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Scientific studies on pottery and pro-porcelain from group of graves in Henglingshan, Guangdong Province

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The findings of the Henglingshan group of graves, Guangdong Province, were appraised as one of the ten major archaeological excavations in 2000. The pottery and proto-porcelain samples excavated from the group of graves in Henglingshan are very important for studying the development history of Guangdong ceramics. In this paper, the chemical compositions, micro-structure and physical properties of the samples were systematically analyzed. The results were subjected to multivariate statistical analysis. Different compositional patterns were found for specimens from different periods. The reasons for these variations were discussed. In addition, compared with the pottery and proto-porcelain samples from different production sites in other provinces of China, the obvious regional characters and unique law of the development for ancient ceramics of Guangdong were also discussed.

energy dispersive X-ray fluorescence analysis, pottery, proto-porcelain, correspondence analysis

1 Introduction

Guangdong Henglingshan group of graves were excavated by Archaeology Institute of Guangdong Province in 2000. This excavation covered an area of about 8500 m^2 and revealed 332 tombs (including 302 Pre-Qin tombs). The number and size of the tombs exceeded any archaeological findings of Pre-Qin tombs in Guangdong province before. The findings of the Henglingshan group of graves, Guangdong Province, were appraised as one of the ten major archaeological excavations in 2000. Besides bronze wares, stone implements and jades, a lot of pottery and proto-porcelain specimens were unearthed. Compared with that in the Neolithic Age, the preparation of pottery during this period had become a specialized handicraft separated from agriculture and other handicrafts. The discoveries had great significance for the study of science and technology development in ancient Dongjiang River Basin, especially for the history of ceramics in Guangdong Province. With the cooperation of Archaeology Institute of Guangdong Province, some pottery, proto-porcelain samples excavated from the tombs during different periods and related clay specimens were collected. The chemical compositions, micro-structure and physical properties of the samples were systematically analyzed. Some new findings are reported.

2 Experimental

2.1 Chemical composition

The EDXRF spectrometer used was an EDAX EAGLE-3, with excitation provided by an target X-Ray tube and using an Si(Li) detector. Tables 1, 2 and 3 list the results.

2.2 Microstructure and physical properties

The phase structure, firing temperature, physical properties of these ceramics samples were analyzed by an X-ray diffractometer (D/max 2550V) and thermal dila-

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Table 1 Major and minor element compositions of pottery bodies from the group of graves in Henglingshan, Guangdong province (wt%)

Code [a)]	Stage [b)]	Name	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	R_xO_y/Al_2O_3 [c)]	SiO_2/Al_2O_3
h1	I	Grey pottery	0.27	1.02	44.04	43.02	0.05	0.12	1.32	9.27	0.25	1.66
h2	I	Grey pottery	0.42	0.53	31.06	59.02	4.98	0.09	0.30	2.27	0.30	3.23
h3	I	Grey pottery	0.35	0.90	35.10	56.60	2.53	0.10	0.69	2.31	0.23	2.74
h4	I	Grey pottery	0.41	0.49	28.27	64.32	2.70	0.14	0.51	3.03	0.27	3.87
h5	I	Grey pottery	0.86	1.69	44.53	38.48	0.10	0.20	1.45	10.90	0.34	1.47
h6	II	Grey pottery	0.44	1.35	31.54	60.23	0.66	0.24	0.63	4.39	0.28	3.25
h7	II	Grey pottery	0.21	0.78	32.27	57.13	0.84	0.10	0.68	6.12	0.25	3.01
h8	II	Grey pottery	0.73	0.94	30.22	58.47	2.42	0.23	0.69	5.04	0.36	3.29
h9	II	Grey pottery	0.21	0.77	30.48	58.21	1.30	0.11	0.69	6.95	0.30	3.25
h10	II	Grey pottery	0.21	0.70	29.62	62.21	1.13	0.11	0.97	3.39	0.23	3.57
h11	II	Grey pottery	0.22	0.41	32.16	60.02	0.88	0.15	0.84	4.22	0.20	3.17
h12	III	Grey pottery	0.65	0.85	42.66	50.34	0.07	0.14	1.21	4.59	0.19	2.01
h13	III	Grey pottery	0.21	0.02	28.89	60.81	3.54	0.24	0.56	4.06	0.28	3.58
h14	III	Grey pottery	0.46	0.86	29.76	55.78	1.82	0.37	0.59	8.15	0.39	3.19
h15	III	Brown pottery	0.63	0.86	24.54	64.22	2.00	0.42	0.59	5.35	0.42	4.45
h16	III	Stoneware	0.21	0.37	28.01	61.01	1.37	0.09	0.64	6.90	0.29	3.70
h17	III	Stoneware	0.20	0.88	24.24	67.22	1.79	0.07	0.57	3.71	0.32	4.71
h18	III	Grey pottery	0.20	1.02	29.57	60.11	1.80	0.28	0.71	4.65	0.31	3.46
h19	III	Stoneware	0.21	0.51	29.89	57.22	0.85	0.11	0.78	8.97	0.32	3.25
h20	III	Stoneware	0.20	0.71	27.85	62.31	1.71	0.16	0.77	4.49	0.29	3.80
h27	IV	Stoneware	0.44	0.64	29.99	60.76	1.30	0.16	0.71	4.74	0.27	3.44
h29	IVh	Orange pottery	0.20	1.01	37.45	52.29	0.28	0.21	0.83	6.24	0.23	2.37
h30	IV	Stoneware	0.20	0.83	26.34	60.13	1.40	0.10	0.57	8.66	0.39	3.88
h31	IV	Stoneware	0.20	0.43	22.24	68.30	1.49	0.11	0.64	5.25	0.33	5.22
h32	IV	Stoneware	0.34	0.67	25.34	65.83	1.84	0.23	0.62	3.69	0.31	4.42
h33	IV	Stoneware	0.29	0.82	28.15	62.24	1.97	0.12	0.73	4.07	0.30	3.76
h34	IV	Stoneware	0.21	0.53	24.32	64.35	1.64	0.15	0.65	7.40	0.38	4.50
h35	IV	Stoneware	0.36	0.63	20.25	71.38	1.64	0.12	0.49	3.73	0.36	5.99
h36	IV	Stoneware	0.20	0.68	28.58	62.91	1.62	0.24	0.69	3.81	0.27	3.74
h43	unrevealed	Faience	0.22	0.75	24.67	66.67	0.28	0.15	1.19	4.67	0.30	4.59

a) Pottery and porcelain samples from group of graves in Henglingshan, Boluo county, Guangdong province.

b) I: during the Shan-Zhou dynasties; II: early Western-Zhou; III: mid-advanced Western-Zhou; IV: Spring and Autumn Period.

c) R_xO_y/Al_2O_3, SiO_2/Al_2O_3, mole ratio.

Table 2 Major and minor element compositions of proto-procelain bodies from Henglingshan, Meihuadun, Raopin and Wubeiling, Guangdong province (wt%)

Code [a)]	Origin	Name	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	SiO_2/Al_2O_3
h21	Henglingshan	Proto-porcelain	0.37	0.49	26.11	67.12	0.76	0.06	1.05	2.62	4.37
h22	Henglingshan	Proto-porcelain	0.30	0.72	31.02	62.47	1.18	0.08	0.69	2.28	3.42
h23	Henglingshan	Proto-porcelain	0.30	0.65	40.48	52.32	1.02	0.04	0.83	2.89	2.20
h24	Henglingshan	Proto-porcelain	0.37	0.53	27.31	64.95	1.66	0.24	0.77	2.99	4.04
h25	Henglingshan	Proto-porcelain	0.21	0.61	24.65	67.98	1.85	0.16	0.70	2.79	4.69
h26	Henglingshan	Proto-porcelain	0.21	0.43	24.79	68.06	1.05	0.08	0.77	3.12	4.67
h37	Henglingshan	Proto-porcelain	0.30	0.45	23.69	69.09	2.76	0.04	0.70	1.77	4.96
h38	Henglingshan	Proto-porcelain	0.45	0.55	28.50	64.36	1.28	0.14	0.83	2.69	3.84
h39	Henglingshan	Proto-porcelain	0.20	0.54	21.76	70.56	2.66	0.06	0.72	1.95	5.51
h40	Henglingshan	Proto-porcelain	0.22	0.99	26.74	65.66	2.41	0.13	0.89	1.86	4.17
h41	Henglingshan	Proto-porcelain	0.37	0.57	23.85	67.07	2.52	0.23	0.55	3.37	4.78
h42	Henglingshan	Proto-porcelain	0.20	0.37	23.16	70.07	1.64	0.11	0.73	2.59	5.14
m1	Meihuadun	Proto-porcelain	0.56	0.34	29.20	61.77	3.05	1.35	1.45	1.28	3.60
m2	Meihuadun	Proto-porcelain	0.52	0.47	24.53	70.10	1.83	0.15	0.60	2.17	4.86
m3	Meihuadun	Proto-porcelain	0.71	0.62	24.35	68.03	2.56	0.12	0.67	1.89	4.75
r1	Raopin	Proto-porcelain	0.29	0.55	29.90	63.52	1.91	0.17	0.56	1.87	3.61
r2	Raopin	Proto-porcelain	0.23	0.54	25.41	65.23	1.39	1.13	1.13	3.28	4.36
r3	Raopin	Proto-porcelain	0.17	0.37	26.39	66.47	0.76	0.29	1.45	3.05	4.28
w1	Wubeiling	Proto-porcelain	1.11	0.73	18.88	73.17	2.52	0.46	0.55	2.15	6.59
w2	Wubeiling	Proto-porcelain	0.61	0.6	19.56	72.95	2.13	0.34	0.67	2.46	6.34
w3	Wubeiling	Proto-porcelain	0.64	0.83	17.27	74.78	2.53	0.5	0.5	2.45	7.36
s1	Meihuadun	Soil sample	0.52	1.97	23.64	68.49	2.07	0.36	0.44	1.39	4.93
s2	Meihuadun	Soil sample	0.67	0.43	30.98	61.21	1.31	0.13	0.43	3.57	3.36
s3	Meihuadun	Soil sample	0.52	0.81	28.71	63.39	2.13	0.22	0.56	2.71	3.75

a) m1—m3: proto-porcelain samples from Meihuadun; r1—r3: Fubin class proto-porcelain samples from Raopin; w1—w3: proto-porcelain samples from Wubeiling; s1: collected nearby the kiln site of Meihuadun; s2: collected from the kiln site of Meihuadun; s3: singtering soil collected from Meihuadun kiln wall.

Table 3 Major and minor element compositions of proto-procelain glazes from Henglingshan, Meihuadun, Raopin and Wubeiling, Guangdong province (wt%)

Code	Origin	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	R_xO_y/Al_2O_3	SiO_2/Al_2O_3
h21-g	Henglingshan	0.53	3.18	15.41	63.94	2.28	11.23	0.48	1.73	2.18	7.05
h24-g	Henglingshan	0.50	3.42	13.82	59.80	3.06	17.18	0.35	1.73	3.31	7.36
h25-g	Henglingshan	0.55	2.76	14.91	67.17	2.48	6.97	0.55	3.54	1.76	7.66
h26-g	Henglingshan	0.54	2.65	13.82	64.62	2.02	12.99	0.35	1.70	2.54	7.95
h37-g	Henglingshan	0.55	3.24	13.05	62.19	3.96	14.63	0.32	1.24	3.17	8.10
h38-g	Henglingshan	0.59	3.74	12.92	65.83	2.14	11.27	0.32	1.93	2.71	8.67
h39-g	Henglingshan	0.52	1.78	17.01	64.10	3.47	9.79	0.40	1.70	1.68	6.41
h42-g	Henglingshan	0.75	0.30	20.91	63.63	2.64	4.43	0.72	5.66	0.83	5.17
m1-g	Meihuadun	0.70	3.98	14.22	61.33	2.42	14.19	0.32	1.84	2.91	7.33
m2-g	Meihuadun	0.69	2.14	16.15	65.72	3.66	8.41	0.43	1.79	1.71	6.92
m3-g	Meihuadun	0.50	2.67	18.19	63.92	3.63	7.58	0.46	1.90	1.49	5.97
r1-g	Raopin	0.36	1.28	16.94	62.97	2.55	6.42	0.97	6.64	1.40	6.32
r2-g	Raopin	0.91	1.41	19.94	61.88	3.65	5.06	0.93	5.14	1.14	5.28
r3-g	Raopin	0.59	1.37	18.06	62.37	3.11	5.77	0.92	5.69	1.28	5.87

tometer (NETZSCH DIL 402C). Table 4 lists the analytical results.

3 Correspondence analysis

Due to the long history and different production sites, the chemical compositions of ancient ceramics are very complicated. Correspondence analysis is a graphical display technique, with advantages over some 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[1]. 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 close together are correlated. This is of great interest in chemical analysis, where it allows new hypotheses to be formulated in archaeometry, and furthermore explains the reasons[2].

The total data for major and trace element composition for all samples were separately subjected to correspondence analysis. The first two or three principal factors (F_1, F_2 and F_3, $F_i = x_1^i A + x_2^i B + \ldots$, 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 was used to convey more statistical formation (see Figures 1—3).

Table 4 Firing temperatures and mineral compositions of some pottery and proto-porcelain samples from the group of graves in Henglingshan, Guangdong province

Code	Stage	Name	Firing temperature (℃)	Mineral compositions
h1	I	Grey pottery	—	Red clay matrix, with more α-quartz and a little α-hematite
h3	I	Grey pottery	~860	Grey clay matrix, with more drab linear micas and a little large particle quartz
h5	I	Red pottery	~870	Red clay matrix, with more α-quartz and a little α-hematite
h8	II	Grey pottery	—	Livid clay matrix, with more α-quartz, a little α-hematite and mullite
h10	II	Grey pottery	~1140	White clay matrix, with more α-quartz and α-hematite, a little mullite
h11	II	Grey pottery	~1190	Grayish white clay matrix, with certain contents of mullite and β-cristobalite, a little fine α-quartz and α-hematite
h12	III	Grey pottery	—	Grayish white clay matrix, with more α-quartz, mullite and α-hematite, a little β-cristobalite
h19	III	Stoneware	~1210	Livid clay matrix, with more α-quartz, α-hematite, mullite and β-cristobalite
h22	III	Proto-porcelain	~1220	Livid clay matrix, with more fine α-quartz, a certain contents of mullite, α-hematite and β-cristobalite
h27	IV	Stoneware	—	Livid clay matrix, with more α-quartz, a ceratain contents of mullite, α-hematite and β-cristobalite
h35	IV	Stoneware	~1250	Yellowish gray clay matrix, with more fine α-quartz, mullite and β-cristobalite, a little glass phase
h40	IV	Proto-porcelain	~1270	With more α-quartz, a certain contents of mullite and β-cristobalite, a little glass phase
h42	Unrevealed	Proto-porcelain	—	With more α-quartz and β-cristobalite, a certain content of mullite

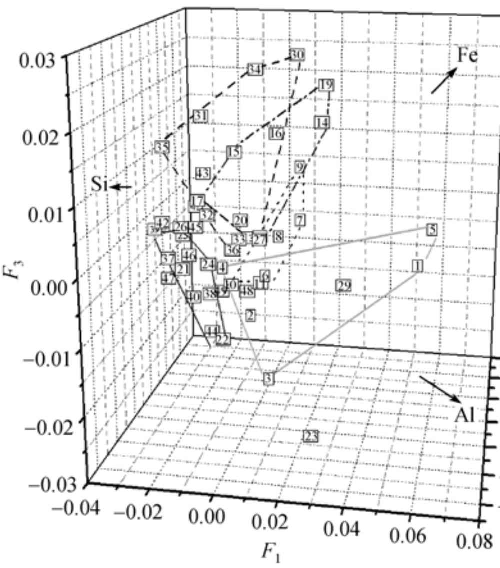

Figure 1 Plot of correspondence analysis with chemical compositions of pottery and proto-porcelain sanmples from Henglingshan of Boluo, Fubing of Raopin, and soil samples from Meihuadun of Boluo. The samples of 1—43 were unearthed from the group of graves Henglingshan. Among them, 1—5 were I stage pottery samples; 6—11, II stage pottery samples; 12—20, III stage pottery samples; 21—26, III stage proto-porcelain samples; 27—36, IVstage pottery samples; 37—40, IV stage proto-porcelain samples; 41—42, Fubin class proto-porcelain samples; 43, Fubin class faience samples; 44—46, Fubin class proto-porcelain samples unearthed from Raopin of Guangdong province; 47—49, soil samples from Meihuadun.

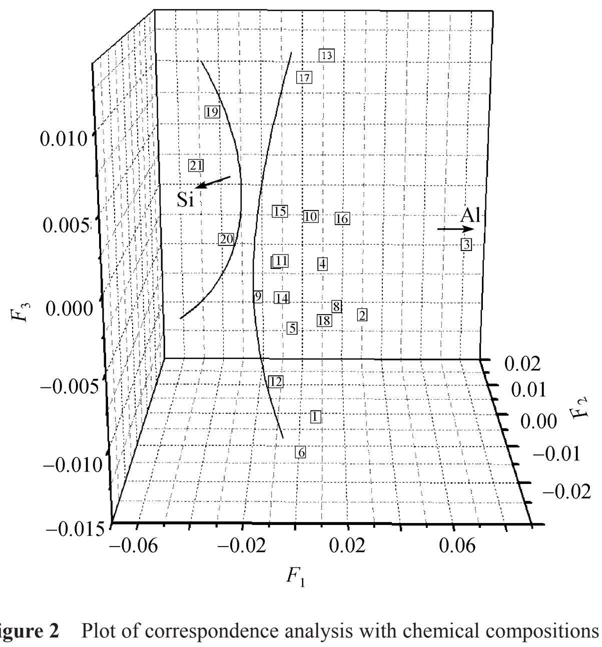

Figure 2 Plot of correspondence analysis with chemical compositions of proto-porcelain bodies from Henglingshan, Meihuadun, Raopin and Wubeiling, Guangdong province. Among them, 1—12 were proto-porcelain samples from Henglingshan; 13—15, proto-porcelain samples from Meihuadun; 16—18, proto-porcelain samples from Raopin; 19—21, proto-porcelain of Wubeiling.

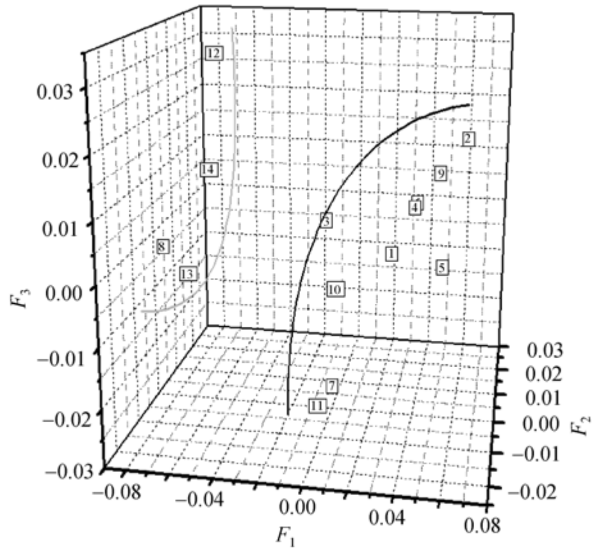

Figure 3 Plot of correspondence analysis with chemical compositions of proto-porcelain glazes from Henglingshan, Meihuadun, Raopin and Wubeiling, Guangdong province. Among them, 1—7 were the first kind proto-porcelain samples from Henglingshan; 8, second kind proto-porcelain samples from Henglingshan; 9—11, proto-porcelain samples from Meihuadun; 12—24, proto-porcelain samples from Raopin.

4 Discussion

The chemical compositions of the pottery samples excavated from Henglingshan tombs vary in a wide range, and one of the conspicuous characteristics is that the pottery body has a very high content of Al_2O_3, especially for the pottery samples in the first and second stages. The contents of Al_2O_3 in most samples are above 30%, and for some samples (such as h1, h2), the contents of Al_2O_3 even exceed 40%. It can be concluded that the raw material is neither general clay nor bauxite. on one hand, the general clay used for pottery preparation doesn't have such high Al_2O_3 content; on the other hand, the content of Fe in general bauxite is much lower than that in the pottery samples excavated from Henglingshan tombs. The raw material used for Henglingshan pottery preparation is most likely to be boehmite with high Al_2O_3 content. Table 5 shows us that the values of R_xO_y/Al_2O_3 of pottery samples excavated from Henglingshan tombs are from 0.2 to 0.4, and the values of SiO_2/Al_2O_3 are mostly between 2 and 4. In fact, the content of the Al_2O_3 in the pottery made in other region is generally about 20%, much lower than that in the pottery body excavated in Henglingshan tombs[2].

The chemical composition's patterns of the pottery samples excavated in Henglingshan tombs during different periods have a clear evolution law. As shown in

Table 5 Values of R_xO_y/Al_2O_3 and SiO_2/Al_2O_3 of pottery and proto-porcelain samples from different production sites in China

Name	Dynasties	Unearthed site	R_xO_y/Al_2O_3	SiO_2/Al_2O_3
pottery	Xia, Shang, Zhou	Zhengzhou, Anyang of Henan province	0.5—0.9	6—9
pottery	Xia, Shang	Hengqu, Houma of Shanxi province	0.5—1.3	7—9
pottery	Shang, Zhou	Yingtan, Qingjiang of Jiangxi province	0.5—0.7	5—11
pottery	Zhou, Chunqiu	Jiangshan, Shaoxing of Zhejiang province	0.4—0.7	4—10

Figure 1, it can be found that the sample point gradually moves to upper left (away from the variable-Al_2O_3). It means that the content of Al_2O_3 in the sample is gradually reducing from the first stage to the fourth stage according to the correspondence analysis rule. In fact, the high content of Al_2O_3 in the pottery is harmful for its sintering process due to the low firing temperature. The average values of SiO_2/Al_2O_3 for the pottery samples from the first stage to the fourth stage are respectively 2.594, 3.26, 3.77, and 4.15. In addition, 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 pottery varied in a wide range. With the accumulation of experience, ancient potters began to strictly choose the raw material used for pottery preparation which would be easy for forming and firing operations of the pottery. As shown in Figure 1, the composition point of the pottery samples excavated from Henglingshan tombs gradually moves to the upper left from the first stage to the fourth stage.

Proto-porcelain samples were discovered by archeologists in the tombs of the third stage and the fourth stage. The compositions of these proto-porcelain samples had little changes, and the only exception is sample h23. As shown in Figure 1, the proto-porcelain samples are confined to a relatively smaller area. In addition, the concentration of Fe in proto-porcelain samples is much lower than that in pottery samples (see Tables 1 and 2). It can be concluded that the raw material used for proto-porcelain is different from that for pottery, 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 proto-porcelain preparation, which is one of important conditions for the successful preparation of proto-porcelain. Although the content of Al_2O_3 in Henglingshan proto-porcelain (~26.84%) is lower than that in early pottery, it is still much higher than that in proto-porcelain made in other regions. Actually, the content of Al_2O_3 in the proto-porcelain samples excavated from Shanxi, Henan, Hebei, Jiangxi , Zhejiang and Shanxi provinces is only about 15%[3]. The obvious difference shows that the proto-porcelain excavated from Henglingshan tombs could not be produced in these provinces. According to Table 2 and Figure 2, it can be found that the compositions of proto-porcelain samples from Wubeiling, Shenzhen city are quite different than those from Henglingshan, Meihuadun and Raoping, Guangdong province. The average value of SiO_2/Al_2O_3 (6—7) for Wubeiling samples is higher than that (3—5) for the samples from Henglingshan, Meihuadun and Raoping. In fact, the chemical compositions of Wubeiling proto-porcelain samples are similar to those of the samples from other provinces in south China, thus indicating that the production site of Wubeiling proto-porcelain samples is not in Guangdong province.

Due to the glaze spalling of proto-porcelain, the chemical compositions of only 14 proto-porcelain samples were systematically analyzed. The proto-porcelain excavated form the group of graves in Henglingshan can be divided into two kinds. The division is related to the main kinds of flux elements used in glaze. The first kind (most of the samples) has relatively high Ca, K and Mg contents. The others with black-green glaze which were named Fubing type have more Fe and Ca contents in glazes. For example, the content of CaO in the glazes of sample h42 is relatively low (~4.43%), but the content of Fe_2O_3 used in glazes is high (>5%). Figure 3 shows us that the first kind of Henglingshan samples and Meihuadun proto-porcelain samples were plotted together. According to the principles of correspondence analysis the samples which are plotted together are similar. In addition, Henglingshan is very close to Meihuadun (about 20 km away). Therefore, Meihuadun is likely to be one of the kiln sites where Henglingshan proto-porcelain samples were produced. As shown in Figure 3, the second kind of Henglingshan samples (Fubing type) and Raoping proto-porcelain samples were plotted together, and the analysis presented here reveals a clear separation between the groups Fubing type and the proto-porcelain samples excavated from Meihuadun. In fact, the proto-porcelain specimen with black-green glaze has not been found in the Meihuadun kiln site, but were produced in a large scale in the Raoping kiln site. So it can be concluded that the proto-porcelain samples of Fubing type excavated from Henglingshan were probably produced in the Raoping kiln site.

As a result of X-ray diffraction phase analysis, microstructure and sintering temperature analysis for the specimens excavated from the group of graves in Henglingshan, it is shown that a major breakthrough in firing technology had been made during the four development stages of Henglingshan ceramics. As shown in Table 4, the sintering temperature of the two specimens produced during the first stage is relatively low (<900℃), the main phases in sample bodies are clay matrix, mica debris and α-quartz crystallite with clear edges and corners (see h3, h5). At the second stage, pottery began to be fired in kiln. With the development of firing technology, the sintering temperature is close to 1200℃ (h11). The α-quartz crystallite with molten corrosion edge, Mullite and cristobalite crystallite could be discovered in the sample bodies. The press marked pottery also began to be successfully manufactured. Up to the third and fourth stages, the sintering temperature of samples had reached about 1250℃. There are more mullite, cristobalite crystallite and some glass phases in the sample bodies, all of this is the typical characteristics usually used to distinguish pottery and porcelain. Undoubtedly, the appearance of proto-porcelain in this region was closely related to the improvement of firing technology.

With the development of firing technology, the sintering temperature of press marked pottery already exceeded 1200℃. And both the evolution of raw material processing techniques and the change of "recipe" provided the conditions for proto-porcelain preparation[4]. Actually, in some way, proto-porcelain could be used instead of bronze ware because of the impermeability of glaze. The emergence of glaze was a major technical breakthrough in the development history of ceramics. It's a key point to study the origin of glaze for the research of proto-porcelain's origin. The origin of glaze was considered to have two ways: 1) the evolution of coating used for the decoration of pottery; 2) inspiration from the forming of kiln sweat in the firing process[1,5]. The specific origin of glaze should be closely related to the local natural resources (raw material, 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 (~500 μg/g). However, it is found that the contents of Mn and P in the glaze of the first type proto-porcelain excavated from Henglingshan and Meihuadun were quite high (~5000 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 the south of China, thus plant ash which also has a high content of Ca would be easy to obtain. It can be concluded that the high concentration of Ca in the proto-porcelain was probably provided by plant ash which was also rich in Mn and P[6,7]. But for Fubin type proto-porcelain samples excavated from Raoping and Henglingshan group of graves, although the concentration of Ca in the glaze is relatively high, the most important flux element is Fe. In addition, the contents of P and Mn in Fubin type samples are far lower than those of the first type proto-porcelain excavated from Henglingshan and Meihuadun. It suggested that the preparation of this kind of glaze was probably derived from the coating with high content of Fe used for the decoration of pottery.

5 Conclusion

The chemical composition of pottery excavated from Guangdong Henglingshan tombs has a clear regional characteristic. The values of R_xO_y/Al_2O_3 and SiO_2/Al_2O_3 for the pottery samples excavated from Guangdong Henglingshan tombs are much lower than those for the pottery samples excavated from other regions of south China.

The science and technology history of ceramics in Guangdong Province was further recognized based on the systemic studies on the pottery and proto-porcelain specimens excavated from Guangdong Henglingshan group of graves. On the one hand, the development of ceramics in Guangdong Province was similar to other regions of south China in some ways, on the other hand, it also has a unique characteristics. As we know, a usual law is that the content of SiO_2 in body gradually increases while the contents of Fe_2O_3, CaO, and MgO gradually decrease in the evolution history from pottery to porcelain in the south China. However, the obvious characteristic for the specimens excavated from Guangdong Henglingshan group of graves is that the content of Al_2O_3 gradually decreases.

With the gradual recognition and treatment of raw material used for ceramics preparation, especially the improvement of firing technology, some glass phase, mullite and cristobalite crystallite could be discovered in Henglingshan ceramics samples during the third and fourth sages, which was generally considered as the typical characteristics of proto-porcelain or porcelain.

The emergence of proto-porcelain was not only related to the development of preparation technique, but also related to the local recourses. And the origin of glaze was considered to have two ways: (i) the evolution of coating used for the decoration of pottery (such as the Fubin type proto-porcelain); (ii) derived inspiration from the forming of kiln sweat in the firing process (such as the proto-porcelain produced in Meihuadun, Guangdong Province).

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