EDXRF Studies on the Chemical Composition of Ancient Porcelain Bodies from Linjiang, Jiangxi, China

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Energy-dispersive x-ray fluorescence was used to study Linjiang porcelains, collected from a newly discovered kiln site and covering the Five Dynasties period to the Ming Dynasty. Major and trace component analysis of the sample bodies was carried out, in addition to principal component analysis with multivariate trace elements. The results show that the Linjiang ware is very similar to that from Jizhou, which is completely consistent with recent archaeological inference. The chemical character of the trace elements obtained would seem to have considerable potential for sensitive discrimination. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

The Jizhou kiln site is located in Yonghe Town, Jian City, Jiangxi Province, China. It is famous for the manufacture of porcelain from the Tang Dynasty (618 AD) to the end of the Yuan Dynasty (1368 AD).[1]

Production involved various styles of ware covering southern and northern systems and beautiful characteristic glazes: blue–green, black, milk-white, blue–white, etc. The black glaze with partridge spots and hare fur motifs are most representative, while the black glaze with appliqué was an original creation known throughout China.

The Linjiang kiln site, a newly discovered porcelain manufacturing site, is located at Linjiang Village, Jian City, very close to Jizhou. From 1991 to 1992 about 15 test pits were excavated over a total area of about 2400 m^2. A ruined workshop was discovered with two U-shaped kilns and more than 16 000 tools, kiln implements, porcelain objects, etc.[2] The accumulative strata was found to be divided into three layers: an upper layer including black, pea-blue, white and blue–white glaze ware, corresponding to the Ming Dynasty (1368–1644 AD), a middle layer including black glaze ware corresponding to the Yuan Dynasty (1271–1368 AD) and a lower layer including milk-white and black glaze corresponding to the Five Dynasties–Song Dynasty period (907–1270 AD).

Recently, energy-dispersive x-ray fluorescence (EDXRF)[3,4] has become established as a powerful tool in the study of Chinese porcelain. In this work, the technique was used to determine the chemical composition of porcelain bodies from Linjiang (LJB) and Jizhou (JZB) and to examine the relationship between the two sites. Comparisons are also given with other wares from Hutian (HTB), Jingdezhen, Jiangxi Province and from the Changsa (CSB) site, Hunan province.

EXPERIMENTAL

The equipment used at City University is an EDAX International DX-95 EDXRF analyser with an Mo target and Si(Li) detector. Twelve thick pellets were made as standard samples at a pressure of 25 ton in^{-2}. Each pellet contained known amounts of the elements of interest (Na, Mg, Al, Si, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Y, Zr and Ba), homogeneously mixed in an agate mortar and pulverized for 8 h. Three calibration lines were constructed for Na–Ca (line 1), Cr–Zn (line 2) and Sr–Ba (line 3) using DELTA-I software.[5] Ti and Rb can also be determined using the curve of $\ln[I/C]$ against $\ln[E]$.[3] (I: intensity caps), C: concentration (μg g^{-1}), E: fluorescent energy (keV).) Each porcelain sample was exposed for 500 s at 15 kV and 200 μA for the group Na–Zn and 45 kV and 15 μA for Rb–Ba.

RESULTS AND DISCUSSION

Major component analysis

The SiO_2 contents in LJB, JZB, HTB and CSB are 66.2–70.8, 66.0–69.1, 74.1–75.6 and 70.0–73.6%, respectively, and the corresponding Al_2O_3 contents are 19.6–23.3, 21.2–23.9, 18.2–19.8 and 19.4–21.9%. There appears to be some negative correlation here; for HTB

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Table 1. General description and chemical composition (wt.%) of porcelain bodies[a]

Sample	Name	Kiln site	Period	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	MnO	RO_2	$RO + R_2O$	PRIN 1	PRIN 2	PRIN 3
LJB-1	Black P.	Linjiang	Song D.	66.73	22.89	1.37	0.77	0.15	0.34	6.94	0.46	0.004	4.81	0.4	−2.14196	−0.66401	−0.305
LJB-2	Black P.	Linjiang	Song D.	67.93	22.55	1.4	0.78	0.16	0.24	6.18	0.42	0.001	4.97	0.35	−1.69533	−0.82123	−0.49019
LJB-3	Black P.	Linjiang	Song D.	66.68	23.03	1.13	0.74	0.14	0.53	6.85	0.5	0.02	4.81	0.41	−2.0114	−0.27281	−0.09615
LJB-4	Black P.	Linjiang	Song D.	66.19	23.33	1.12	0.75	0.19	0.54	6.03	0.49	0.007	4.72	0.38	−2.0262	−0.16451	−0.23548
LJB-5	Black P.	Linjiang	Song D.	67.61	22.64	1.74	0.69	0.22	0.61	4.77	0.25	0.04	4.88	0.32	−1.35507	1.36494	−0.0759
LJB-6	Black P.	Linjiang	Song D.	67.83	23.11	1.72	0.7	0.53	0.58	4.88	0.2	0.05	4.8	0.34	−1.14626	1.3538	0.72304
LJB-7	Celadon	Linjiang	Yuan D.	70.49	20.08	1.95	0.24	0.37	0.46	5.38	0.26	0.07	5.63	0.38	0.06517	1.04666	0.15137
LJB-8	Celadon	Linjiang	Yuan D.	70.7	19.56	1.93	0.25	0.56	0.4	5.4	0.32	0.07	5.8	0.41	0.51499	0.78579	0.35006
LJB-9	Black P.	Linjiang	Song D.	67.93	21.23	1.05	0.78	0.28	0.28	5.23	0.28	0.1	5.31	0.34	−0.41874	−0.59792	1.10221
LJB-10	Black P.	Linjiang	Song D.	66.43	22.76	1.18	0.72	0.78	0.5	6.7	0.49	0.03	4.84	0.45	−1.24111	−0.13599	1.06931
LJB-11	B.-W. P.	Linjiang	Ming D.	69.8	20.59	1.21	0.48	0.59	0.33	5.3	0.67	0.08	5.58	0.41	0.60845	−0.70111	0.59813
LJB-12	B.-W. P.	Linjiang	Ming D.	70.44	20.95	1.2	0.08	0.56	0.2	5.06	0.42	0.07	5.52	0.36	0.35951	−0.794	0.78167
LJB-13	B.-W. P.	Linjiang	Ming D.	70.78	21.11	1.18	0.07	0.54	0.19	5.01	0.11	0.07	5.51	0.32	0.00602	−0.52382	0.99776
JZB-1	Black P.	Jizhou	S. Song D.	66.77	23.33	1.31	0.7	0.12	0.31	6.63	0.45	0.001	4.74	0.37	−2.2201	−0.78713	−0.34164
JZB-2	Black P.	Jizhou	S. Song D.	66.68	23.85	1.28	0.69	0.11	0.34	6.5	0.18	0.002	4.63	0.34	−2.65081	−0.36921	−0.05523
JZB-3	Black P.	Jizhou	S. Song D.	67.25	23.07	0.96	0.74	0.11	0.14	6.9	0.49	0.001	4.86	0.37	−2.05659	−1.88877	−0.27114
JZB-4	Black P.	Jizhou	S. Song D.	68.13	23.3	0.94	0.73	0.11	0.24	6.01	0.14	0.001	4.88	0.32	−2.16082	−1.01653	−0.10452
JZB-5	Black P.	Jizhou	S. Song D.	67.96	21.62	1.28	0.8	0.18	0.38	6.91	0.41	0.01	5.19	0.43	−1.53656	−0.53998	−0.35444
JZB-6	Black P.	Jizhou	S. Song D.	68.37	21.15	1.36	0.79	0.2	0.3	6.6	0.41	0.16	5.32	0.41	−1.20596	−0.6768	−0.36553
JZB-7	Black P.	Jizhou	S. Song D.	69.13	21.41	1.02	0.72	0.12	0.55	5.98	0.67	0.003	5.36	0.42	−0.88161	−0.47749	−1.02171
JZB-8	Black P.	Jizhou	S. Song D.	69.1	21.84	1.01	0.72	0.12	0.49	5.79	0.54	0.01	5.27	0.39	−1.03826	−0.47337	−0.70229
JZB-9	Celadon	Jizhou	Song D.	67.06	22.56	0.99	0.06	1.05	0.46	6.33	0.37	0.07	4.92	0.46	−0.54757	−0.18495	2.22191
JZB-10	Celadon	Jizhou	Song D.	66.03	21.9	0.95	0.05	1.07	0.47	6.4	0.43	0.08	4.99	0.49	−0.4177	−0.2983	2.27069
HTB-1	Celadon	Hutian	Song D.	74.12	18.18	0.83	0.05	0.59	0.21	2.97	1.4	0.04	6.74	0.38	3.21286	−2.1683	−1.28554
HTB-2	Celadon	Hutian	Song D.	74.79	18.35	0.88	0.05	0.56	0.2	2.71	1.38	0.04	6.72	0.36	3.29206	−2.064	−1.38903
HTB-3	Celadon	Hutian	Song D.	75.23	19.28	1.45	0.1	0.71	0.37	2.48	0.69	0.07	6.33	0.31	2.68733	0.14775	−0.24948
HTB-4	Celadon	Hutian	Song D.	74.96	18.05	1.4	0.09	1.05	0.36	2.24	1.05	0.08	6.73	0.37	3.87155	−0.26578	−0.00008
HTB-5	Celadon	Hutian	Song D.	75.6	18.22	0.94	0.25	0.41	0.39	2.32	1.01	0.03	6.84	0.32	2.8657	−0.88071	−1.71259
HTB-6	Celadon	Hutian	Song D.	74.39	19.81	0.92	0.24	0.61	0.29	2.28	0.64	0.03	6.21	0.27	2.05689	−0.77811	−0.65248
CSB-1	Celadon	Changsa	Tang D.	72.14	20.63	1.49	0.64	0.19	0.65	3.3	0.44	0.007	5.71	0.29	0.3216	1.11879	−1.43111
CSB-2	Celadon	Changsa	Tang D.	73.63	19.37	1.48	0.64	0.19	0.63	3.38	0.47	0.005	6.19	0.31	0.9252	0.98918	−1.73122
CSB-3	Celadon	Changsa	Tang D.	72.91	20	1.39	0.65	1.29	0.58	2.29	0.35	0.1	5.97	0.34	2.51566	1.41239	1.62255
CSB-4	Celadon	Changsa	Tang D.	73.42	19.99	1.02	0.64	1.08	0.48	2.31	0.57	0.23	6.09	0.34	3.55409	0.58463	3.0638
CSB-5	Celadon	Changsa	Tang D.	70.73	20.65	3.15	0.7	0.4	0.9	2.84	0.17	0.03	5.34	0.28	0.12457	4.39068	−1.09051
CSB-6	Celadon	Changsa	Tang D.	70.03	21.93	3.25	0.65	0.38	0.84	2.42	0.2	0.03	4.99	0.24	−0.22959	4.35024	−0.98873

[a] P = porcelain; B-W = blue and white; S = southern; RO_2 in mol; $RO + R_2O$ in mol; PRIN 1, PRIN 2 and PRIN 3 = principal components 1, 2 and 3.

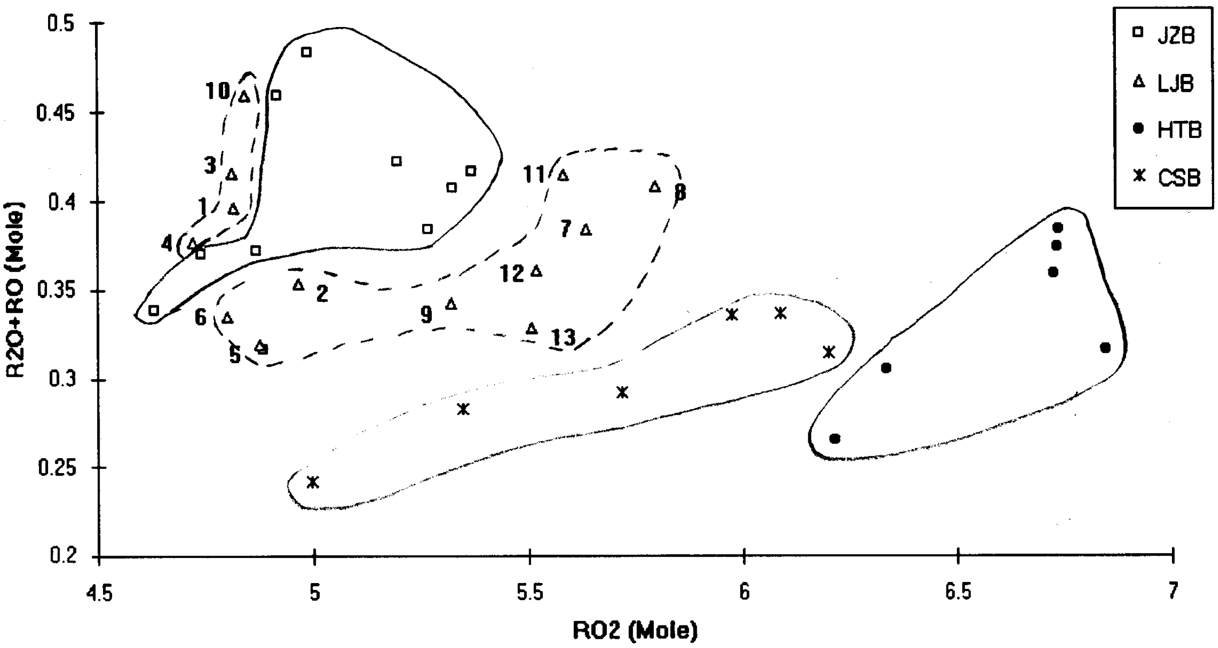

Figure 1. Plot of RO_2 (mol) against $R_2O + RO$ (mol). JZB: Jizhou wares; LJB; Linjiang wares; HTB: Hutian wares; CSB: Changsa wares.

Table 2. Trace element composition ($\mu g\ g^{-1}$)

Sample	Cr_2O_3	NiO	CuO	ZnO	Rb_2O	SrO	Y_2O_3	ZrO_2	BaO	Sum	PRIN 1	PRIN 2	PRIN 3
LJB-1	27	128	50	38	213	167	68	522	487	1700	0.75322	−1.3361	0.58802
LJB-2	94	147	70	39	210	157	67	523	496	1803	1.01646	−0.1743	0.71329
LJB-3	93	127	48	21	230	157	68	504	454	1702	1.03253	−0.7717	0.25617
LJB-4	96	101	35	10	234	151	68	512	439	1646	1.15447	−1.2106	−0.3376
LJB-5	99	118	52	14	173	112	56	537	355	1516	0.91431	−0.4522	−0.563
LJB-6	90	92	53	20	175	114	58	533	385	1520	0.91591	−0.768	−0.9346
LJB-7	57	58	42	64	292	65	52	369	305	1304	−0.6689	−1.0143	−2.0488
LJB-8	52	125	92	104	293	68	57	347	303	1441	−1.2423	0.4613	−0.6783
LJB-9	67	79	37	10	239	179	80	471	415	1577	1.01925	−1.9248	−0.445
LJB-10	48	105	41	22	231	186	80	486	452	1651	0.89771	−1.746	0.23239
LJB-11	87	132	62	106	103	240	73	311	249	1363	−0.2209	−0.7954	0.25919
LJB-12	90	125	32	110	836	52	61	92	141	1539	−3.0925	0.08788	−1.0709
LJB-13	95	141	47	116	876	59	65	142	164	1705	−2.996	0.49317	−0.5691
JZB-1	112	129	99	29	198	176	63	530	643	1979	1.78003	−0.0234	0.7296
JZB-2	127	100	67	25	199	174	76	514	593	1875	1.65338	−0.6202	0.10022
JZB-3	112	194	67	16	194	191	80	510	717	2081	1.83761	0.01299	2.32175
JZB-4	85	139	68	47	202	196	75	514	631	1957	1.36322	−0.6358	1.17007
JZB-5	172	133	70	12	210	160	59	521	699	2036	2.18945	0.21394	0.56551
JZB-6	122	131	66	34	195	155	61	521	598	1883	1.48207	−0.15300	0.44367
JZB-7	68	167	34	4	215	160	67	527	717	1959	1.67591	−0.9300	1.61028
JZB-8	95	155	49	45	212	145	64	526	722	2013	1.33714	−0.2576	1.19518
JZB-9	62	171	52	89	1525	57	270	132	170	2528	−4.9977	0.19443	2.63539
JZB-10	41	130	50	86	1563	55	274	105	144	2448	−5.195	−0.4675	1.90218
HTB-1	76	90	47	32	390	83	38	66	100	922	−1.4673	−0.8551	−2.1146
HTB-2	66	164	68	47	365	79	42	50	121	1002	−1.7946	−0.18874	−0.6288
HTB-3	35	141	59	81	614	62	56	126	157	1331	−2.5235	−0.1307	−0.6504
HTB-4	44	137	45	103	583	58	52	150	146	1318	−2.6389	−0.1066	−0.8817
HTB-5	152	107	23	31	221	124	64	524	259	1505	−0.66113	−0.4239	−0.99
HTB-6	114	127	14	21	224	118	65	524	265	1472	−0.50974	−0.7053	−0.5164
CSB-1	241	114	80	21	173	53	57	540	496	1775	1.50379	1.65817	−1.1016
CSB-2	207	103	46	6	180	62	60	534	480	1678	1.47137	0.61931	−1.1919
CSB-3	222	129	298	24	227	73	61	535	435	2004	1.60923	4.34194	−0.4111
CSB-4	179	195	168	98	232	67	56	539	425	1959	0.23819	3.41787	0.69202
CSB-5	193	102	103	79	259	79	69	511	262	1657	0.10734	1.53324	−1.3226
CSB-6	100	205	143	75	244	70	69	512	331	1749	−0.2859	2.27933	1.04141

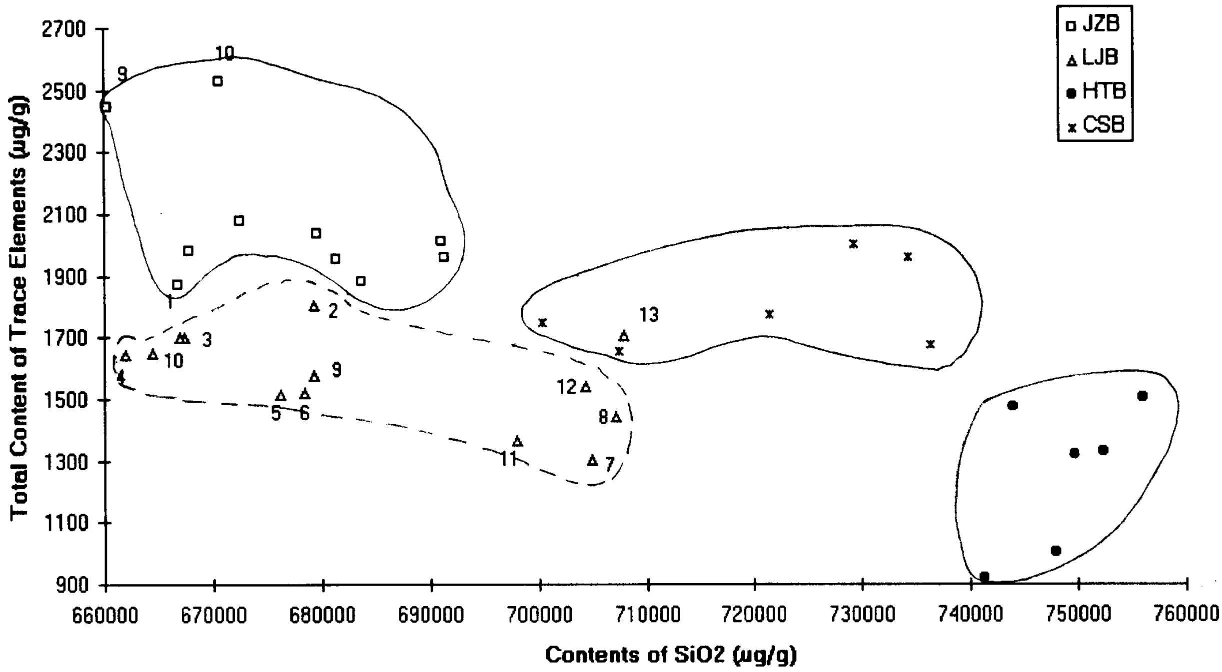

Figure 2. Plot of SiO_2 ($\mu g\ g^{-1}$) against total trace elements from Cr_2O_3 to BaO ($\mu g\ g^{-1}$). JZB: Jizhou wares; LJB: Linjiang wares; HTB: Hutian wares; CSB: Changsa wares.

the highest SiO_2 value corresponds to the lowest Al_2O_3 value, and for LJB and JZB the lowest SiO_2 value corresponds to the highest Al_2O_3 value, the data from both areas showing very similar trends. The concentration of Fe_2O_3 in the wares from all four sites is less than 2% except for CSB-5 and CSB-6, which contain 3.15 and 3.25%, respectively. The low concentration of Fe_2O_3 in the samples is a marked characteristic of good quality ancient porcelain.[6]

Based on the porcelain sample formula,[7] Table 1 shows the results in terms of [RO_2 (mol)] and [R_2O + RO (mol)], where [RO_2] consists of $SiO_2 + TiO_2$ (mol) and [R_2O + RO] consists of $K_2O + Na_2O$ (mol) and CaO + MgO (mol). Figure 1 shows the graph of [RO_2] against [R_2O + RO]. Again, the data for LJB and JZB are very similar. The diagram shows that the LJB data points are clearly divided into two areas with the JZB data points lying in between. Both sets are far

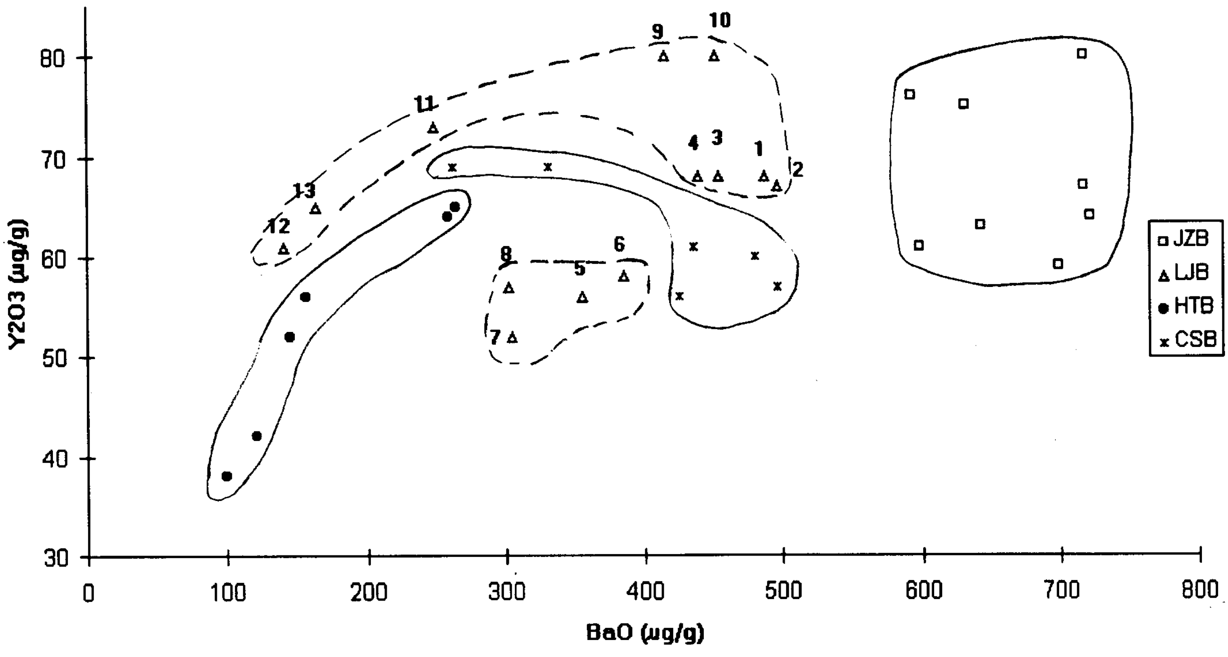

Figure 3. Plot of content of BaO ($\mu g\ g^{-1}$) against that of Y_2O_3 ($\mu g\ g^{-1}$). JZB: Jizhou wares; LJB: Linjiang wares; HTB: Hutian wares; CSB: Changsa wares.

away from the HTB and CSB data points. Some of the LJB and JZB points are very close together, one pair even overlapping. This indicates that the raw material from LJZ and JZB are very similar, which might be expected as the kiln sites are only *ca* 10 km apart.

Trace component analysis

Table 2 shows the concentration of trace elements (Cr–Ba) and the sum of total trace elements for LJB, JZB, HTB and CSB ware. The plot of SiO_2 concentration against the total amounts of trace elements (Fig. 2) indicates that the four kiln sites are clearly discriminated into four separate areas. Looking closely at the distribution of the LJB data, it can be seen that it divides into two subgroups: one (LJB-1, -2, -3, -4, -5, -6, -9 and 10) on the left side of the LJB area represents the black ware of the Song Dynasty (960–1270 AD), while the other (LJB-7, -8, -11, -12, and -13) on the right side represents the celadon and blue–white ware of the Yuan–Ming Dynasty period (1271–1644 AD). It can also be seen that two samples (JZB-9 and -10), both celadon ware, are situated in the upper part of the JZB area while the remaining JZB samples (black ware) are clustered in the lower part of that area.

Several alternative diagrams relating the trace elements can be plotted. Figure 3 shows BaO against Y_2O_3 and again indicates that the sample points from the four sites divide into separate areas with, again, two sub-areas in the LJB ware. Two data points, JZB-9 and -10 (both celadon), are in fact located outside the upper-left side of Fig. 3 as they contain very high concentrations of Y_2O_3 (270 and 274 $\mu g\ g^{-1}$) and very low Ba contents (170 and 144 $\mu g\ g^{-1}$).

Clearly, the trace element chemical composition is a sensitive tool with the potential for discriminating samples with various glazes and from different age periods, as well as discriminating different production kilns (see Fig. 2).

Principal component analysis

Principal component analysis[8] was applied with multiple variables made up from the major element concentrations of Si, Al, Fe, Ca, Mg, K, Na and Mn oxides. The cumulative contributions of the three resulting principle eigenvalues (PRIN 1, PRIN 2 and PRIN 3) reach 46, 71 and 87%, respectively, which means that the data are highly correlated and can be indicated by the three PRIN components. The plot of PRIN 1 against PRIN 2 (Fig. 4) shows that the samples divide clearly into four areas relative to their provenance. The LJB area is again closer to the JZB area than to the others, with two samples (LJB-1 and -2) falling inside the JZB area.

Principal component analysis applied to the trace element concentrations (Cr–Ba) gives three principle components (PRIN 1, PRIN 2 and PRIN 3) with cumulative contributions of 42, 61 and 76%, respectively (Fig. 5). Again, the samples are located in four separate areas with the LJB and JZB groups close. However, five data points still show some scatter. JZB-9 and -10 (celadon) are to the far left side, while LJB-8, -12 and -13 are to the middle-left side of Fig. 5. This is due to the relatively abnormal concentration of a number of trace elements (e.g. Rb, Sr, Y and Ba).

These findings again show the sensitivity of chemical indices/trace elements techniques for discrimination

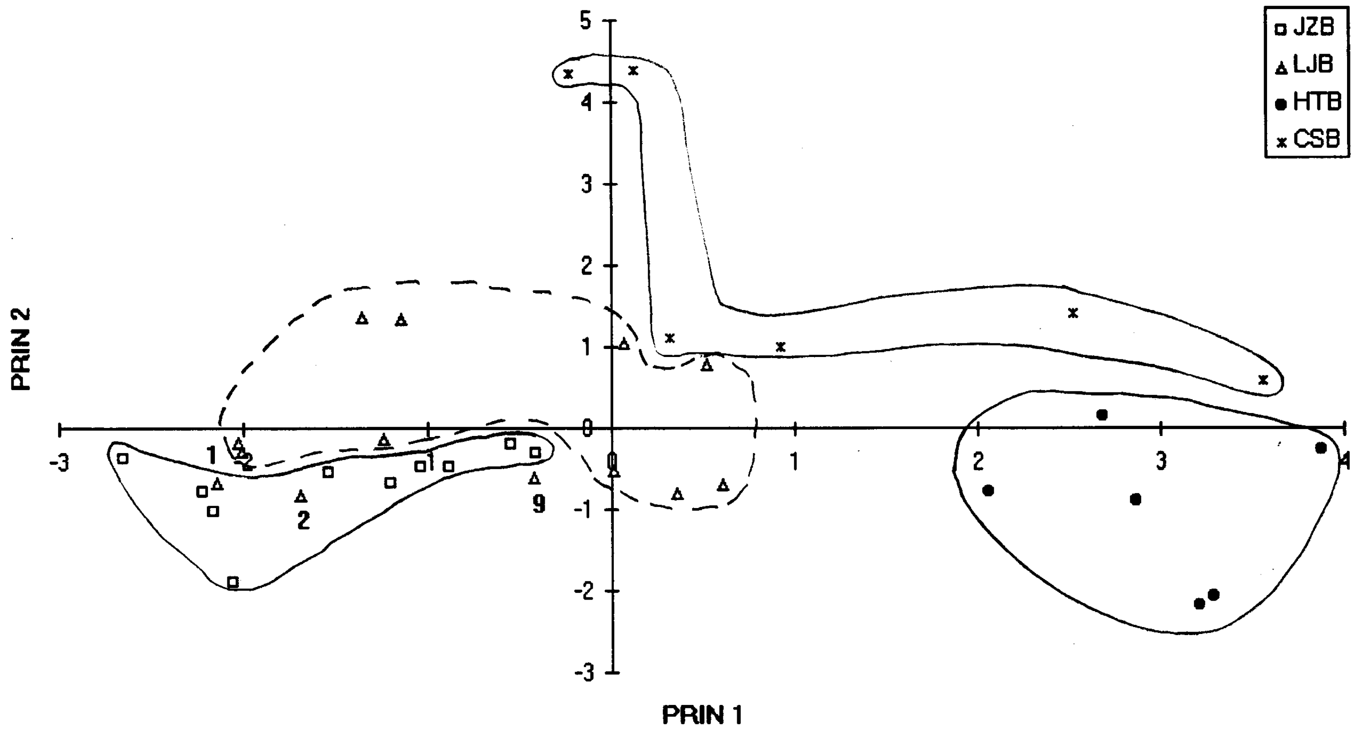

Figure 4. Plot of first two principal components with the concentrations of elements Si–Mn. JZB: Jizhou wares; LJB: Linjiang wares; HTB: Hutian wares; CSB: Changsa wares.

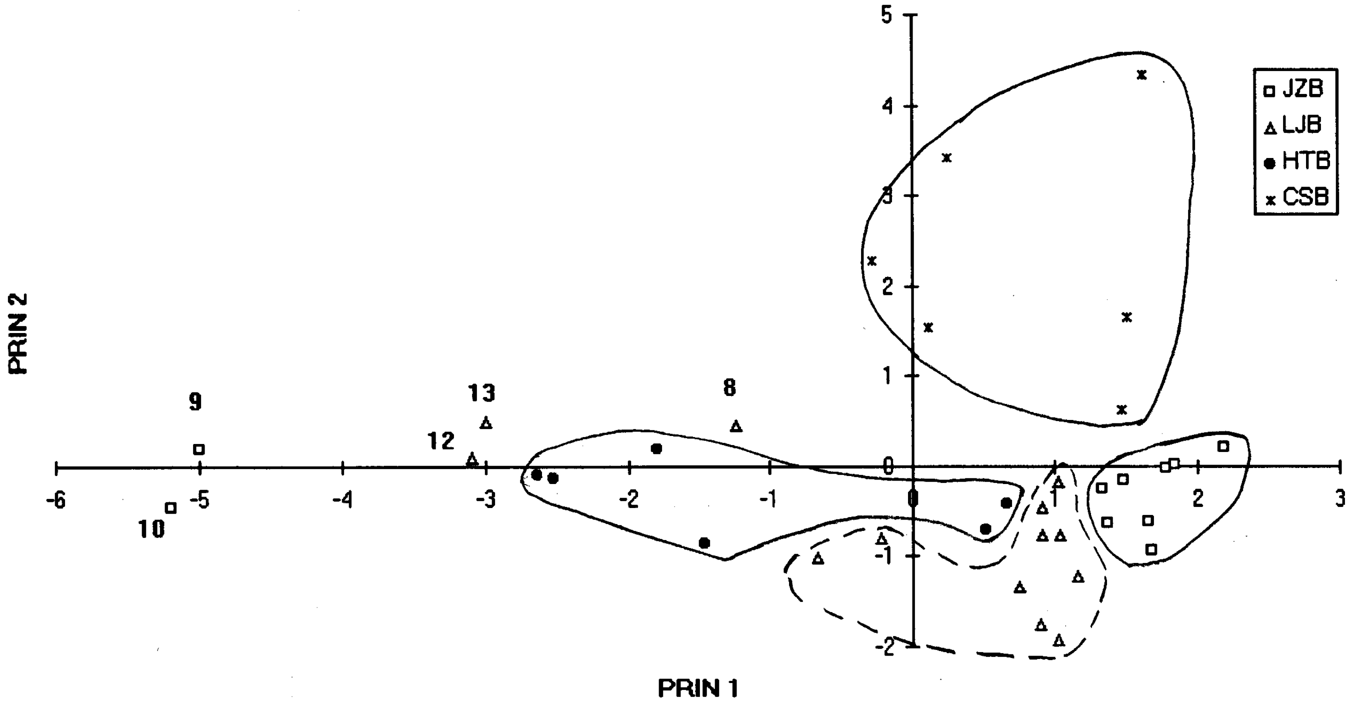

Figure 5. Plot of first two principal components with the concentrations of elements Cr–Ba. JZB: Jizhou wares; LJB: Linjiang wares; HTB: Hutian wares; CSB Changsa wares.

studies. In future studies, more samples of celadon and blue–white ware will be investigated in order to improve the correlation.

CONCLUSION

The chemical composition of Linjiang porcelain body from a newly discovered kiln site has been reported. It is clearly shown that the chemical characteristics may be used as 'fingerprinters' to discriminate between sites of origin. The sample distribution of the LJB data is close to that of the JZB data for most combinations of variables. The results not only reflect the short distance (*ca* 10 km) between the two sites, but are also consistent with the findings of an archaeological study covering vessel style, glaze colour, time period and manufacturing technique, etc., in 1995,[2] which concluded that the Linjiang ware belonged to the Jizhou kiln system. The chemical indices of the trace elements seem to provide a more sensitive method in recognizing the category (e.g. provenance and/or date) of a sample from its body characteristics, despite differences in glazes, e.g. black, blue–white, of samples from the same site. As more data accumulate over the next few years, a data bank of major and trace elements can be concentrated which will provide a major resource for the study of archaeological science.

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REFERENCES

1. Jiangxi Cultural Relic Team, *Archaeology* **5**, 184 (1982).
2. Jiangxi Provincial Institute of Cultural Relics and Archaeology, *J. Archaeol.* **2**, 243 (1995).
3. C. T. Yap, *Appl. Spectrosc.* **45**, 584 (1992).
4. J. Z. Li, H. J. Luo and L. M. Gao, in Proceedings of the International Symposium ISAC92, Shanghai, edited by J. Z. Li and X. Q. Chen, p. 1. Shanghai Scientific Technical Publishers, Shanghai (1992).
5. J. C. Russ, R. B. Shen and R. Jenkins, *EXAM: Principles and Practical Experiments*, p. 62. Publication No. 111-0-E-1277, Part No. 80-01201-00, EDAX International, Mahwah, NJ (1978).
6. J. Z. Li, in *Scientific and Technical Achievement in Ancient Chinese Pottery and Porcelain*, edited by J. Z. Li and X. Q. Chen, p. 1. Shanghai Scientific Technical Publishers, Shanghai (1985).
7. S. P. Chen and X. Q. Chen, *Comprehensive Summary of Chemical Composition of Various Ancient Chinese Pottery and Porcelain*, p. 31. Shanghai Scientific Technical Publishers, Shanghai (1984).
8. J. T. Tou and R. C. Gonzalez, *Pattern Recognition Principle*. Addison-Wesley, New York (1981).

