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The multivariate statistical analysis and XRD analysis of pottery at Xigongqiao site

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Abstract

A series of pottery samples excavated from the Xigongqiao site in Tengzhou city of Shandong province was determined using inductively coupled plasma atomic emission spectrometry. Together with excavation data and archaeological analysis, the potential for provenance and technology of unearthed ancient pottery was studied by using multivariate statistical analysis and X-ray powder diffraction pattern (XRD) analysis. In order to characterize and classify these earthenware samples, the major and minor/trace element concentrations were studied with both cluster analysis and principal component analysis. The results showed that there were three different groups in cluster analysis dendrogram in good correlation with their colors. This indicated that the potteries were made from clays of different composition. These results were in agreement with the results of principal component analysis. XRD analysis further assessed the validity of multivariate statistical analysis.

Keywords: Xigongqiao site; Provenance of ancient pottery; Inductively coupled plasma atomic emission spectrometry; Multivariate statistical analysis; X-ray powder diffraction pattern

1. Introduction

The first evidence for pottery making in China was associated with the beginning of the Neolithic, nearly 10,000 BP, when human groups adopted a sedentary lifestyle. The pottery industry witnessed a distinct evolution from the Yangshao to Dawenkou and Longshan stages during the Neolithic period. Characteristic of the Yangshao culture (7000–6000 BP) are hand-made gray coarse earthenware and light-red painted fine earthenware. The succeeding late stage of Dawenkou and Longhan culture (5000–4000 BP) are characterized by thin wheel-made black earthenware. There are also white wares in the latter indicating the careful selection of additional materials for pottery making.

The Xigongqiao site is located to the southwest of Xigongqiao village, Guanqiao town, Tengzhou city, Shandong province, and occupies an area of 50,000 m^2. These cultural remains are assigned to the Dawenkou culture, from the later middle to the late stage, and dated to 5000–4500 BP [1]. It was first excavated in 1998, dug out 48 tombs and over 200 ash-pits and unearthed more than 1000 pottery, stone implements and bone articles in all. The excavation of Xigongqiao site is one of the largest archaeological exhumation in Tengzhou city. The categories and amounts of earthenware are so many that they are unique at Dawenkou culture sites. The provenance of pottery has considerable relevance to the aspects of ancient economy, trade, life style and customs or so. Therefore the pottery is a very important material to better understand ancient societies.

The determination of the chemical composition of pottery is a means of exploring its origin and relevant issues. This study is an attempt to explore the potential of chemical composition analysis in characterizing pottery sources and technology through the study of

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earthenware artifacts at Xigongqiao site, and further to assess the validity of this result by X-ray powder diffraction pattern (XRD).

2. Testing analysis and data processing

2.1. Analytical technique

The first step in the study of the provenance of pottery was to look at the typology and decoration. Then the study evolved to determine the chemical composition, especially the trace element composition. The rationale of the testing is based on the premise that different clay sources possess unique chemical compositions and therefore pottery made of these clays can be distinguished [2]. Compared with major elements, contents of minor and trace elements are in ppm magnitude, which can effectively reflect on region composition character [3,4]. The samples consist of 48 sherd specimens from various types of earthenware at Xigongqiao site. Most of them are black (33); others are gray (9), white (5) and brown (1). Chemical compositions of these sherds were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Despite the elements analysis was widely applied in these study, but sometime the results from phase analysis could operate the key action. In fact, it could be seen the action in this paper, so the obtained samples were identified by the XRD.

Procedure of sample disposal: both inner and outer surfaces of the sherd were scraped using a tungsten-carbide drill burr. The scraped specimens (the initial weight of 2 g or so) were brushed with a brush and washed with distilled water and alcohol in an ultrasonic vessel, then dried at the room temperature. An agate mortar and pestle was used to crush and grind each specimen into fine powder to ensure better homogeneity, filtered with copper sieve mesh of 0.074 mm and sealed in a plastic bag for ICP-AES analysis and XRD analysis.

The ICP-AES analyses were carried out on a French JY38S inductive plasma atomic emission spectrometer. Standard soils of GBW07401, GBW07402 and GBW07408 were used.

The obtained samples were characterized by the XRD which was carried out on a Japanese Mac Science MXP18AHF X-ray diffractometer using CuK_α radiation ($\lambda = 0.154178$ nm). Range for diffraction angle: 10–65°, sampling width: 0.02°, scanning speed: 8.00°/min.

2.2. Data processing

In order to obtain actual and credible information about the provenance of the pottery, we must choose high independent, stable and homogenous elements for basic variable. Three groups elements should be removed.

1. P element, which has a high volatility.
2. Hg, U, Pb, Li elements, which have low stability in soil.
3. Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu, Y rare earth elements, which have high correlation, so only La, Ce, Sm, Eu, Yb elements are chosen, which accord with the independence of variable [5].

Therefore 24 elements were selected for multivariate statistical analysis. These elements are La, Ce, Sm, Eu, Yb, Rb, Cs, Ba, Co, Cu, Ni, Zn, As, Cr, Sb, Th, Si, Al, Fe, Mg, Ca, Na, K, Mn. Table 1 records the concentrations of the 24 elements for 48 specimens. Each element of major, minor and trace is in an equal weight degree through standardization of raw data by Z scores. It is very important in statistical analysis.

3. Discussion

The samples were analyzed by using the statistics package for social science (SPSS) for windows. It is indispensable to employ multivariate statistics that use the correlation between element concentrations as well as the absolute concentrations themselves to characterize different types and sources of pottery [6].

3.1. Cluster analysis

Instead of distributing the samples into typological categories, we have found it more useful to keep all the data together and to employ the multivariate statistical technique of hierarchical cluster analysis (HCA) to emphasize the structure in the data [7]. The grouping that resulted from chemical analysis of the sample is presented in the dendrogram of Fig. 1. This shows the result of aggregative HCA using as similarity measure the mean Euclidean distance among the concentrations of 24 elements, the linking criterion used was the average between-groups linkage. The result of clustering is the separation of the samples into three groups (Fig. 1).

The first group contains all the black pottery. Two samples of ash-pit 186, 33, 193, 127 and 188, respectively consist of a subgroup (sample 33 and 34, 6 and 8, 39 and 40, 19 and 20, 36 and 37). Three samples of ash-pit 211 consist of a minor subgroup (sample 44, 45 and 46); two samples of ash-pit 31 consist of a minor subgroup (samples 2 and 4). It is very important to realize that all the black pottery constitute group I, which indicates that all the black pottery could be made from identical clays.

The second group contains all the gray pottery (9), two black pottery (samples 13 and 24) and one brown pottery (sample 5). Samples 5 and 29 consist of

Table 1
Chemical composition of the studied earthenware specimens (La-Cu:ppm, SiO_2-MnO:%) B: black earthenware; C: gray earthenware; D: brown earthenware; G: white earthenware

Code	La	Ce	Sm	Eu	Yb	Ni	Zn	As	Cr	Sb	Th	Rb	Cs	Ba	Co	Cu	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO
XH31-1Bb	35.18	71.86	6.05	1.23	2.74	75.1	130	8.3	110	0.16	13.2	127	14	1268	16.1	37.9	60.12	16.42	6.8	1.72	2.11	1.11	2.82	0.04
XH31-2Ba	35.08	65.07	5.7	1.18	2.51	55.7	102	9.8	113	0.61	13.3	124	9	1478	17.2	30.2	60.9	16.01	6.69	1.48	2.19	1.09	2.67	0.05
XH31-3Cc	37.07	73.68	6.22	1.25	2.82	60.4	101	2.1	93	0.25	13.4	109	7	1098	17.5	23.9	67.3	14.83	5.51	1.5	2.21	1.19	2.25	0.05
XH31-6Be	35.64	62.53	5.43	1.14	2.53	66.3	120	4.4	96	0.13	13	115	10	1397	16.2	31.2	62.77	15.29	5.91	1.51	2.08	1.2	2.61	0.05
XH33-1Dg	35.93	77.78	6.56	1.32	3.15	59.7	85	9.2	115	0.76	14.2	76	6	1179	18.4	26.1	60.8	16.77	7.03	1.22	1.58	1.1	1.95	0.1
XH33-2Ba	38.6	70.64	6.58	1.38	2.98	65.8	100	10.4	114	0.37	13.8	115	10	1517	16.1	32.7	58.38	16.25	7.03	1.25	2.05	1.14	2.59	0.06
XH33-3Bc	40.98	71.51	6.56	1.42	2.96	63.5	91	13.4	118	0.43	14.5	126	13	1899	15.9	34.8	53.31	17.69	7.55	1.3	2.25	0.99	2.66	0.03
XH33-4Bh	38.46	69.34	6.64	1.37	2.75	69.8	101	9.3	111	0.37	12.9	110	9	1840	16.6	33.2	58.39	15.85	6.59	1.58	2.36	1.54	2.5	0.05
XH36-1Ba	34.53	63.08	5.77	1.19	2.63	79.8	142	8.9	101	0.29	13	134	11	1442	18.6	39.9	61.02	16.34	6.78	1.76	1.88	1.08	2.68	0.04
XH36-2Bc	38.8	69.32	6.22	1.32	2.78	71.1	128	13.1	90	0.74	14.6	144	14	1347	19.2	36	56.44	17.97	7.86	1.83	2.13	0.73	2.89	0.11
XH36-3Cc	29.23	59.12	5.14	1.08	2.35	37.5	74	7.2	86	0.61	11.5	104	7	1124	13.6	21.3	70.05	13.52	5.05	1.18	1.54	1.46	2.01	0.04
XH36-4Gl	44.06	93.88	5.73	1.21	3.15	18.8	33	0.4	69	0.02	15.9	63	5	333	6.1	19.4	68.78	22.89	2	0.76	0.82	0.86	1.74	0.02
XH54-4Ba	36.11	68.08	5.73	1.14	2.58	50.7	83	5.2	80	0.36	12.5	95	8	1191	14.3	22.1	66.25	13.96	5.61	1.34	2.07	1.38	2.19	0.04
XH54-5Ca	35.29	76.95	6.14	1.21	2.82	44.5	79	1.3	99	0.19	12.9	116	11	664	17	27	70.41	14.25	5.93	1.8	1.46	1.46	2.42	0.05
XH63-1Ba	41.65	80.89	7.01	1.44	3.07	64.1	115	6.8	118	0.64	15.1	137	14	1459	22	41.4	57.56	17.46	7.11	2.07	2.47	0.78	3	0.07
XH63-2Bg	39.41	74.85	6.42	1.31	2.74	66.9	127	11.2	105	0.47	13.4	141	15	1456	19.5	38.1	60.06	16.2	6.88	1.74	2.28	1.04	2.73	0.05
XH94-1Bb	34.02	87.64	5.89	1.18	2.7	74.6	99	15.4	89	0.93	12.8	109	12	1252	21.9	34.8	63.48	14.91	6.38	1.5	2.02	1.13	2.16	0.08
XH94-2Ba	32.96	63.05	5.33	1.12	2.47	57.4	107	8.7	91	0.95	13.8	109	11	961	14.8	32.5	65.11	15.21	6.27	1.54	1.85	1.18	2.28	0.05
XH127-1a	36.21	61.49	5.76	1.24	2.7	51.3	116	8.8	102	0.78	15.5	153	12	1064	15.8	31.2	62.4	17.79	7.44	1.88	1.66	1	3.01	0.04
XH127-2c	39.29	72.17	6.49	1.34	2.88	55.8	112	8.3	123	0.58	15	142	10	1167	17	34.7	59.91	17.25	6.88	1.71	1.98	0.94	2.97	0.06
XH128-1Bk	32.89	60.54	5.65	1.13	2.73	60.7	83	20.4	98	0.84	12	102	9	1189	20.7	34.3	61.87	15.63	6.91	1.39	2.22	1.1	1.95	0.14
XH128-2Bc	37.48	65.82	6.01	1.26	2.69	58	84	20.5	85	0.54	13.2	118	7	1444	14.9	29.9	61.66	15.1	6.42	1.47	2.34	1.13	2.57	0.05
XH128-3Ca	37.8	79.23	6.47	1.3	3.18	48.5	83	1.9	99	0.22	10.6	124	9	785	16.9	26	68.57	15.81	6.56	1.7	1.05	1.04	2.55	0.1
XH138A-2B	36.73	60.19	5.85	1.21	2.63	52.6	83	8.2	89	0.26	11.1	113	7	1191	15.8	24.8	66.31	14.19	5.49	1.65	2.02	1.39	2.52	0.06
XH138B-1B	38.68	68.5	6.23	1.33	2.76	65.9	118	8.2	101	0.56	14	152	15	1157	20.5	34.7	60.37	17.37	6.63	2.11	2.09	0.94	2.74	0.06
XH138B-2B	45.01	75.78	6.79	1.46	2.97	57.4	102	7.8	109	0.74	15.4	147	9	1411	21.1	34.7	60.56	18.38	6.9	2.05	2.12	0.89	2.93	0.12
XH138B-4C	40.85	66.84	6.52	1.39	2.86	45.5	100	2.3	108	0.09	13.5	103	7	976	16.1	25.5	66.56	15.89	5.62	1.99	1.51	1.48	2.28	0.07
XH171-1Bn	45.31	61.19	6.4	1.41	2.58	74.9	106	7.1	83	0.46	12.5	130	9	1044	18.2	39.5	61.91	16.76	6.37	1.95	1.83	1.47	2.54	0.06
XH171-4Cg	41.35	65.72	6.25	1.35	2.85	38.7	76	9.5	130	0.36	14	51	3	1663	15.1	26.1	58.01	15.56	6.29	1.08	2.42	1.08	1.62	0.05
XH172B-1G	50.47	78.28	6.2	1.34	2.77	22.6	45	1	81	0.19	17	83	5	543	5.7	27.3	67.11	23.08	2.6	0.7	0.77	0.79	1.9	0.04
XH186-2Ch	27.64	52.66	5.64	1.13	2.47	43.9	80	1.7	100	0.18	14	130	11	835	16.9	26.1	69.56	15.01	5.93	1.67	1.52	1.25	2.42	0.05
XH186-4Ca	33.82	68.54	5.85	1.21	2.6	42.2	90	2.1	104	0.24	14.1	144	9	753	20.1	27	69.05	15.25	6.21	1.88	0.89	1.18	2.74	0.06
XH186-5Bh	41.98	80.65	6.97	1.41	2.75	63.5	101	10.7	129	0.59	13.4	116	10	1535	16.8	42	59.8	16.07	6.73	1.68	2.14	1.48	2.29	0.1
XH186-6Ba	43.94	79.18	7.07	1.46	2.76	65.3	100	9.4	131	0.4	13.6	118	8	1648	17.2	42.8	59.02	16.02	6.74	1.63	2.21	1.43	2.28	0.1
XH188-1Ca	34.25	61.56	5.9	1.18	2.71	36	71	2.5	101	0.34	13.1	133	11	724	12.6	24.3	70.76	13.86	5.28	1.49	1.8	1.47	2.36	0.04
XH188-2Bh	35.44	60.04	5.79	1.21	2.63	59.3	104	6.8	109	0.4	12.9	121	10	1420	15.1	30.7	62.42	15.22	5.84	1.48	2.29	1.11	2.53	0.08
XH188-3Ba	38.74	64.96	6.47	1.32	2.79	53.9	110	5.3	109	0.28	13.9	127	10	1441	15.1	24.2	62.04	15.38	6.11	1.54	2.3	1.06	2.67	0.07
XH188-4Bk	35.61	72.08	5.9	1.29	2.63	51.6	97	6.8	138	0.41	11.9	124	10	1335	15.9	31.2	60.27	16.31	6.62	1.62	2.26	1.03	2.71	0.05
XH193-1Bk	38.09	74.76	6.05	1.31	2.77	72.9	127	6	177	0.51	13.9	127	10	1435	18.9	32.3	60.21	16.63	6.8	1.92	2.12	0.98	2.62	0.04
XH193-2Bc	41.42	79.35	6.14	1.37	2.71	64.8	122	7.4	151	0.52	13.7	121	11	1376	19.5	35	60.18	16.65	6.56	2	2.22	0.92	2.62	0.05
XH193-4Gl	58.39	127.5	9.69	2.15	3.23	26.4	59	1.8	78	0.19	15.4	98	6	980	6.8	25.2	64.53	21.55	3.48	0.62	1.17	0.8	2.18	0.02
XH206-1Gl	58.26	129.44	9.08	2.02	4.11	15.7	34	0.9	82	0.09	15.5	69	6	411	5.6	12.7	67.8	23.39	1.86	0.75	1.06	0.89	1.83	0.03
XH206-3Ba	27.37	63.4	4.92	1.07	2.41	52.1	89	12.7	107	0.85	12.1	106	9	1427	15.8	32.8	62.61	15.54	6.38	1.6	2.17	1.05	2.09	0.04
XH211-2Bk	28.08	61.12	5.01	1.07	2.39	50.8	100	8.7	122	0.5	12.8	130	11	1597	16.6	29	63.16	15.85	6.44	1.59	1.98	1.01	2.79	0.08
XH211-3Bg	36.03	71.75	5.7	1.26	2.68	52.6	90	10	95	0.65	11.7	144	11	1593	17	30.4	61.99	15.43	6.3	1.52	2	1.19	2.63	0.1
XH211-4Bd	30.08	60.9	5.07	1.11	2.38	68.6	138	6.3	97	0.32	12.5	129	11	1238	16.7	38.1	62.4	15.61	6.42	1.71	1.94	1.11	2.66	0.09
XH211-5Ba	47.17	105.4	7.54	1.6	2.9	59.8	117	8.8	125	0.51	14.6	150	11	1427	19.2	38.1	59.52	17.25	7.32	2.06	2.06	0.99	2.83	0.06
XH211-6Gl	53.97	143.9	10.7	2.47	3.85	20.3	65	2.4	68	0.12	15.4	107	9	770	8	32.6	66.5	21.84	2.76	0.73	1.3	1.01	2.06	0.04

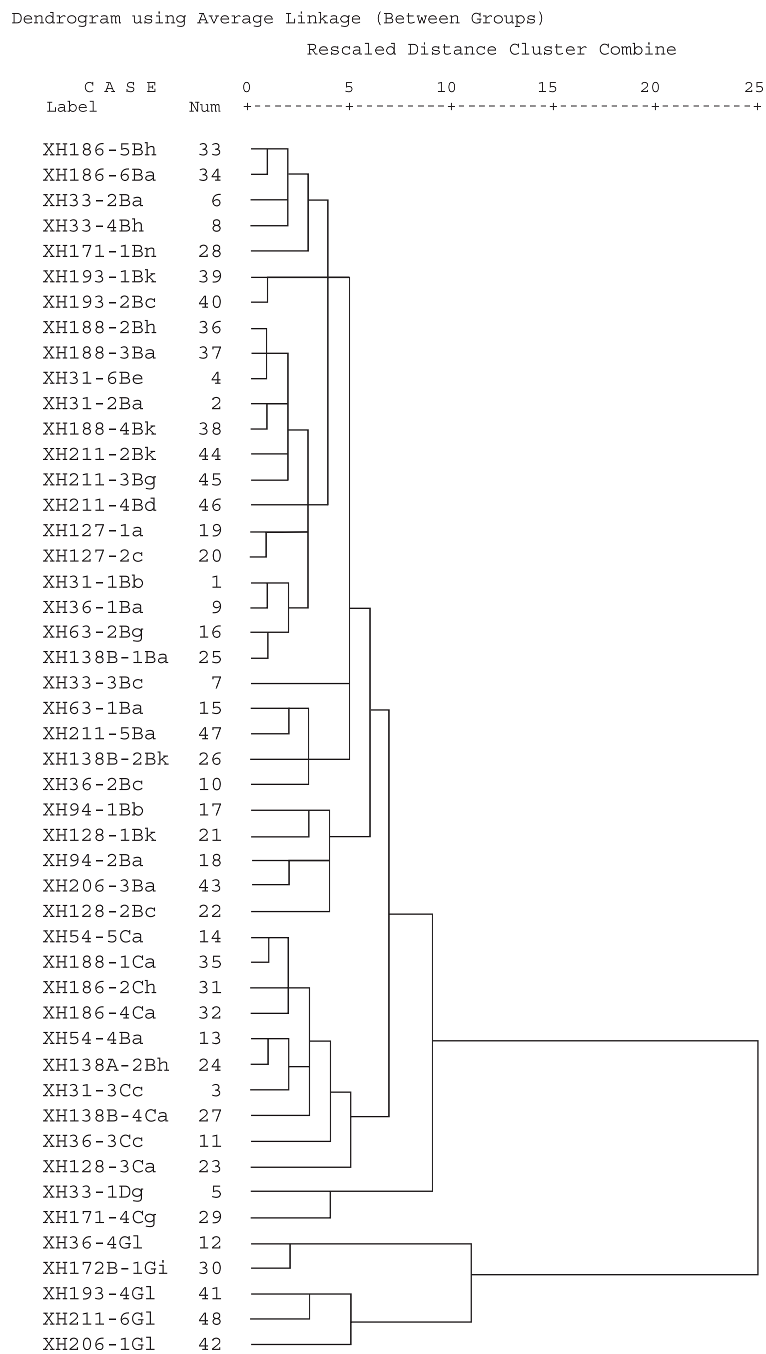

Fig. 1. Hierarchical cluster analysis dendrogram obtained on the basis of 22 element compositions using average linkage (between groups).

a subgroup, other pottery consist of another subgroup. Through careful observation of fresh cleavage insection, pottery body of samples 5, 13 and 24 were gray. The different colors on the surface likely caused of sintering atmosphere and surface cementite. Generally speaking, the surface colors of pottery are based on not only chemical compositions, but also sintering atmosphere and technology [8]. The conditions of atmosphere and temperature in the firing and post firing phases could affect the body of the pottery, provided that the duration of the different phases and the local atmospheres created among the pots being fired allow the dominating gases to act on the surfaces of the pots, and sometimes to penetrate into the body. However the body colors of pottery are primarily correlated to chemical composition of raw clay. Accounting for this point, the kind of samples 5, 13 and 24 could be likely identical to other gray pottery.

The third group contains all the white pottery Gui tripod. In comparison with group I and group II, they had higher concentration of Al_2O_3 and SiO_2 and lower concentrations of Fe_2O_3, CaO and MgO, which were most likely to be made of porcelain clay in the northern China. The earthenware filled with many colors and types in the later middle and the late stage of Dawenkou culture. The most distinctive characteristic seemed to show that pottery production and technology had made a greater progress in that stage. Based on the intended functionality of pottery vessels, different clays were carefully chosen from mud soil, fine paste clay by adding fine grain sand or coarse grain sand. Some cooking vessels such as Gui tripod were made from porcelain clay or higher contents of aluminum clay [9,10]. Thus, the separation between earthenware from different groups is likely to reflect the variability of raw clay materials in their chemical composition. This may shed some new light on how the first protoporcelain was invented. At the beginning, potters might accidentally or deliberately used porcelain clay to fire earthenware. They might have discovered that high-fired earthenware bodies were harder, less porous, and better quality. Then, they might have intentionally raised firing temperature so as to produce protoporcelain. Therefore, the availability of porcelain clay as a suitable raw material was crucial for the production of those partially vitrified and non-deformable protoporcelain wares. The earliest protoporcelain was produced during the Shang and Zhou dynasties (the next period of Dawenkou culture) in China.

3.2. Principal component analysis (PCA)

The principal component analysis was used as a tool to examine graphically the grouping pattern of the samples in terms of chemical composition, i.e. to see if there were partitions in terms of pottery type. The first two components, which describe most of the total variance in the elemental variables, usually best separate the different groups of samples; they were often used for the study of the provenance of artifacts [7].

Fig. 2 showed the scatter plot of pottery samples at Xigongqiao site, based on PCA of SPSS. At the outset, the PCA was conducted on the entire data set consisting of all 48 earthenware sherd specimens. The first two principal components subsume 62.95% of the total variance in the data set (PC I 45.25%, PC II 17.70%), revealing a well segregated pattern between earthenware. This separation can be attributed to the use of different componential raw materials in making earthenware. The samples of group III located at the left-above region at Fig. 2. The samples of group I located at the right-center of PC II at Fig. 2. Most samples of group II located at right-down of PC I, with the exception of sample 11 approach PC I nearly. It indicated that three groups of pottery could be separated at PCA plot. Although PCA only made use of 62.95%

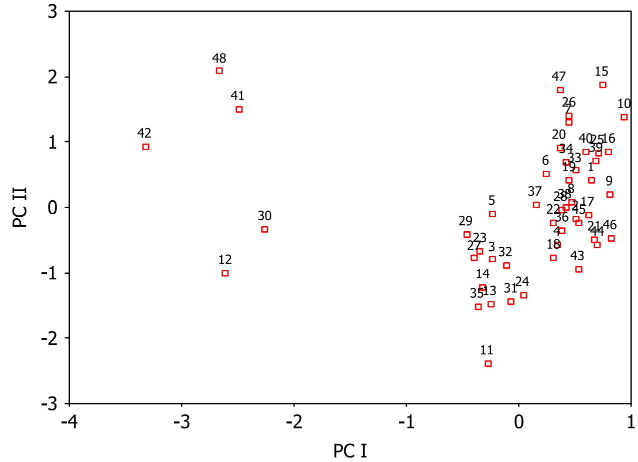

Fig. 2. Scatter plot of the first two principal components showing the grouping of 48 earthenware specimens.

information about the raw data, the results of classification were almost in agreement with that of HCA.

3.3. X-ray powder diffraction pattern (XRD) analysis

In order to assess the validity of pottery classification, the typical earthenware of three groups was characterized by XRD. Fig. 3 shows the XRD results.

Fig. 3a shows the similar XRD results of sample 6, 7 and 10, which were in group I at HCA dendrogram. The peaks of quartz are high and narrow (especially d = 0.334 nm), showed a good crystal state. But plagioclase feldspar had wide peaks (especially d = 0.319 nm, 0.449 nm), showed a worse crystal state.

Fig. 3b shows the similar XRD results of sample 11, 13 and 24, which were in group II at HCA dendrogram. Both quartz and alkali feldspar show good crystal state, there were narrow peaks of quartz (especially d = 0.334 nm) and keen peaks of alkali feldspar (especially d = 0.383 nm, 0.402 nm). Samples 13 and 24 should be assigned to gray pottery, on the surface of them, black or brown must be the result during firing. The two principal feldspar groups (alkali feldspar and plagioclase) can be recognized by their different peak positions in XRD pattern, so they maybe have important implications for future provenance determination.

Fig. 3c shows the XRD result of sample 12, which was evidently different from those of groups I and II. Besides of the distinct peaks of quartz and alkali feldspar, there were characteristic peaks of γ-Al_2O_3 crystalline (d = 0.140 nm, 0.198 nm, 0.239 nm), which was in agreement with high contents of Al_2O_3 in ICP-AES analysis. It indicated that white pottery was made from blending porcelain clay (included hydrous alumina such as Boehmite or Gibbsite) and other clays (included alkali feldspar). so there are alkali feldspar peaks and gamma-alumina peaks. The former shows a good crystal

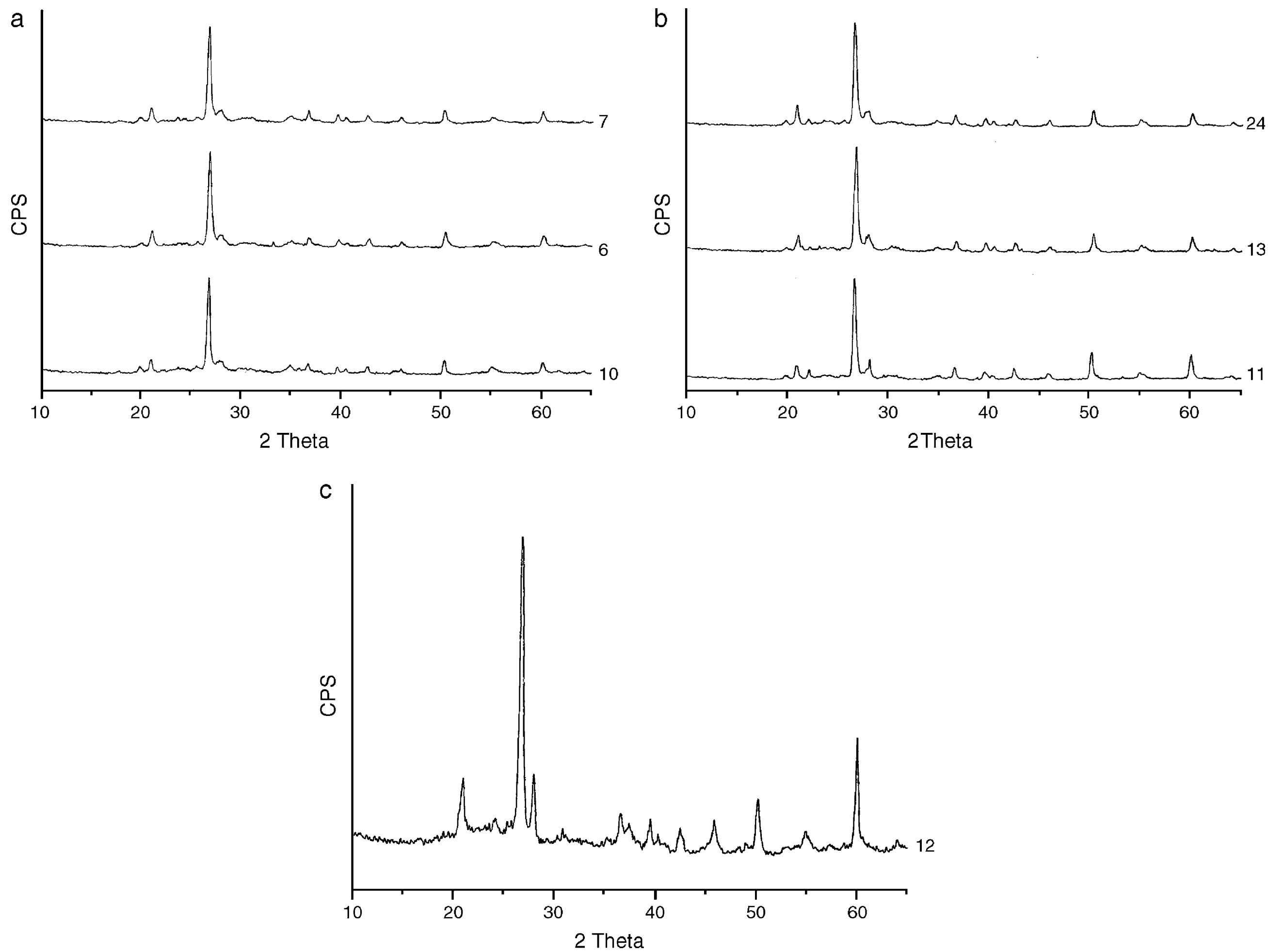

Fig. 3. The XRD results of 48 earthenware specimens. (a) Group I samples 6, 7 and 10. (b) Group II samples 11, 13 and 24. (c) Group III sample 12.

mineral, the latter represents dehydration of hydrous alumina phases on firing at 500–600 °C.

Therefore XRD further showed that three groups of pottery in cluster analysis were made from different clay raw materials.

4. Conclusions

By using ICP-AES technology, the major and minor/trace composition of 48 pottery objects of different types excavated from the ruins of Xigongqiao were determined. The potential for provenance and technology of unearthed ancient potteries were studied by using cluster analysis and principal component analysis. The results showed that there were three different groups in cluster analysis dendrogram in good correlation with their colors. This indicated that the pottery were made from clays of different composition. These results were in agreement with the results of principal component analysis. XRD further assessed the validity of the multivariate statistical analysis. The two principal feldspar groups (alkali feldspar and plagioclase) can be recognized by their different peak positions in XRD pattern, so their correct identification maybe have important implications for future provenance determination. It indicated that black pottery were possibly made from local clays, gray pottery were possibly made from other clays and white wares were possibly made from raw materials of making protoporcelain in the north of China. Although three different groups have been identified, the provenance of them would be still ongoing and should be attempted by petrographic examination and characterizing production sites. However, we could highlight the important fact that the white wares may be as the first step to the achievement of the protoporcelain.

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