun Tomb	celadon	mean	2970	110	180	70	140	270	40	360	4560
		S.D.	630	50	50	10	20	120	10	50	900
Fengjiashan Kiln site	celadon	mean	2900	90	130	50	120	310	40	360	4570
		S.D.	1600	30	40	20	20	150	10	70	1890
Tingziqiao Kiln site	celadon	mean	2170	110	160	20	110	370	40	370	4840
		S.D.	570	30	30	30	20	160	10	40	1770

1.2 Microstructure and physical properties

The phase structure, firing temperature, physical properties of the ceramic samples were analyzed by an X-ray diffractometer (D/max 2550V) and thermal dilatometer (NETZSCH DIL 402C). Table 5 lists the analytical results.

2 Correspondence analysis

Due to long history and different production places, the chemical compositions of ancient ceramics are very complicated. Correspondence analysis is a graphical display technique, with advantages over the more familiar data analytical techniques such as multi-dimensional scaling and cluster analysis. Correspondence analysis is an improved form of factor analysis, first suggested by Benzeic in 1970 [3]. In addition to providing correlation among all samples, it also shows correlations between variables and samples. Samples which are plotted together are similar, and elements plotted closely together are correlated. This is of great interest in chemical analysis, where it allows new hypotheses to be formulated in archaeometry, and furthermore it allows to explain the reasons [4].

The total data for major and trace element composition for all samples were separately subjected to correspondence

Table 5 Physical properties and phase compositions of the samples from the Noble Burials of the Yue State at Hongshan and Yue-kiln site of Deqing County

No.	Site	Name	Volume density (%)	Water absorption (%)	Apparent porosity (g/cm^3)	Firing temperature (^{o}C)	Mineral compositions
WQ-3	Qiuchengdun	celadon	2.01	6.3	13	~1283	α-quartz, a little cristobalite and a certain content of mullite
WQ-7	Qiuchengdun	celadon	2.16	2.4	5	~1283	α-quartz, a certain content of cristobalite and mullite
WQ-24	Wanjiafen	impressed stoneware	2.18	4.8	10	~1200	α-quartz, little cristobalite and mullite
WQ-36	Laohudun	celadon	2.07	8.1	17		
WQ-42	Laohudun	celadon	2.06	8.4	17		
WQ-43	Laohudun	celadon	2.03	8	16	~1291	α-quartz, a certain content of cristobalite and mullite
Feng-2	Fengjiashan	celadon	2.35	1.9	4	~1293	α-quartz, a certain content of cristobalite and mullite
Feng-8	Fengjiashan	celadon	2.15	2.7	6	~1296	α-quartz, a certain content of cristobalite and mullite
Ting-3	Tingziqiao	celadon	2.15	2	4	~1217	α-quartz, a little cristobalite and mullite
Ting-5	Tingziqiao	celadon	1.88	7	13	~1265	α-quartz, a little cristobalite and mullite

analysis. The first two or three principal factors (F_1, F_2 and F_3, $F_i=x_1^iA+x_2^iB+\ldots$, where A, B, … are element concentrations and x_1^i, x_2^i, … are factor scores), summarizing 80% of the total variability (providing most of the likely correlations), were selected. A 3D scatter graph is used to convey more statistical information (see Figures 2 and 3).

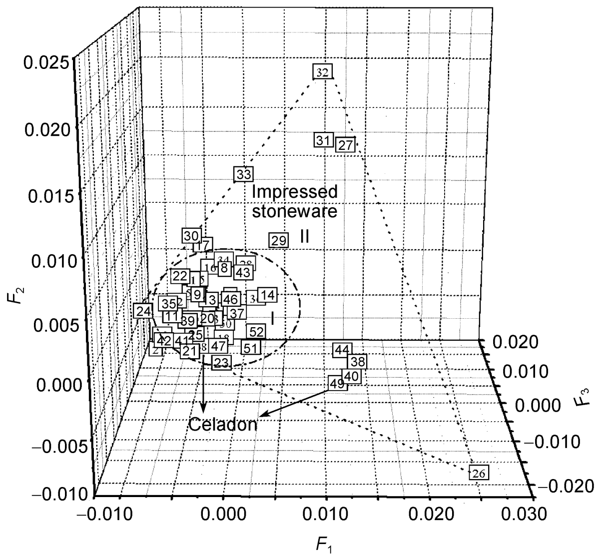

Figure 2 Correspondence analysis with chemical compositions of the sample bodies from the Noble Burials of the Yue State at Hongshan and Yue-kiln site of Deqing County. The Noble Burials of the Yue State at Hongshan: 1–17, celadon samples from Qiuchengdun; 18–25, celadon samples from Laohudun; 26–33, impressed stoneware samples from Wanjiafen. Deqing Kiln: 34–46, celadon samples from Fengjiashan; 47–52, celadon samples from Tingziqiao.

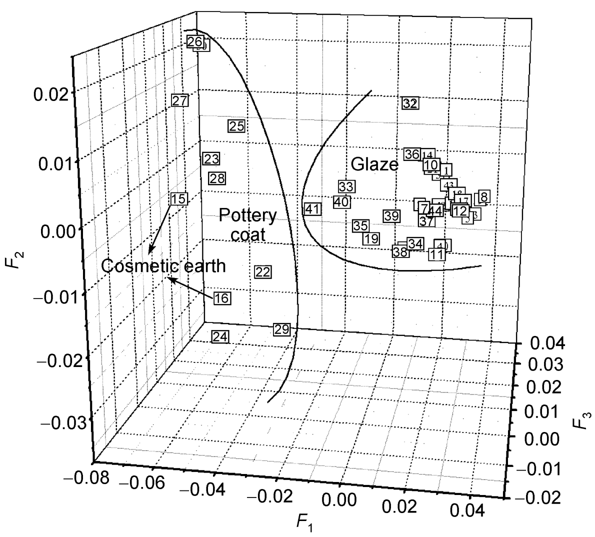

Figure 3 Correspondence analysis with chemical compositions of the sample glazes, slip coatings from the Noble Burials of the Yue State at Hongshan and Yue-kiln site of Deqing County. The Noble Burials of the Yue State at Hongshan: 1–14, glaze of celadon samples from Qiuchengdun; 15–16, slip coating of celadon samples from Qiuchengdun; 17–22, glaze of celadon samples from Laohudun; 23–30, slip coating of impressed stoneware samples from Wanjiafen. Deqing Kiln: 31–39, glaze of celadon samples from Fengjiashan; 40–45, glaze of celadon samples from Tingziqiao.

3 Discussion

3.1 Chemical composition analysis

The concentration of SiO_2 in the bodies of celadon samples excavated from Qiuchengdun and Laohudun varies in a small range (70%–75%). The concentration of Al_2O_3 is between 15% and 20%. The average value of the SiO_2/Al_2O_3 is about 4.12. The composition characteristic is similar to that of porcelain stone in southern China. The content of flux in the bodies of the impressed stoneware samples unearthed in Wanjiafen is relatively high, the average value of flux (K_2O, Na_2O, CaO, MgO, Fe_2O_3) is about 8.82% and higher than that of the celadon samples excavated from Laohudun (see Table 1). The difference is mainly due to the change of Fe_2O_3 content. According to the usual development law of Chinese ceramics, one of the variation characteristics from pottery to porcelain was mainly shown in the change from high content of SiO_2 and R_xO_y, low concentration of Al_2O_3 to low concentrations of SiO_2 and R_xO_y, high concentration of Al_2O_3 in southern China. It is an established principle that ancient potters would make use of local resources. And for lack of experience, the chemical composition of the early impressed stoneware samples varies in a wide range, as shown in Table 1 and Figure 1, but the compositions of all celadon samples had little changes, those samples are confined to a relatively small area. In addition, the concentration of Fe in celadon samples is much lower than that in the impressed stoneware samples (see Table 1). It can be concluded that the raw material used for celadon preparation is different from that for the impressed stoneware, as the potters at that time had not found effective method to reduce the concentration of Fe in the raw materials, the observed differences in compositions can indicate the relevant selection of raw materials. That is to say, the raw material with low concentration of Fe had been chosen for celadon preparation, which is one of the important conditions for the successful preparation of celadon. However, compared with the celadon samples produced in Yue kiln site of Shangyu County during the late Eastern Han Dynasty (25–220 A.D.), which have been widely recognized to be up to the standard of porcelain, the concentrations of impurity elements, such as Fe_2O_3, TiO_2, etc., in celadon samples excavated from the Noble Burials of the Yue State at Hongshan are still relatively high (~3%, see Table 1), and the content of Fe_2O_3 in the celadon samples produced in Shangyu County is only about 1.5% due to the evolution of raw materials processing techniques and the origin of the raw materials [5].

With the emergence of celadon artifact, it had gradually taken the role of bronze ware in daily life because of the impermeability of glaze. It was found that the content of CaO was about 17%, significantly higher than that of alkali oxide in the glazes of the celadon samples excavated in the Noble Burials of the Yue State at Hongshan (see Table 2). This kind of glaze should belong to the typical high-temperature calcium-glaze series. In addition, a kind of thin layer similar to pottery coating was found on the surface of the impressed stoneware and celadon samples unearthed in the Noble Burials of the Yue State at Hongshan, which has never been reported in early archaeological discoveries. Table 2 shows us that the kind of thin layer has a low content of CaO (about 1%–4%), but high contents of K_2O and Na_2O. There are obvious differences in chemical compositions compared with other glaze specimens (see Figure 3). The thin layer is similar to slip coating usually used in the preparation of white porcelain. The emergence of glaze was a major technical breakthrough in the development history of ceramics. It is a key point to study the origin of glaze for the research of the origin of celadon. The origin of glaze was considered to have two ways: 1) the evolution of coating used for the decoration of pottery; 2) derived inspiration from the forming of kiln sweat in the firing process [5, 6]. The specific origin of glaze should be closely related to the local natural resources (raw material and fuel etc.). Generally, limestone with high content of Ca was one of the raw materials used for the preparation of glaze, and the usage of limestone cannot increase the contents of Mn and P in glaze. However, it is found that the contents of Mn and P in the glazes of the celadon samples excavated from the Noble Burials of the Yue State at Hongshan are quite high (~4000 μg/g). It means that another kind of raw material with high contents of Mn and P should be used. In fact, firewood was the main fuel used for the ceramics production in southen China, thus plant ash which also has high content of Ca would be easy to be obtained. It can be concluded that the high concentration of Ca in the celadon samples was probably provided by plant ash which was also rich in Mn and P [6, 7].

The appearance of porcelain is related closely to the abundance of porcelain stone in southern China. Early celadon artifacts produced in southern China were a type of quartz-mica ceramic. Porcelain stone was the only raw material used for celadon bodies. In this condition, the composition pattern of those celadon artifacts would directly depend on the raw material used. In order to confirm the exact production site of the celadon artifacts excavated from the Noble Burials of the Yue State at Hongshan, Deqing County was selected as the first possible kiln site based on the suggestions of archaeologists. In fact the Noble Burials of the Yue State at Hongshan is very close to Deqing County, and celadon artifacts were produced on a large scale during the Warring States Period. As shown in Figures 2 and 3, the celadon samples excavated from the Noble Burials of the Yue State at Hongshan and the celadon samples produced in Deqing County are plotted together, it indicates that their major element compositions are similar to each other. Furthermore, the trace element compositions of all the samples were also analyzed (see Tables 3 and 4). There are high similarities for the contents of Mn, Cu, Zn, Rb, Sr, Y and Zr in the celadon samples from the two sites. Therefore, it can be concluded that Deqing County is likely to be one of the kiln sites where the celadon samples excavated from the Noble Burials of the Yue state at Hongshan were produced.

3.2 Physical properties and microstructure

The phase structure, firing temperature, and physical properties of the ceramic samples unearthed in the Noble Burials of the Yue State at Hongshan were analyzed by an X-ray diffractometer (D/max 2550V) and thermal dilatometer (NETZSCH DIL 402C). Table 5 shows us that the celadon samples excavated in Qiuchendun and Laohudun sites were fired at high temperature (~1290°C). There are more mullite, cristobalite crystallite and some glass phase in the sample bodies, all of these are the typical characteristics usually used for distinguishing pottery from porcelain. Undoubtedly, the appearance of celadon in this region was related closely to the improvement of firing technology. In addition, those celadon samples feature beautiful patterns and excellent manufacturing, then, should those celadon artifacts belong to proto-porcelain or porcelain series? In general, the appearance characteristics of porcelain distinguished from pottery mainly include: 1) The body of porcelain artifact is fine and close in texture, the color of the body is usually white or slightly grey and the section of the body has a glassy luster; 2) There are relatively high strength, low porosity and water absorption for porcelain artifact; 3) There are more glass phase and a certain content of mullite crystallite in body, and a layer of even and well adhesive glaze on body [8]. As shown in Table 5, for the ceramic samples excavated in the Noble Burials of the Yue State at Hongshan, the volume density is around 2.1 g/cm^3, porosity is above 2% and water absorption is 5%–17%. Undoubtedly, compared with the celadon samples produced in Yue kiln site of Shangyu County during the late Eastern Han Dynasty, which have been widely recognized to be up to the standard of porcelain, the physical properties of those excavated celadon samples are still not up to the standard of porcelain. For example, the water absorption of the celadon artifact produced in Yue kiln site of Shangyu County is usually lower than 0.5% [8]. And the layer of glaze is rather thin and easy to be stripped for the celadon samples excavated in the Noble Burials of the Yue State at Hongshan. In addition, although there is a certain content of mullite crystallite in body for the samples excavated in the Noble Burials of the Yue State at Hongshan, the content of glass is still relatively low. Furthermore, the electron microprobe analysis for the middle layer between body and glaze shows that there is no anorthite crystal, which is easy to be found in the celadon samples produced in Yue kiln site of Shangyu County (see Figures 4 and 5). That is also one of the reasons why the glaze is easy to be stripped for the celadon samples excavated in the Noble Burials of the Yue State at Hongshan. To sum up, the celadon samples excavated in the Noble Burials of the Yue State at Hongshan should still belong to proto-

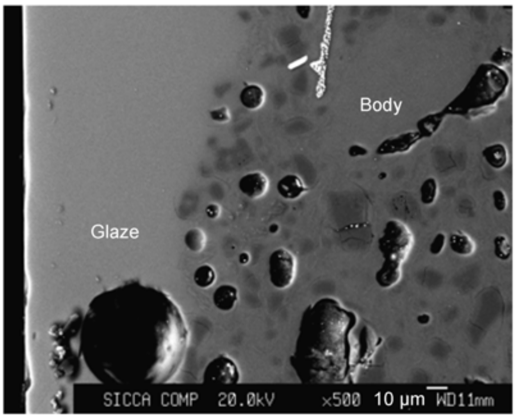

Figure 4 Microstructure of the celadon sample from the Noble Burials of the Yue State at Hongshan.

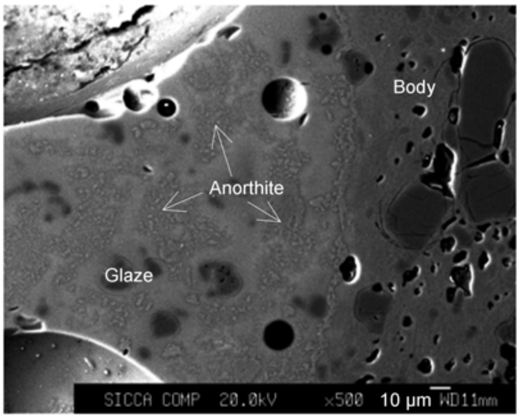

Figure 5 Microstructure of the celadon samples produced in Yue kiln site of Shangyu County.

porcelain series based on the chemical compositions, microstructure and physical properties.

4 Conclusions

(1) The composition characteristic of high content of silicon and low content of aluminum in the celadon sample bodies excavated in the Noble Burials of the Yue State at Hongshan is similar to that of porcelain stone in southern China. It was found that the content of CaO in the glaze is above 17%, this kind of glaze should belong to the typical high-temperature calcium-glaze series. In addition, a thin layer similar to pottery coating was found on the surface of the impressed stoneware and celadon samples unearthed in the Noble Burials of the Yue State at Hongshan, which has never been reported in early archaeological discoveries.

(2) Although the celadon samples excavated in the Noble Burials of the Yue State at Hongshan feature beautiful patterns and excellent manufacturing, to sum up, the celadon samples should still belong to proto-porcelain series based on the chemical compositions, microstructure and physical properties.

(3) Based on the major and trace element composition pattern of the celadon samples from different production sites, it can be concluded that Deqing County is likely to be one of the kiln sites where the celadon samples excavated from the Noble Burials of the Yue State at Hongshan were produced.

This work was supported by the National Natural Science Foundation of China (Grant No. 50762006), the Origin Exploring of Chinese Civilization Projects (second) (Grant No. 2006BAK21B03), and Jiangxi Provincial Department of Education (Grant No. LS0908).

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