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Multiple-analytical study on the initiation and technology of Zhaili celadon from the late sixth to the seventh centuries

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Abstract:

Zhaili kiln is considered one of the earliest kilns sites in northern China, however, there is currently little comprehensive research on the Zhaili production. Therefore, in this study, scanning electron microscope-energy dispersive spectrometer and X-ray diffraction were performed on thirty pieces of typical Zhaili celadon from the late sixth to seven centuries to explore their raw material feature and manufacturing technique. In addition, the motivations for the initiation of Zhaili celadon were also further explored.

1.Introduction

The sixth-seventh centuries AD were a significant period for the ceramic production in the north China. After more than three hundred years production of southern celadon, starting from the Yue celadon of the late of second century AD, the celadon manufacturing techniques was introduced to the north and grew maturity rapidly since late of the sixth century. Shandong province is one of the important celadon production areas in northern China during the period, but the study of early celadon in Shandong provincehas been long ignored due to the lack of archaeological materials and the poor quality of celadon.



Fig.1 Location of Zibo city and Zhaili kiln

Zhaili kiln, located in Zibo city, Shandong province (Fig.1), was considered as one of the earliest celadon kilns in northern China (Chinese ceramic society 1982:

163). It was unknown until the cultural relics survey in 1957. The archaeological investigation and tentative excavation were performed from 1976 to 1977 subsequently (The commission of Zibo ceramic history et al., 1984). However, no systematic excavation has been performed on Zhaili kiln, thus the whole appearance of the kiln still remains unknown. According to the archaeological evidences so far, the production of Zhaili kiln was differentiated into three phases. The first phases started at least since the Eastern Wei dynasty (AD 534-543), which is the initiation stage. The celadons in this phase were clearly low quality, shown by the unsintered coarse body and brownish glaze. The second was the mature phase, which from the Northern Qi (AD 550-577) to the Sui dynasties (AD 581-618). The fine sintered body and greenish glaze showed a great improvement of ceramic technology in this phase. The third phase was the Tang dynasty (AD 618-907), which is the decaying stage. The color of glaze became darker and some of them turned to be brown even black, the quality of body was also declining. The celadons in this phase have quite a few similarities with their counterparts from early Cicun kiln in terms of typology and decoration (The commission of Zibo ceramic history et al., 1984).

Zhaili kiln was the key to studying the introduction of northern celadon, however, there is current limited research because of the lack of archaeological materials. Zhang (2016) performed a typological research of kiln tools from several kilns in the Northern Dynasties, indicating that the technology of celadon production in Zhaili kiln were likely to be introduced by the potters from Jiangsu or Zhejiang province directly. The research of Huang et al. (2020) has analyzed 8 pieces of Zhaili celadon shards in microstructure and chemical composition, which is the only scientific research on the celadon of Zhaili kiln. It suggested that the bodies of Zhaili celadon were less sintered compared to its counterparts from other contemporary kilns and loess may be added into glazes.

To further understand the origin, development and inheritance of the celadon production technology of Zhaili kiln, scanning electron microscope-energy dispersive spectrometer (SEM-EDS) and X-Ray diffraction (XRD) were performed on thirty pieces of Zhaili celadon shards from the Northern Dynasties to the early Tang Dynasty. The features and manufacturing techniques of Zhaili celadon were discussed in details. In addition, the reasons for the initiation of Zhaili kiln were also discussed based upon analytical results, historical background and archaeological evidence.

2. Materials and methods

2.1 Sample description

Thirty shards of celadon from Zhaili kiln (Fig.2) formed the basis of research. Due to the scarcity of Zhaili celadons, only three shards, respectively ZHL-1，ZHL-2，ZHL-3, from the Northern Dynasties, the initiation phase of Zhaili kiln. The other shards from the late of Nothern Dynasties to the early Tang Dynasty, the mature phase of Zhaili kiln.

In addition, twenty-three of Tang to Jin periods celadon (Fig.2), white porcelain and black glaze ware shards from several kilns in Zibo city were determined as

comparison group. They are not discussed in detail here but their data are presented in this article (Supplementary table1).



Fig.2. Photographs of Zhaili celadon and typical comparison group in this study
(ZHL represents samples from Zhaili kiln; CG represents samples from comparison group)

2.2 Analytical methods

2.2.1 Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) analysis

The bulk elemental compositions of ceramic samples were determined by X-ray energy dispersive spectrometer (EDS) produced by Bruker, Germany, coupling with Thermo Scientific Quattros field emission scanning electron microscope (SEM). The samples were analyzed at least three times at voltages of 20KV, counting time of 90s. The results were showed in the form of oxides and standardized to 100%. The results were also corrected by the standard curve method and the detection limit of the instrument was 0.01%.

2.2.2 X-ray Diffraction analysis

The phase structure of samples was determined by Smartlab 9KW X-ray diffraction produced by Rigaku, Japan. Each sample was taken 2g of body, washed and dried, then crushed into powder (the particle-size was less than 200 mesh). The samples were analyzed by PB mode, at voltages of 45KV, electric current of 200mA, scanning speed 15/min, scanning scope of 4°-70°.

3. Results

3.1 The microstructure features of Zhaili celadons

Celadon samples show relatively similar microstructures under SEM, while subtle differences can be observed. As shown in the Fig.3, celadon samples were composed of a thin glaze layer, usually no more than 200um, and a body with unmelted quartz, irregular pores and continuous vitrification. Besides, no decorative clay layer was observed in celadon samples.

The glaze of Zhaili celadon was uneven and transparent with few cracks, barely no crystal can be found. Crystals of calcium plagioclase are only found at the glaze-body interface of few samples (Fig.3b). Irregular grains of quartz with cracks are extensive in the body. The size of the quartz was coarse, grains beyond 100um can be observed commonly. The irregular shape and the coarse size of the quartz indicate they are likely to be extrinsic to the clay. Bright particles of TiO_2, probably derived from rutile or anatase in the clay (Huang et al., 2023), are general in the body. The pores in body are irregular and fine. All the features suggest that the bodies of Zhaili celadon are merely sintered.

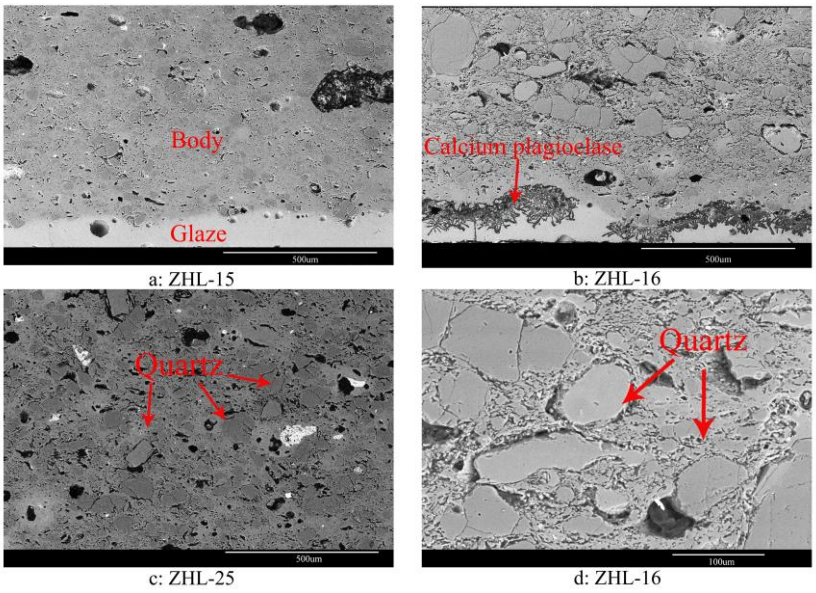


Fig.3. BSE image of typical samples by SEM

3.2 The features of bodies

The bulk compositions of the Zhaili celadon pastes are shown in the Table 1. The total compositions of SiO_2 and Al_2O_3 in the body ranges from 89.37 to 95.51wt.%, with an average of 93.89wt.%, and the Zhaili celadon bodies shows a feature of relatively high contents of Al_2O_3 (19.49wt.%-29.25wt.%) and low SiO_2 (64.38-75.36wt.%), which conform with the kaolin clay tradition for the northern stoneware and porcelain production (Zhou et al., 1960, Guo et al., 1980, Guo 1984). The balance consists of fluxing oxides, which are CaO, MgO, Na_2O, K_2O, FeO. Almost all samples have low contents of CaO (<1wt.%), MgO (<0.5wt.%) and Na_2O (<0.5wt.%), but 1.23-2.39wt.% contents of K_2O. Besides, high contents of Fe_2O_3 and TiO_2 are obviously characteristics of Zhaili celadon body, which gives the body a deep color. In specific, the Fe_2O_3 content ranges from 1.17 wt.% to 2.63wt.% and averages 1.72wt.%, while the TiO_2 content in a range of 0.66-4.56wt, with an average of

1.44wt.%.

Table 1 Bulk compositions of body determined by SEM-EDS (wt.%)

Samples No.	SiO_2	Al_2O_3	CaO	Na_2O	MgO	K_2O	TiO_2	Fe_2O_3
ZHL-1	68.73	24.45	0.88	0.31	0.45	1.84	1.70	1.63
ZHL-2	68.16	24.40	0.82	0.26	0.47	1.85	2.17	1.87
ZHL-3	69.93	23.51	0.45	0.32	0.46	1.69	1.78	1.87
ZHL-4	70.60	24.18	0.68	0.26	0.47	1.36	1.09	1.36
ZHL-5	63.61	25.73	0.98	0.32	0.49	1.77	4.59	2.52
ZHL-6	68.68	25.61	0.47	0.17	0.44	2.05	1.48	1.04
ZHL-7	69.36	23.74	1.06	0.24	0.26	1.28	1.99	2.03
ZHL-8	69.98	24.19	0.45	0.21	0.39	1.51	1.48	1.78
ZHL-9	70.43	23.69	0.52	0.24	0.35	1.23	1.31	2.21
ZHL-10	65.11	27.74	0.79	0.25	0.36	1.55	1.61	2.56
ZHL-11	69.81	24.38	0.74	0.26	0.41	1.82	1.30	1.25
ZHL-12	67.26	26.60	0.47	0.40	0.46	2.01	1.42	1.38
ZHL-13	66.66	27.17	0.50	0.28	0.52	1.61	1.74	1.48
ZHL-14	66.64	26.97	0.56	0.38	0.54	1.76	1.39	1.76
ZHL-15	73.36	21.84	0.32	0.49	0.18	1.75	0.76	1.08
ZHL-16	67.46	27.42	0.39	0.16	0.10	1.66	0.88	1.93
ZHL-17	64.38	29.25	0.68	0.49	0.11	2.39	1.03	1.64
ZHL-18	69.85	25.46	0.27	0.22	0.3	1.59	0.84	1.48
ZHL-19	66.62	26.22	0.46	0.27	0.28	1.60	1.68	2.63
ZHL-20	65.86	28.28	0.50	0.30	0.36	2.28	0.99	1.41
ZHL-21	70.85	23.78	0.38	0.31	0.55	1.93	1.03	1.17
ZHL-22	72.27	21.62	0.58	0.23	0.58	1.60	1.12	2.01
ZHL-23	70.03	24.32	0.46	0.23	0.40	1.42	1.30	1.83
ZHL-24	74.96	19.49	0.16	0.52	0.10	1.66	1.75	1.23
ZHL-25	75.36	20.15	0.49	0.49	0.15	1.25	0.66	1.47
ZHL-26	70.43	23.48	0.51	0.32	0.47	1.56	1.37	1.84
ZHL-27	68.33	24.59	0.67	0.25	0.58	1.90	1.38	2.28
ZHL-28	71.14	23.71	0.44	0.20	0.37	1.30	1.02	1.80
ZHL-29	68.17	25.67	0.55	0.20	0.50	1.89	1.42	1.58
ZHL-30	69.39	25.71	0.35	0.34	0.14	1.60	0.92	1.55

Due to the similarity in the main elemental compositions of the analyzed Zhaili celadon bodies, three samples were randomly selected for XRD testing to further discuss their mineral composition. The XRD results shown in Fig.4 indicate that all the Zhaili celadon bodies have similar mineral components, which consist of quartz, mullite and cristobalite. Wei et al (2005) indicate that the mullite will crystallize when the kaolin stone is heated to 1100℃， and extensive grains of mullite and few grains of cristobalite will crystallize when it heated to 1200-1300℃. Therefore, the present of mullite and cristobalite in the bodies indicates that Zhaili celadons were fired at least 1200℃, even the celadon samples (ZHL-2 and ZHL-3) produced in the initiation stage of Zhaili kiln could reach the temperature. Combined with the barely sintered body observed in the BSE image, we infer that the firing temperature of Zhaili celadon might be above 1200℃ but hard to reach to 1300℃. The low sintered body might be ascribed to the short heat preservation.

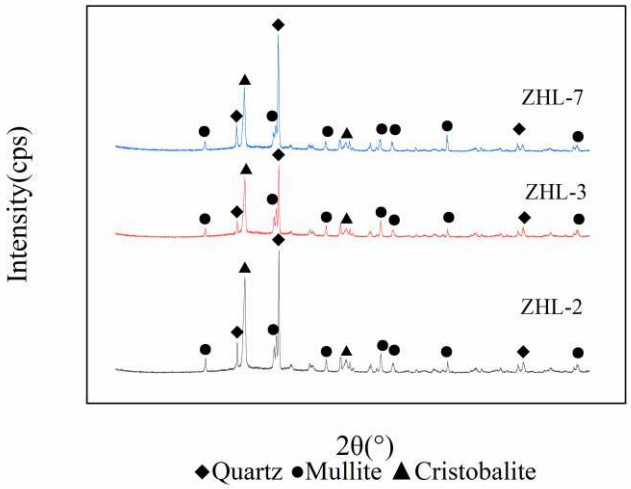


Fig.4. Mineral component of typical celadon samples

3.3 The features of glazes

The major compositions of glazes are presented in Table 2. Most samples are similar in elemental compositions, the major compositions SiO_2 plus Al_2O_3 range from 63.02-82.79 wt.%, with 51.04-61.64 wt.% SiO_2 and 11.98-23.31 wt.% Al_2O_3, and high contents of CaO as flux range from 7.69wt.% to 25.74 wt.%. As shown in Fig.5a, CaO contents have a negative relationship with the concentrations of SiO_2 and Al_2O_3 in glazes. Three early Zhaili samples distribute on the low flux and high siliceous area, averaging 9.97 wt.% CaO and 81.25 wt.% SiO_2 plus Al_2O_3, while the others have opposite pattern, at around 16.86 wt.% CaO and 76.04 wt.% siliceous contents. In addition, Fig.5b indicates all Zhaili glazes are characterized by high concentrations of Fe_2O_3 and TiO_2. The Fe_2O_3 contents of Zhaili glazes are clustered in a region of 1.84 wt.%-4.82 wt.%, averaging 3.13 wt.%, which is obviously higher than the other contemporary glazes produced in the Xing kiln, Ding kiln (Cui et al, 2012, Lu et al., 2012, Huang et al., 2020, Huang et al., 2023). The TiO_2 of Zhaili celadon are also in high contents, ranging from 0.72 wt.% to 1.60 wt.%, with an average of 1.00 wt.%.

Table 2 Bulk compositions of glaze determined by SEM-EDS (wt.%)

样品编号	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	MnO	TiO_2	Fe_2O_3
ZHL-1	61.64	21.15	7.69	1.54	0.77	2.38	0.29	0.00	1.45	3.09
ZHL-2	57.61	23.31	10.58	1.19	0.96	3.01	0.28	0.01	1.18	1.87
ZHL-3	57.72	22.30	11.64	0.92	0.87	2.34	0.23	0.00	1.16	2.82
ZHL-4	54.82	15.31	17.56	2.08	0.97	1.70	0.46	0.13	1.25	2.64
ZHL-5	56.76	16.62	15.23	2.08	0.63	2.39	0.42	0.17	1.60	4.10
ZHL-6	58.17	18.59	13.43	1.71	0.78	3.20	0.14	0.11	1.35	2.53
ZHL-7	58.78	14.48	16.57	2.25	0.85	1.49	0.82	0.11	1.01	3.64
ZHL-8	58.27	17.67	14.90	1.77	0.61	1.92	0.29	0.08	1.22	3.28
ZHL-9	59.69	16.77	13.60	1.77	0.85	3.03	0.32	0.07	1.01	2.89
ZHL-10	59.22	16.52	12.59	1.98	0.96	4.37	0.19	0.12	1.12	2.92
ZHL-11	58.23	11.97	20.88	2.03	1.22	2.66	0.80	0.00	0.37	1.84
ZHL-12	56.47	18.83	13.17	1.70	0.74	2.46	0.38	0.05	1.33	2.73
ZHL-13	53.03	15.84	21.65	2.30	0.80	2.33	0.54	0.09	0.94	2.47
ZHL-14	51.46	12.81	19.92	3.54	1.12	2.60	0.92	0.13	1.06	3.25
ZHL-15	56.02	14.42	16.80	2.63	0.94	2.16	2.82	0.13	0.72	3.37
ZHL-16	55.79	14.14	15.72	2.77	0.72	1.84	3.29	0.08	0.86	4.82
ZHL-18	56.43	15.59	17.63	2.22	0.64	2.36	1.15	0.13	0.79	3.08
ZHL-19	58.34	16.14	16.23	1.98	0.58	2.22	0.32	0.14	0.91	3.16
ZHL-20	56.68	14.82	17.86	2.58	0.39	1.87	1.68	0.13	0.71	3.31
ZHL-21	51.79	12.41	24.43	2.83	1.26	2.54	1.01	0.16	0.82	2.75
ZHL-22	60.90	18.17	11.25	1.92	0.83	2.40	0.45	0.14	0.98	2.96

ZHL-23	60.38	17.32	12.61	2.18	0.29	1.97	0.61	0.13	1.17	3.34
ZHL-24	57.82	17.29	13.37	2.03	0.82	2.12	2.97	0.06	0.90	2.63
ZHL-25	54.83	14.34	19.13	2.63	0.87	1.88	2.34	0.11	0.73	3.26
ZHL-26	54.36	14.85	20.68	2.51	0.63	2.11	0.60	0.11	0.96	3.20
ZHL-27	56.14	13.94	15.18	2.31	1.35	5.58	0.61	0.09	0.89	3.91
ZHL-28	55.00	15.55	17.57	2.31	1.10	2.62	0.70	0.10	1.07	3.98
ZHL-29	51.04	11.98	25.74	2.71	1.11	2.01	0.90	0.12	0.79	3.58
ZHL-30	57.33	16.71	14.69	2.59	0.83	1.84	1.68	0.06	0.81	3.48

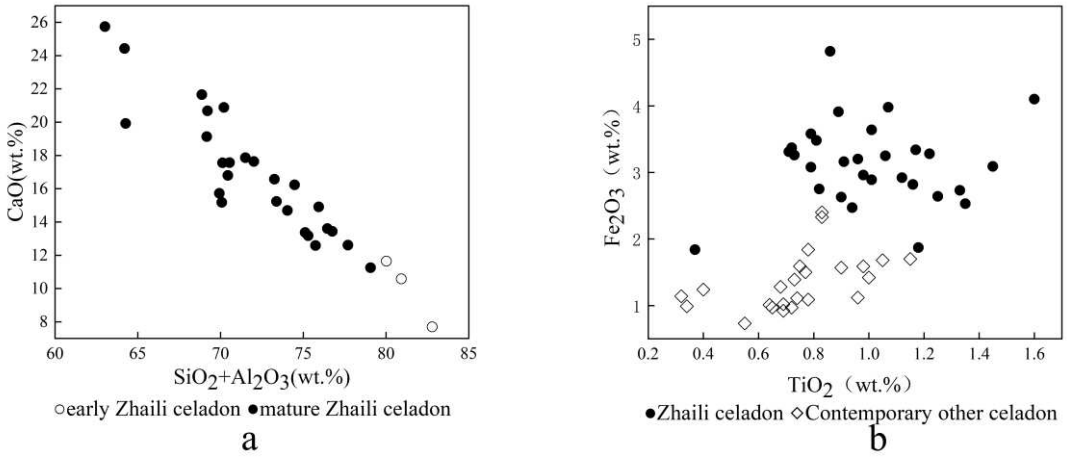


Fig.5. Scattered plot of Zhaili celadon glazes. a: Concentrations of SiO_2 plus Al_2O_3 versus CaO in the celadon glaze. b: Concentration of TiO_2 and Fe_2O_3 in the Zhaili celadon glaze and other contemporary celadon glazes (Huang et al., 2020)

4. Discussion

4.1 Body material of Zhaili celadon

Song et al. (1986) indicates that the raw material of Zhaili celadon body paste was a kaolin clay associate with the coal layer, which complies with the chemical compositions in this study. To further study the features of the body clay of Zhaili celadon, we analyzed the stoneware and porcelain samples from other kilns of the Tang to Jin dynasty (618-1234 AD) in Zibo city (so called Zibo kilns) and collected the data of common kaolin clay (Li 2005:28) in Zibo city for comparison (Seen in Fig.6a, the chemical composition of ceramic samples from Zibo kilns and kaolin clay can be seen in Supplementary Table 1). As seen in Fig.6a, the bodies of Zhaili celadon have relatively low contents of Al_2O_3 and high SiO_2. In specific, the Al_2O_3/SiO_2 ratio of Zhaili body is obviously lower than the bodies from Zibo kilns and local common kaolin clay. As calculated, the Al_2O_3/SiO_2 ratios of Zhaili celadon is around 1:2.79, which is evidently lower than those found in celadon wares made in later Zibo kilns and local common kaolin clay, around 1:1.81 and 1:1.24 respectively. Huang et al. (2020) also suggested that Zhaili celadon bodies also have relatively low Al_2O_3/SiO_2 compared to the contemporary counterparts produced at other northern kilns site.

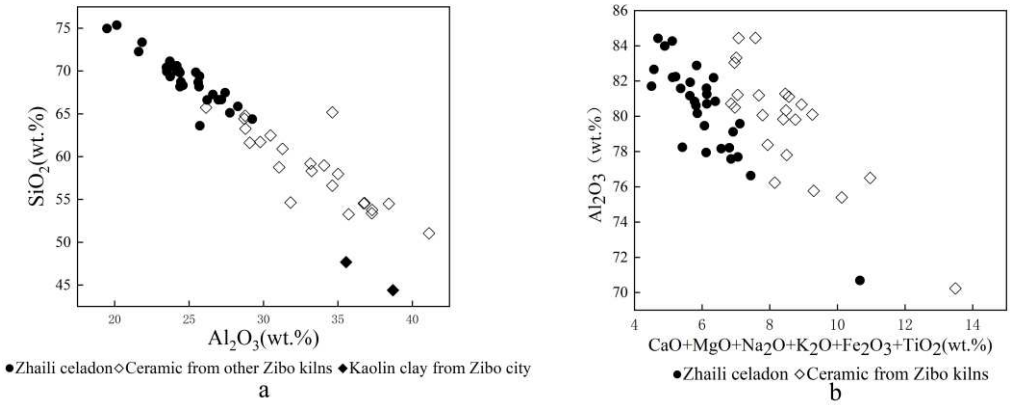


Fig.6. Scattered plots of bodies of Zhaili and Zibo kilns

a: Concentrations of Al_2O_3 versus SiO_2 in ceramic body in this study and published early data (Li 2005:28).

The data of ceramics from Zibo kilns was shown in Supplementary Table1.

b: Normalized concentrations of ceramic body in this study

Table 3 Normalized composition of bodies from Zhaili and Zibo kilns (wt.%)

Body	Al_2O_3	CaO	Na_2O	MgO	K_2O	TiO_2	Fe_2O_3
Zhaili kiln	80.35	1.78	0.98	5.48	4.61	5.57	19.69
Zibo Kilns	79.67	2.67	1.55	4.12	4.63	6.10	20.33

The low Al_2O_3/SiO_2 ratios and low contents of potassic and calcium oxide, indicates that the potters in Zhaili kiln might choose a special clay with relatively low Al_2O_3 and high SiO_2 or add additional quartz into the body paste. However, as shown in Fig.3c, 3d, the grains of quartz are coarse and angular which can interpret as a material, such as crushed quartz pebbles or milled sand (Huang et al., 2023), thus we prefer the deduction that additional quartz was added.

To determine this deduction, we remove the SiO_2 content from the compositions of Zhaili bodies and Zibo kilns bodies and normalized to 100 wt.% (the results are shown in Table 4 and Fig.6b). As shown in Table 4 and Fig.6b, the samples from Zhaili kiln and Zibo kilns show a relatively similar elemental composition except SiO_2. It is indicated that the body of Zhaili celadon was made using similar kaolin clay to the body of Zibo kilns, except for the addition quartz.

The direct result of adding additional quartz is reduce the Al_2O_3/SiO_2 ratio, while the decrease of Al_2O_3 content could reduce the firing temperature (Lu 2005:33, Li 2005:27), thus we may infer that the quartz was added to reduce the fire temperature of body. The merely sintered bodies shown in Fig.3c and 3d present the primitiveness of firing techniques in Zhaili kiln, which support the conclusion. Therefore, the purpose of adding additional quartz to the body by the potter of Zhaili kiln may be to adapt to the low firing temperature of the primitive kiln.

4.2 Glaze recipe of Zhaili celadon

Traditional Chinese celadon glaze was made using siliceous material and calcium or calcium-alkali flux, as well as Zhaili Celadon. The high contents of CaO (around 16.15wt.%) and low contents of K_2O (around 2.46wt.%) of Zhaili glazes indicates that most of them were made with high lime flux, while the high contents of P_2O_5 (around 0.94wt.%) and MgO (around 2.17wt.%) in glaze indicate the calcium

flux was vegetal ash.

The clay used to make body paste was usually also added into glaze as siliceous material. To determine the siliceous material in Zhaili body, the method, proposed by Hurst et al., (1996) and Tite et al. (1998), has been widely used in determining the constituent of lead glaze is modified to the calcium glaze. The modified method was proposed by Huang et al. (2020) and had been performed on the research of celadon. Based on the approach, if the glaze was made using the body clay and ash flux, while the ash has minor clay components like SiO_2, Al_2O_3, Fe_2O_3 and TiO_2, then the ratio of clay components should be similar with in both body and glaze. We calculated the Al_2O_3/SiO_2, Fe_2O_3/Al_2O_3 and TiO_2/Fe_2O_3 ratios in both body and glaze of the celadons from Zhaili and Zibo kilns and plotted into Fig.7.

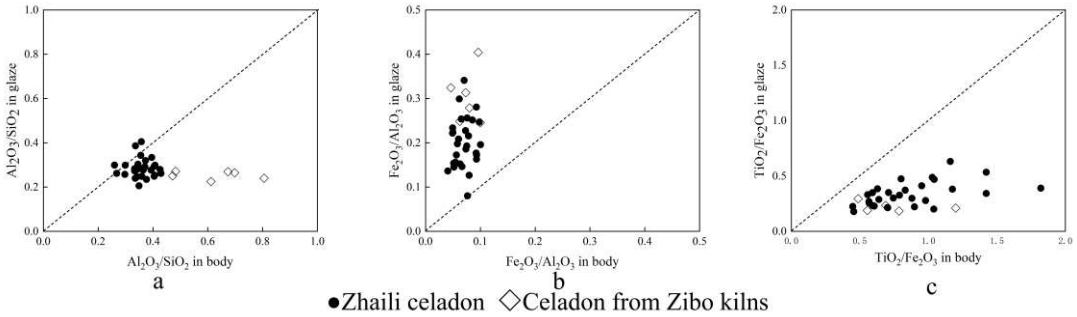


Fig.7. Comparison of clay component ratio of bodies from Zhaili and Zibo kilns with glazes, the 1:1 line is indicated

As shown in Fig.7, barely the samples from both the Zhaili and Zibo kilns departure from the 1:1 line, indicating that the components of raw material in glaze are different from the body clay. The distribution of samples in Fig.7 suggests that there are more contents of SiO_2 and Fe_2O_3 in glazes compared to the bodies. The lime in glaze derives from vegetal ash, which cannot provide neither the SiO_2 or Fe_2O_3, while the body clay cannot fulfill such high contents in glaze as well, therefore, there are another material into the glaze. In addition, as discussed, additional quartz was added into the body paste of Zhaili celadon, however, the Fig.7a indicates that the siliceous material in glaze still have higher contents of SiO_2 than the body clay with quartz.

Loess, a common clay in north China, at around 59.81 wt.% SiO_2, 11.88 wt.% Al_2O_3, 2.77 wt.% Fe_2O_3 (Wu et al., 1995), could meet the require of high SiO_2 and Fe_2O_3. However, the content of Al_2O_3 (11.88 wt.%) was too low in loess to conform with the Al_2O_3 content (around 16.10 wt.%) in glazes. Therefore, we infer that the siliceous component was mixed by loess and kaolin clay. To confirm the deduction, we collected the average chemical compositions of Chinese loess and normalized the clay components to 100wt.%, as well as the glazes and bodies in this study. The clay components, such as SiO_2, Al_2O_3, Fe_2O_3 and TiO_2 were compared and plotted into Fig.9. The clay components of glazes will distribute between the clay components of bodies and loess if it consists of them.

As shown in Fig.8, most glazes distribute between the loess and bodies, indicating that loess could be the additional material. Few bodies are close to the

glazes in the Fig.8a because of the additional quartz in body. In addition, some glazes seem to beyond the Fe_2O_3 contents of loess in Fig.8c, 8d, it due to the data of loess incited was an average while the Fe_2O_3 content is easy to fluctuate. Therefore, it is reliable that loess, kaolin clay (probably the body clay), and vegetal ash formed the ternary recipe of Zhaili and Zibo kilns. This conclusion conforms with early research (Huang et al., 2020). However, few samples close to the body (Fig.8a, 9b) suggest that the loess was not used in all the Zhaili glazes. The technical difference may derive from the different periods or the unstable glaze recipe.

Loess is a fusible clay used to make black glaze in the northern provinces, such as Henan, Shanxi, Shaanxi and Shandong (Wood 2011:139, Li et al., 1988: 151, Wang 2000: 142). Except high contents of SiO2, loess also has high CaO contents, average 7.79wt.% (Wu et al., 1995), indicating that it could not only fulfill the demand of siliceous components, but also provide sufficient calcium flux. The results in this research indicates that loess was used in the glaze formular of Zhaili kiln and lasted to the later Zibo kilns (at least Jin dynasty). This special formular, which is rare in the history of Chinese celadon, could be seen as the feature of the celadon produced in the ancient Zibo city, while Zhaili kiln, the earliest celadon kiln in Zibo city, were likely to be the inventor of the recipe. Although reasons for adding loess still need further study, adding as part of calcium flux seem to be reasonable. Shandong province has widespread and abundant loess while the vegetal resource is relatively rare and vulnerable, thus the loess is more accessible and convenient compared to vegetal ash. The accessibility and convenience of loess could be the reasons of adding into glaze as both the siliceous raw material and flux.

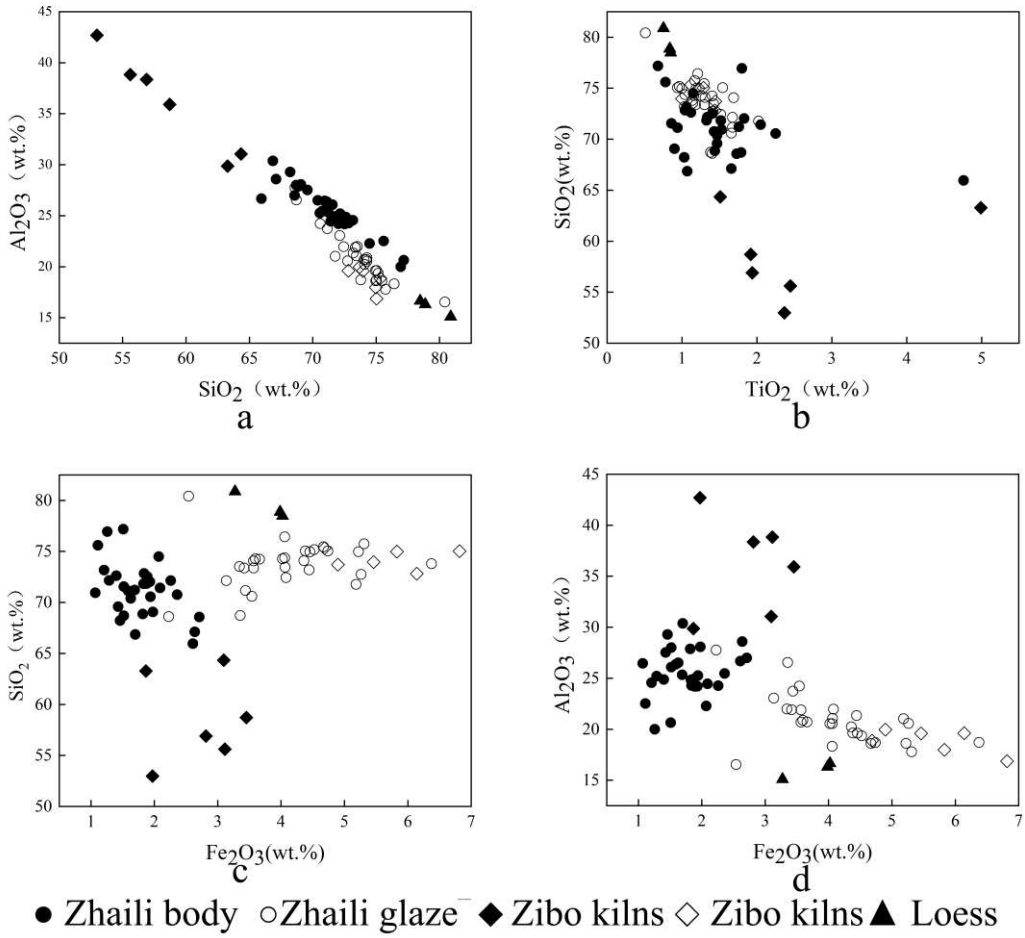


Fig.8. Comparison of clay compositions of loess with celadon bodies and glazes analyzed in this research

The high contents of P_2O_5 and MgO in glaze indicates the presence of vegetal ash in glaze formular, while the different CaO/K2O shows the diversity of vegetal ash (Fig.9). To determine the difference of vegetal ash, we normalized the ash-related compositions in the glaze to 100wt.% and collected the compositions of possible vegetal ash, as well as loess, and normalized in the same way (Table 4).

Table 4 Normalized ash composition of Zhaili celadon glaze (Table 2) and northern Chinese vegetal ashes (Li, 1998:100-102, Wu et al., 1995). (wt.%)

Glazes	CaO	MgO	K2O	P2O5	MnO
Group 1	75.14	10.16	9.08	5.16	0.47
Group 2	69.94	9.67	18.18	1.86	0.35
Ashes	CaO	MgO	K2O	P2O5	MnO
Loess	61.87	18.67	17.87	1.11	0.48
Poplar	68.97	3.30	13.94	13.79	0.00
Pine	67.75	7.59	15.31	4.67	4.67
Straw	34.14	10.62	34.84	16.24	4.16

As shown in Table 4, the glazes are divided into two groups based upon the difference of CaO and K_2O. Group 1 is consisted of the glazes with 65.06 wt.%-81.77 wt.% CaO and 6.39 wt.%- 11.78 wt.% K_2O, while glazes from Group 2 have 63.86 wt.%-76.93 wt.% CaO and 13.85 wt.%-20.00 wt.% K_2O. The obvious difference can ascribe to the diversity of vegetal ash used in the glaze formular. As shown in Table 4,

the wood ash, like poplar and pine, usually has relatively high contents of CaO and low K_2O, while the grass ash, like straw, has opposite pattern. Therefore, we may infer that the glazes in group 1 are fluxed by loess and wood ash while the group 2 are fluxed by loess and grass ash.

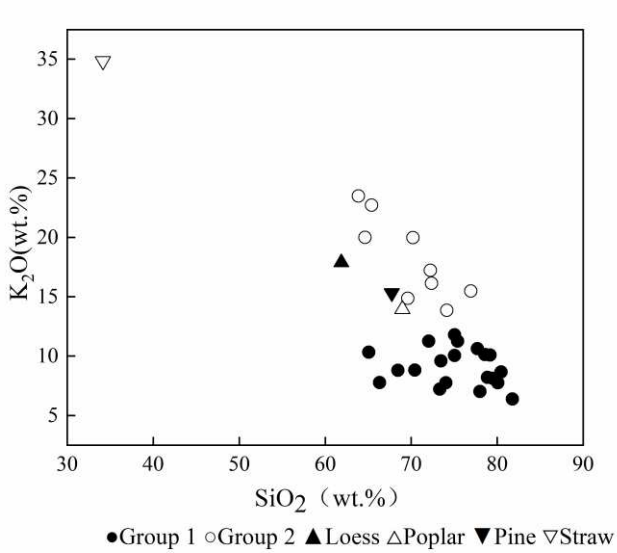


Fig.9. Normalized concentration of CaO versus K2O in glazes of this study and Northern Chinese vegetal ashes (Li 1998: 100-102; Wu et al., 1995)

4.3 The motivations for the Zhaili celadon

Celadon is a stoneware covered by a green glaze layer, which is fluxed by calcareous materials and colored by ferrous materials. The history of southern celadon could date back to 1500 BCE, however, the north of China had not produced celadon until the late sixth century. The geological inaccessibility and high fire-resistance are the main reasons (Wood, 2011: P108-109). So why did the Zhaili kiln become one of the earliest celadon kilns in the north China?

The production of white pottery in Shandong province could date back to the the late of Neolithic Age (Luan 2010; Li 1998:32; The Chinese ceramic society 1982: 38), which indicated that the people in Shandong province began to exploit kaolin clay since then. After a long-term interruption, the white pottery reproduced in Western H an and lasted to at least Western Jin dynasty in Shandong province. The long-term history of using kaolin clay showed the advanced exploitation technology of kaolin clay, which indicated that the kaolin clay was relatively available in Shandong province.

Although the kaolin clay was relatively available, the high-fire resistance still prevented the emergence of northern celadon until late of the sixth century. In this study, we find that additional quartz was added into the body paste of Zhaili celadon. The additional quartz decreased the ratio of Al_2O_3 in body, which reduced the fire-resistance of kaolin clay. This approach solved the difficulties of the high fire-resistance of kaolin clay and produced Zhaili celadon successfully.

The improvement of celadon technology was the main reason of the innovation of Zhaili celadon. The development of technology is complicate, while we may understand the inherent motivation through the historical and political background.

Sixth century was a divisive era in the history of China, so called the Northern and Southern Dynasties period. Long-term disruption facilitated the migration of population, as well as the communication of ceramic technology objectively. Zhang (2016) indicated that the frequent floods and famines in the Yangtze River Delta, a production center of southern celadon, may compel local potters to move to the Shandong province. The potters who became refugees were likely to be recruited into the manorial estate of great Clan Landowners, like bankrupt farmers.



Fig.10 Kiln pillars with potters' name found in Zhaili and Hejiadian kiln

a: Kiln pillars from Zhaili kiln (The Commission of Zibo Ceramic History et al., 1984)

b: Kiln pillars from Hejiadian(Shandong Institute of Cultural Relics and Archaeology., 2017)

Zhaili kiln seem to be the properties of the manorial estate owned by the clan great Landowners. The deduction is supported by the archaeological evidence. The investigation of Zhaili kiln during 1976-1977 found some kiln pillars (Fig.10a), a tool used during the firing procedure, carved with names of potters (The commission of Zibo ceramic history et al., 1984). The same inscription was also seen at kiln pillars (Fig.10b) in the Hejiadian kiln, a contemporary kiln with Zhaili kiln in Qufu, Shandong province (Shandong Institute of Cultural Relics and Archaeology et al., 2017). The sign left on the tool rather than products was interpreted as a managing measure of potters, and this management lasted to nearly the twentieth century in China. It indicated that the potters were under the supervision of their employers, excluding the possibility that Zhaili kiln was a union of family workshop. Combined with the historical background, it is reliable that Zhaili kiln was the properties of the Great clan Landowners. The handcrafts of great Clan were characteristics by adequate fund and advanced technology, which provide the material condition for the invention of Zhaili celadon.

The political influence was another inherent motivation. The Clan Landowners in Shandong province was deeply influenced by the Southern Dynasties in culture, not only because of the close distance in geography but also the special political background. Before occupied by Northern Wei dynasties, ruled by nomadic Xianbei Turks, the Shandong province was under the reign of the Southern dynasties, ruled by Han nationality, for nearly sixty years. Therefore, the local great Clans prefer the culture of Southern dynasties than the Northern Wei founded by foreign nomad. The burials research (Ni, 2015) indicated that the cultural factors of Southern dynasties

were seen at the burials of great Clans in Shandong province, showed a discontent with foreign rulers.

Celadon as a typical southern ware, was also affected by Shandong Clans. Typical southern celadons were found in the local nobles' tombs, such as the lion-shaped water pot unearthed from Cui You's (464-511 CE) tomb (Zibo Museum et al., 1985), the tiger-shaped urine pot, dragon tripod, box and lamp from Fang Yue's (472-541 CE) tomb (Shandong Museum., 1975). The production of traditional southern style vessels in Shandong kilns, like the bowl with lotus pattern and the high-foot plate, also reflects the preference for Southern celadons. However, southern celadons are relatively rare in quantity and only found in the high-level nobles' tombs. Therefore, the contradiction of the poor import of southern celadons and the preference of nobles was likely to facilitate the attempt of producing celadon in local kilns. In addition, as the Landowners industry, satisfying the pursuit for luxury of landowners was one of the main purposes of Zhaili kiln (Wei., 2004: 30), which drove the invention of northern celadon as well.

Based upon the technical development, special historical background and political situation, potters in Zhaili kiln produced celadon successfully eventually. The celadon body was made by kaolin clay and additional quartz, covered with glaze fluxed by vegetal ash and loess. Compared to contemporary celadon and other Zibo ceramic, the technology of Zhaili celadon was unique, thus we would infer it may originate individually in terms of the southern vegetal-ash glaze formular and local raw material. Using loess and vegetal ash to make celadon glaze was a characteristic of Zhaili kiln, and the special formular lasted to the Jin dynasty (1115-1234) at least in kilns from Zibo city. The reasons of adding loess still need further study, we inter that the loess is added as part of flux because of its accessibility and cheapness.

However, the application of loess in celadon glazes has the merit of cheapness and convenience, but it limited the improvement of celadon quality and development of the celadon technology because of its high content of Fe_2O_3. As recorded, the color of Zhaili celadon turned to be brown even black after Tang dynasty (The commission of Zibo ceramic history et al., 1984). This transition reflected the improvement of Fe_2O_3 ratio in glaze. As discussed, the loess brought more Fe_2O_3 contents into Zhaili glaze compared to body clay and vegetal ash, thus we can interpret the improvement of Fe_2O_3 as the rise of loess proportion in glaze. The reasons for the transition still need further study, but the influence of this transition is obvious that the mainstream product in Zibo kilns changed from celadon to black glaze ware since then. In specific, Cicun kiln, nearly 25 kilometers away from Zhaili kiln, started from the mid Tang dynasty when the Zhaili kiln was declining. The main product of Cicun kiln in Tang dynasty is black glaze ware, which probably effected by the loess and vegetal ash formular glaze of Zhaili kiln. Celadon had never become the main product again in ancient Zibo kilns since then.

Nevertheless, after short-term firing in Tang dynasty, Zhaili kiln faded away gradually. The reasons for the disappear of Zhaili kiln still need further study. It may relate to the exhaust of raw materials and fuel (firewood) brought by long-term firing.

Conclusion

The research indicates that, as one of the earliest celadon kilns in north China, the celadon manufacturing technology of Zhaili kiln was relatively independent. Additional quartz was added into the body pastes to adapting the low fire-temperature of primitive kiln. The glaze was mixed by body clay, vegetal ash and loess. Loess was added into glaze as flux because of its accessibility and cheapness in Shandong province. However, the high Fe_2O_3 of loess also limited the development of the celadon technology, which turned the mainstream product in Zibo city change from celadon to black glaze ware. In addition, the special historical background of divisive era and the preference of Shandong Clans influenced by politics provide the inherent motivation for the development of celadon technology.

Author contributions

C. Geng: Investigation, Resources, Formal analysis, Writing – original draft, Data curation. **J.Y. Shen:** Conceptualization, Methodology, Data curation, Writing – review & editing, Project administration, Funding acquisition. **J.F. Lang:** Resources, Methodology, Project administration, Writing – review & editing. **Z.L. Chen:** Resources, Writing – review & editing. **C. Lu:** Resources, Visualization. **W. Liu:** Formal analysis

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Ethics declarations

Competing interests The authors declare no competing interests.

Data availability The authors declare that the data supporting the findings of this study are available within the article and its supplementary information files.

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