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EDXRF studies on blue and white Chinese Jingdezhen porcelain samples from the Yuan, Ming and Qing dynasties

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The chemical compositions of blue and white Chinese Jingdezhen porcelain samples were analysed using energy-dispersive x-ray fluorescence (EDXRF) techniques. The results were subjected to multivariate statistical analysis. Different compositional patterns were found for specimens from different periods (Yuan, Ming and Qing dynasties) and for different intended usage (imperial or common). The reasons for these variations are discussed. From the analysis a discriminant function is generated that is capable of classifying samples with high efficiency.

INTRODUCTION

In recent years, chemical composition analysis has been increasingly employed in attempts to determine the data and provenance of porcelain products. By establishing a database of major and trace element compositions of ceramic samples from known sites and of known age, it is possible to produce effective mechanisms based on statistical methods for identifying unclassified samples.

Jingdezhen has been a ceramic production centre since the Yuan dynasty (1280–1368 AD) when the famous blue and white Jingdezhen porcelain began to be produced on a large scale. From that time, it has always remained one of the most important representatives of Chinese ancient ceramics from the Yuan (1280–1368 AD), Ming (1368–1644 AD) and Qing dynasty (1644–1911 AD) periods. The search for a non-destructive method to ascribe the exact period of manufacture of Jingdezhen porcelain has received considerable attention. Assignation between the Yuan and Ming dynasties is particularly problematic owing to the similarity of the major element compositional characteristics and to the difficulty in collecting reliable specimens from the Yuan dynasty.[1,2]

Following the excavations of ceramics at the site of the Imperial Factory at Zhushan, Jingdezhen, a large quantity of imperial porcelain was discovered that had been deliberately smashed and concealed at the factory because it fell below the standard of perfection demanded by the court, but could not be allowed to pass into the hands of the common people. In this work, 37 specimens of blue and white porcelain excavated at Jingdezhen were selected from reliable strata and were chosen as being typical and representative of their respective periods. The samples covered both imperial and common usage. The imperial specimens were taken from the Yuan (JYI), Ming (JMI) and Qing (JQI) dynasties, with 5, 20 and 7 samples, respectively. The five common specimens represented the Yuan (JYC) dynasty. All samples underwent energy-dispersive x-ray fluorescence (EDXRF) analysis, a technique now well established as a powerful tool providing quick, non-destructive analysis, involving easy sample preparation and good reproducibility. The results were subjected to a multivariate statistical analysis.

EXPERIMENTAL

The EDXRF spectrometer used was a Philips DX-95, with excitation provided by an Mo target x-ray tube and using an Si(Li) detector. A collimator was used to choose smaller, 'flat' regions of analysis, thus reducing errors caused by surface irregularities. The diameter of the collimator was 12 mm. Twelve thick pellets were made as standard samples at a pressure of 3.875 ton cm^{-2}. These contained Na, Mg, Al, Si, Ti, Ba, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Rb, Sr, Y and Zr. A calibration line was constructed for all elements. The tube was operated at 18 kV, 500 μA for the group Na–Zn and 50 kV, 45 μA for Pb–Zr. An exposure time of 600 s was used for all samples. Tables 1 and 2 list the analytical results obtained, and Table 3 gives the means and variances of trace elements concentrations.

MULTIVARIATE STATISTICAL ANALYSIS

Correspondence analysis

Correspondence analysis is an improved form of factor analysis, first put forward in 1970 by Benzeic. In addition to providing correlations among all samples, it also shows

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Table 1. Concentrations of major element (wt%)

No.	Name	Period (dynasty)	Type	Na	Mg	Al	Si	K	Ca	Fe
1	JYC1	Yuan	Common	0.812	0.586	14.6	78.3	3.70	0.438	1.45
2	JYC2	Yuan	Common	0.661	0.225	18.0	76.3	3.48	0.204	1.08
3	JYC3	Yuan	Common	1.06	0.237	20.1	72.8	3.83	0.383	1.46
4	JYC4	Yuan	Common	0.861	0.131	17.5	76.5	3.49	0.394	0.997
5	JYC5	Yuan	Common	0.925	0.475	17.4	76.0	3.57	0.326	1.01
6	JYI1	Yuan	Imperial	0.606	0.968	17.5	75.5	3.80	0.217	1.30
7	JYI2	Yuan	Imperial	0.578	0.993	17.9	75.1	3.88	0.208	1.24
8	JYI3	Yuan	Imperial	0.511	1.07	17.1	75.7	3.89	0.222	1.34
9	JYI4	Yuan	Imperial	0.665	0.939	17.7	75.3	3.82	0.227	1.28
10	JYI5	Yuan	Imperial	0.614	1.09	17.4	75.5	3.74	0.245	1.23
11	JMI1	Ming	Imperial	1.01	1.06	16.1	76.8	3.68	0.284	0.952
12	JMI2	Ming	Imperial	0.819	0.956	16.8	76.4	3.65	0.310	0.956
13	JMI3	Ming	Imperial	0.603	1.062	16.9	76.3	3.84	0.238	0.930
14	JMI4	Ming	Imperial	0.633	1.14	18.5	74.9	3.68	0.158	0.817
15	JMI5	Ming	Imperial	0.458	0.980	18.4	75.7	3.30	0.153	0.873
16	JMI6	Ming	Imperial	0.542	0.764	17.0	76.7	3.61	0.334	0.923
17	JMI7	Ming	Imperial	0.775	0.824	17.4	75.7	3.74	0.463	0.975
18	JMI8	Ming	Imperial	0.768	1.21	18.3	75.2	3.38	0.170	0.869
19	JMI9	Ming	Imperial	0.645	1.15	21.1	71.9	4.07	0.159	0.960
20	JMI10	Ming	Imperial	0.597	0.881	16.8	76.6	3.52	0.609	0.899
21	JMI11	Ming	Imperial	0.879	1.10	16.7	76.4	3.36	0.547	0.886
22	JMI12	Ming	Imperial	0.913	1.06	18.9	74.5	3.45	0.303	0.833
23	JMI13	Ming	Imperial	0.883	0.706	17.3	77.5	2.24	0.254	1.02
24	JMI14	Ming	Imperial	0.569	0.923	21.2	72.7	3.40	0.159	0.924
25	JMI15	Ming	Imperial	0.486	0.646	16.6	76.9	3.65	0.618	0.925
26	JMI16	Ming	Imperial	0.636	0.907	19.6	73.9	3.95	0.152	0.848
27	JMI17	Ming	Imperial	0.921	0.795	16.2	76.7	4.19	0.197	0.930
28	JMI18	Ming	Imperial	0.646	0.819	14.4	78.7	4.05	0.467	0.859
29	JMI19	Ming	Imperial	0.593	0.356	15.0	78.1	4.51	0.408	0.889
30	JMI20	Ming	Imperial	0.703	0.817	16.9	76.3	4.19	0.169	0.844
31	JQI1	Qing	Imperial	0.750	0.510	26.1	68.6	3.47	0.251	0.915
32	JQI2	Qing	Imperial	0.732	0.520	23.1	70.3	4.66	0.470	0.897
33	JQI3	Qing	Imperial	0.763	0.841	24.6	67.8	4.49	0.418	0.902
34	JQI4	Qing	Imperial	0.798	0.934	25.0	67.6	4.22	0.437	0.931
35	JQI5	Qing	Imperial	0.677	0.422	24.5	69.4	3.92	0.230	0.842
36	JQI6	Qing	Imperial	0.657	0.502	22.9	69.9	4.94	0.213	0.860
37	JQI7	Qing	Imperial	0.664	0.474	23.8	69.4	4.50	0.218	0.847

correlations between significant variables and samples.[3] This is of great interest in chemical analysis, where it allows new hypotheses to be formulated in archaeometry, and furthermore explains the reasons.

The data for major and trace element composition for all sample bodies were separately treated using correspondence analysis. The first three principal factors (F_1, F_2 and F_3), summarizing 90% of the total variability (providing most of the likely correlations), were selected. These principal factors were plotted in a similar manner to the scattergams, except that each plot axis has positive and negative factor scores ($F_i = x_1^i A + x_2^i B + \ldots$, where $A, B, \ldots$ are element concentrations and x_1^i, x_2^i, $\ldots$ are factor scores), and a 3D scatter graph is used to convey more statistical information (see Figs 1 and 2).

Figure 1 shows a reasonable separation between the groups JYI, JMI, JYC and JQI. Although group JYI cannot be completely distinguished from JMI, it is confined to a relatively smaller area. Group JQI is close to Al but not to Si. According to the principles of correspondence analysis, group JQI is characterized by Al. As shown in Fig. 3(a) (a simple plot of Si against Al), there is obviously a higher Al content and lower Si content in JQI compared with other groups. In addition, the Fe concentration of JYI and JYC is relatively high [see Table 1 and Fig. 3(b)].

Figure 2 reveals a clear separation of all the groups. Group JYI is close to Ti and far from Mn. In contrast, JQI is near to Mn but far from Pb and Cr. Groups JYC and JMI are located between JQI and JYI. Figure 4(a), (b) and (c) show plots of Mn against Pb, Ba against Cu and Cr against Ti, respectively. These indicate significant differences between the four groups. The Mn and Cu concentrations in JQI are the highest amongst all the groups. JYC has the next highest Mn content. The Pb, Ba and Cr contents in JQI are lower than in any other group. In particular, the Ti concentration in JYI is much higher (nearly five times) than in any other group.

Discriminant analysis

Correspondence analysis and cluster analysis provide grouping information based on similarities/dissimilarities between porcelain samples. A problem with these approaches is that the assessment of data for one or a new piece of porcelain requires reprocessing of all the previous analytical data. Discriminant analysis is a

Table 2. Concentrations of trace element (μg g^{-1})

No.	Name	Ba	Ti	Cr	Mn	Ni	Cu	Zn	Pb	Rb	Sr	Y	Zr
1	JYC1	182	610	142	988	84	24	78	54	290	58	22	117
2	JYC2	212	408	173	974	113	23	37	26	224	40	34	129
3	JYC3	226	338	96	1020	103	17	99	55	290	53	44	114
4	JYC4	183	572	137	859	124	27	82	75	224	55	31	126
5	JYC5	196	395	149	936	112	19	85	63	225	55	32	119
6	JYI1	241	2450	183	573	99	33	44	65	207	48	26	191
7	JYI2	203	2450	106	559	96	35	52	56	204	50	25	191
8	JYI3	287	2620	201	580	126	35	37	79	209	46	27	198
9	JYI4	217	2230	192	590	94	31	41	59	205	48	27	183
10	JYI5	250	1850	152	617	48	26	64	85	200	56	22	203
11	JMI1	173	497	172	781	90	31	56	96	213	37	26	124
12	JMI2	240	410	102	718	115	44	59	146	212	39	26	126
13	JMI3	282	412	149	709	127	25	46	97	206	35	33	123
14	JMI4	269	374	193	400	132	8	12	253	207	22	24	121
15	JMI5	279	411	164	447	111	21	49	169	191	28	21	120
16	JMI6	201	445	96	561	125	26	11	114	205	44	24	137
17	JMI7	167	667	125	621	136	25	15	126	211	55	25	143
18	JMI8	243	493	148	431	118	24	13	113	192	27	24	126
19	JMI9	260	579	127	503	111	22	84	170	191	27	28	137
20	JMI10	184	431	126	631	115	30	45	249	209	62	27	130
21	JMI11	183	449	126	554	102	14	40	230	208	60	22	134
22	JMI12	208	428	162	511	103	2	46	92	204	40	25	130
23	JMI13	141	145	166	659	168	36	49	190	201	71	33	191
24	JMI14	217	447	75	418	121	25	7	33	195	24	25	132
25	JMI15	183	414	114	535	120	29	23	90	203	39	20	61
26	JMI16	293	439	128	351	94	26	23	29	197	26	11	127
27	JMI17	253	349	181	519	83	23	51	157	212	47	31	126
28	JMI18	207	356	206	648	100	27	19	81	210	39	30	126
29	JMI19	290	326	184	678	102	16	64	98	218	45	28	133
30	JMI20	166	617	123	432	100	25	30	62	201	46	20	133
31	JQI1	155	130	46	1369	123	49	46	0	239	77	41	139
32	JQI2	137	550	42	1269	113	79	65	21	245	43	51	147
33	JQI3	144	116	26	1439	94	59	65	11	268	63	45	123
34	JQI4	146	78	20	1513	92	55	72	8	274	70	54	110
35	JQI5	132	226	25	1014	102	49	24	15	218	55	16	150
36	JQI6	141	396	38	986	80	89	51	13	255	79	25	141
37	JQI7	136	275	31	981	96	74	38	12	245	70	20	144

Table 3. Means and variances of trace elements concentrations

	JYC		JYI		JMI		JQI	
	Mean (μg g^{-1})	Variance	Mean (μg g^{-1})	Variance	Mean (μg g^{-1})	Variance	Mean (μg g^{-1})	Variance
Ba	200	362	240	1050	222	2230	142	58
Ti	465	14200	2320	87300	434	12200	253	29100
Cr	139	779	167	1500	143	1210	33	93
Mn	956	3840	584	472	555	14700	1220	52100
Ni	107	224	93	790	114	362	100	203
Cu	22	16	32	14	24	84	65	250
Zn	76	543	48	114	37	449	52	292
Pb	55	326	69	160	130	4240	11	42
Rb	251	1290	205	12	204	62	249	352
Sr	52	50	50	15	41	183	65	163
Y	33	62	25	4	25	26	36	239
Zr	121	40	193	58	129	479	136	210

powerful method of distinguishing sample groups. Instead of looking for natural groupings in the data, it produces functions that separate known groupings.[3] Once groups have been identified it would be convenient if the routine analysis of a few key elements could be used to classify new porcelain into previously identified groups.

Correspondence analysis indicates that the present samples may be divided into four groups: imperial porcelain samples from the Yuan dynasty (JYI), imperial from Ming (JMI), imperial from Qing (JQI) and porcelain samples for common usage from the Yuan dynasty (JYC). To complement this, major and trace element compositions for all

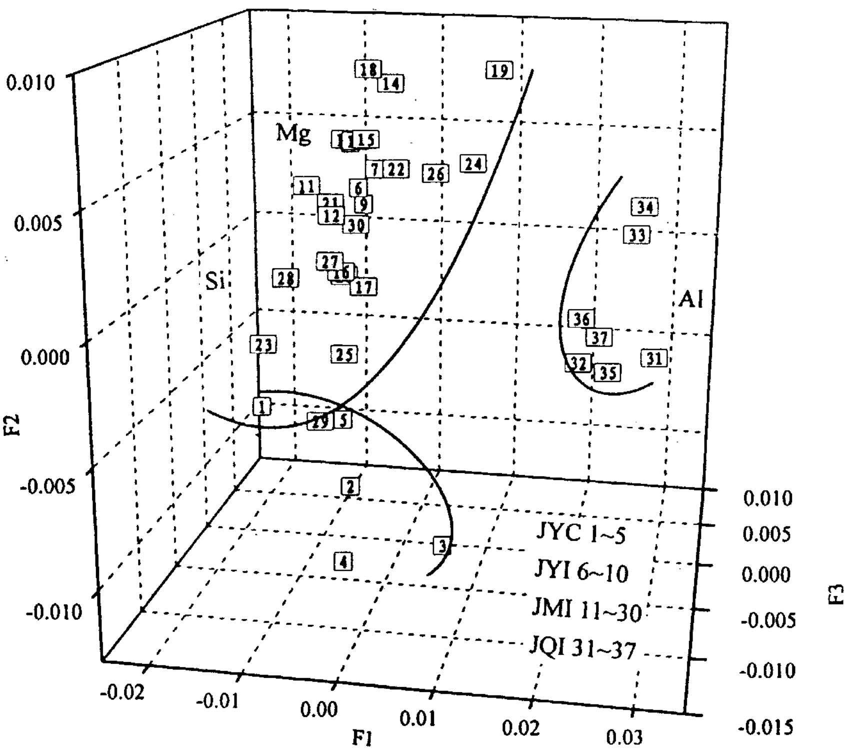

Figure 1. Plot of the first three factors with the concentration of major elements.

sample bodies were treated using the stepwise discriminant technique capable of selecting significant variables. Setting the F value to 3.5 and 2.7 for selecting and removing variables, respectively, the discriminant functions predicted for Blue and White Jingdezhen porcelain over time are as follows:

$$S_1(\mathrm{JYC}) = -2133 + 0.0159C_{\mathrm{Mg}} + 0.00546C_{\mathrm{Si}} + 0.0281C_{\mathrm{Fe}} - 0.01287C_{\mathrm{Ti}} - 0.4121C_{\mathrm{Mn}} - 2.2963C_{\mathrm{Cu}} + 5.3377C_{\mathrm{Y}}$$

$$S_2(\mathrm{JYI}) = -2376 + 0.0176C_{\mathrm{Mg}} + 0.00562C_{\mathrm{Si}} + 0.0293C_{\mathrm{Fe}} + 0.06367C_{\mathrm{Ti}} - 0.4298C_{\mathrm{Mn}} - 2.6288C_{\mathrm{Cu}} + 5.6274C_{\mathrm{Y}}$$

$$S_3(\mathrm{JMI}) = -2279 + 0.01898C_{\mathrm{Mg}} + 0.00572C_{\mathrm{Si}} + 0.0245C_{\mathrm{Fe}} - 0.0286C_{\mathrm{Ti}} - 0.4642C_{\mathrm{Mn}} - 2.1888C_{\mathrm{Cu}} + 5.8756C_{\mathrm{Y}}$$

$$S_4(\mathrm{JQI}) = -1593 + 0.0155C_{\mathrm{Mg}} + 0.00471C_{\mathrm{Si}} + 0.0179C_{\mathrm{Fe}} - 0.0244C_{\mathrm{Ti}} - 0.3066C_{\mathrm{Mn}} - 1.3028C_{\mathrm{Cu}} + 4.2179C_{\mathrm{Y}}$$

Any unknown sample can be classified in this way; C_{Mg}, C_{Si}, C_{Fe}, C_{Ti}, C_{Mn}, C_{Cu} and C_{Y} represent the element concentrations. When these values are substituted for any sample, the group function that delivers the highest value indicates the group to which the sample most probably belongs.

The relative discriminatory power of the variables employed was assessed by the approximate Bartlette χ^2 distribution:

$$\chi^2 = -\ln V[(N-1) - (L+M)/2]$$

$$r(\text{degrees of freedom}) = L(M-1)$$

where N = number of samples, L = number of variables employed, M = number of groups and V = Wilks statistical value. With N, L, M and V equal to 36, 7, 4 and 0.000275, respectively, then $\chi^2 = 241.87$. Referring to tables of χ^2 distribution values, $\chi^2_{0.005}(r) = 41.4 < 241.87$. This clearly shows that the discriminant function is effective.

DISCUSSION

In general, the variation in chemical composition of Jingdezhen porcelain would be expected to depend on (i) the 'recipe' used, i.e. the types and proportions of raw materials required, (ii) the origin of the raw materials and (iii) the production process, e.g. the elutriation technique used and the firing conditions etc.

Change of 'recipe'

Owing to improvements in firing conditions, the firing temperature of Blue and White porcelain during the Qing dynasty (~1300 °C) would be higher than that in the Yuan and Ming periods (~1250 °C).[4] This allowed changes in the raw materials. Higher proportions of kaolin, with high Al concentration, were added to the sample bodies. This also accounts for the different patterns of trace element composition, e.g. variations in Mn, Pb, Ba and Cr concentration, between the groups.

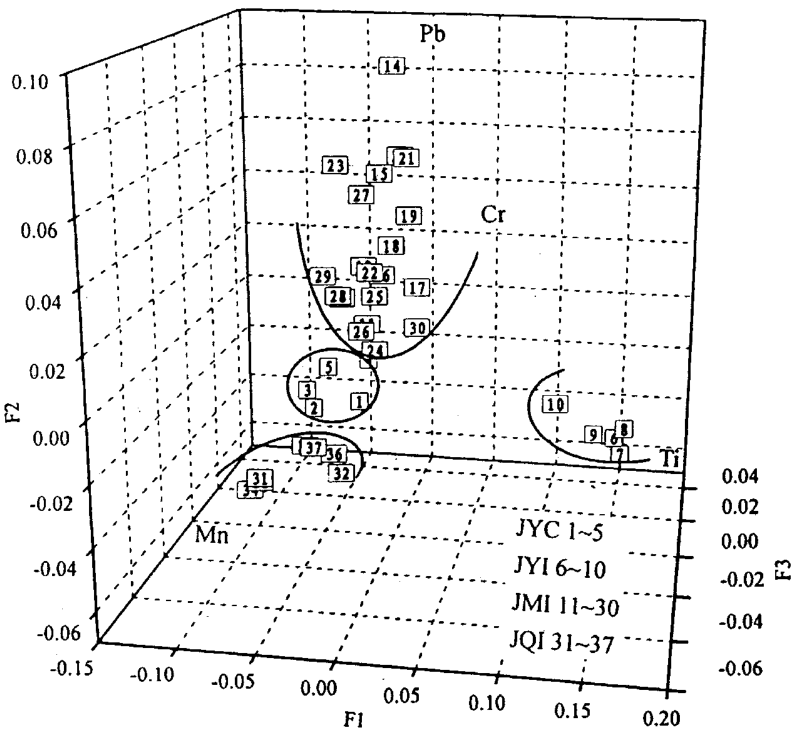

Figure 2. Plot of the first three factors with the concentration of trace elements.

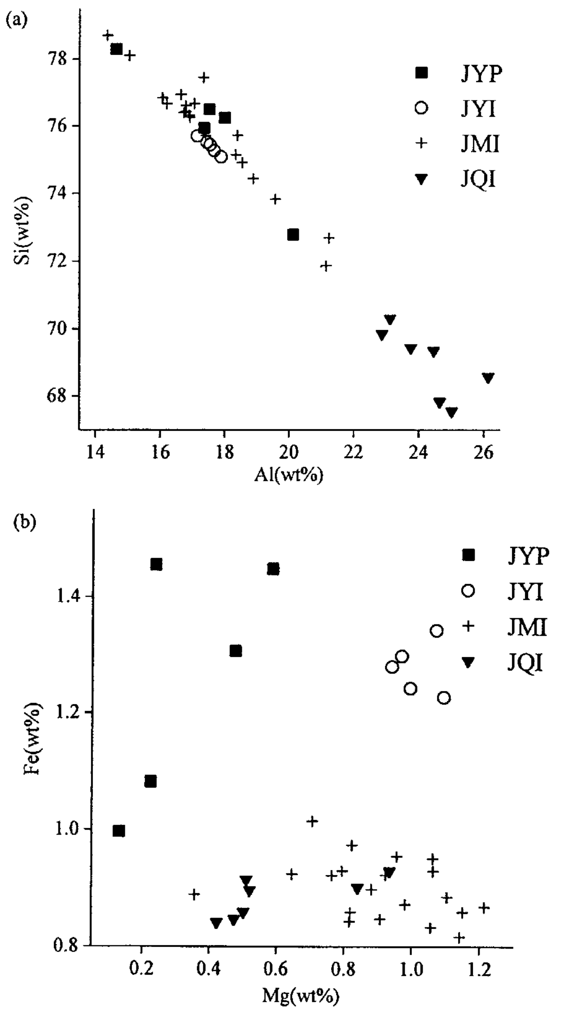

Figure 3. Scattergrams of major elements: (a) Si against Al; (b) Fe against Mg.

Origin of raw materials

Table 1 and Fig. 1 show that the major element composition of all the specimens from the Yuan to the Ming dynasty remains almost unchanged. This indicates that the abnormally high Ti content found in the trace element composition of group JYI specimens may relate more to the origin of the raw materials used. Better quality raw materials would be expected to be reserved for the production of imperial porcelain.[5] It is highly possible that the origin of the raw materials for imperial and common porcelain differ despite sharing the same period and region. Hence the compositional pattern of JYI is apparently very dissimilar to that of JYC.

Production process

The inclusion of Fe, found as a colouring agent in clay from southern China, can lead to products of relatively poor quality. With the evolution of raw material processing techniques (selection, wet elutriation, etc.), potters were probably able to remove iron better in the Ming and Qing dynasties. This is shown by the lower Fe content in specimens from the Ming and Qing dynasties compared with those from the Yuan dynasty.

CONCLUSION

The different compositional patterns of Blue and White Jingdezhen porcelain from different periods and for different usage (imperial or common) can be interpreted in terms of the raw material 'recipe,' the evolution of raw materials processing techniques and the origin of the raw materials. Although the major element compositions

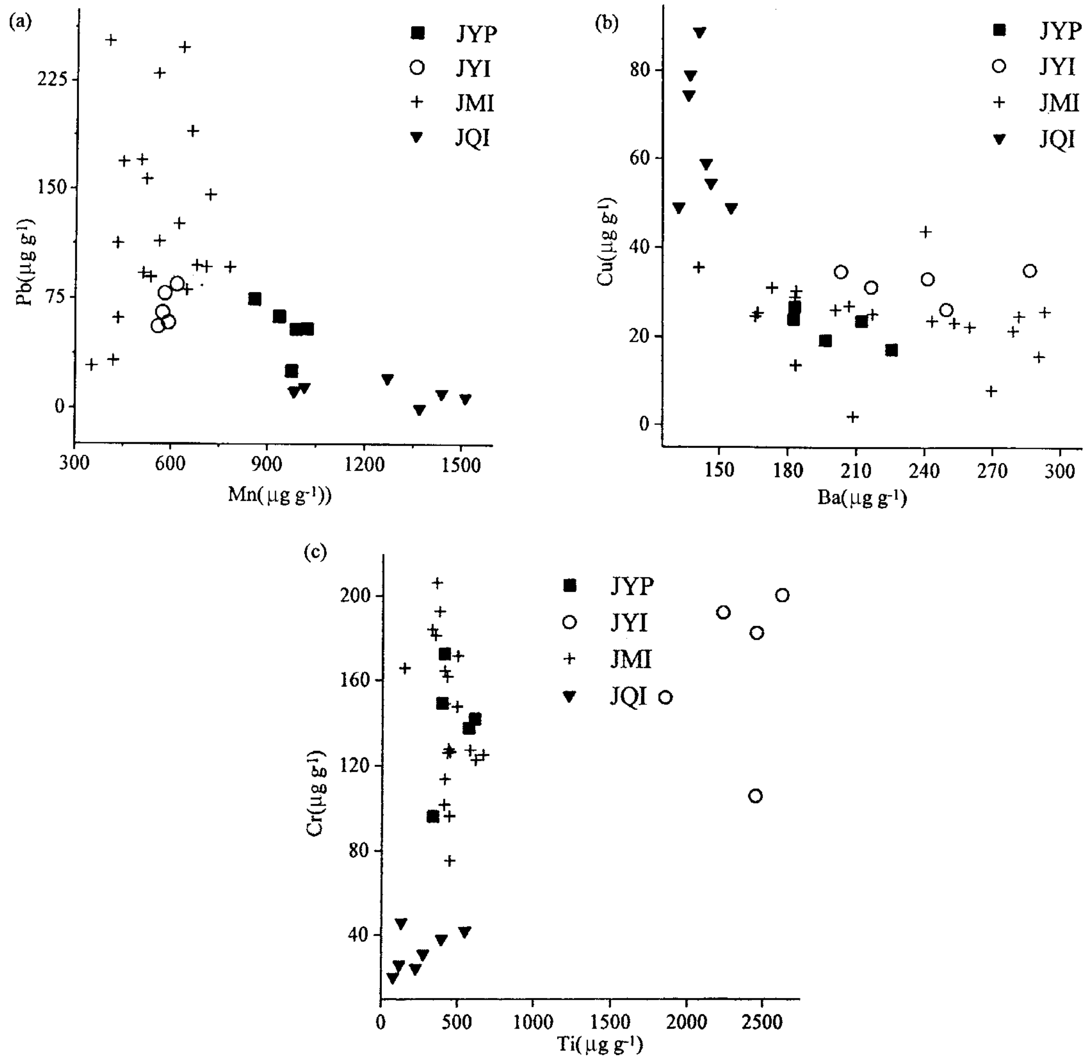

Figure 4. Scatterams of trace elements: (a) Mn against Pb; (b) Ba against Cu; (c) Cr against Ti.

of specimens from the Yuan and Ming dynasties show high similarity, differences in trace element compositions (in particular the high Ti concentration in specimens from group JYI) provide a basis for accurate classification. At the time of the Qing dynasty both major and trace element compositions changed owing to the increase of kaolin in sample bodies. In addition, the compositional pattern of imperial ware differs from that of common ware of the same period owing to the origin of the raw materials employed. The use of stepwise discriminant analysis provides a high discriminatory power in classifying blue and white Jingdezhen porcelain according to age and usage. Unknown samples can be classified effectively by a few key element concentrations, C_{Mg}, C_{Si}, C_{Fe}, C_{Ti}, C_{Mn}, C_{Cu} and C_{Y} using these functions.

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