EDXRF studies of porcelains (800–1600 A.D.) from Fujian, China with chemical proxies and principal component analysis

P. L. Leung,[1]* Z. C. Peng,[2] M. J. Stokes[1] and Mike T. W. Li[1]

[1] Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong
[2] Department of Earth and Space Science, University of Science and Technology of China, Hefei, China

Dehua white porcelain was an important product for exportation in China since the Song Dynasty (1000 A.D.). The energy-dispersive x-ray fluorescence technique was applied to the study of 41 pieces of Dehua porcelain from Fujian Province, China. The chemical proxies and principal component analysis show that most of the samples are basically distributed in three areas, corresponding to their origins of production, but a few of the samples are scattered owing to the abnormal concentration of the trace elements. These findings indicate the sensitivity of chemical proxies/trace element techniques for discriminating the provenance postulations. Copyright © 2000 John Wiley & Sons, Ltd.

INTRODUCTION

Dehua County, located at 118°12′E and 25°25′W in Fujian Province, is near to the south-eastern coast of China. It began to manufacture celadon in the Tang Dynasty (800 A.D.) and to produce white porcelain in the Northern Song Dynasty (960 A.D.).[1] Since the products were exported to Southern-East Asia European countries in the Song Dynasty (1000 A.D.), Dehua ware has become the famous 'Fujian Porcelain Capital,' well known throughout the world as being the same as Ru ware, Guan ware and Ding ware in northern China and Ge ware and Jingdezhen ware in southern China.

Dehua White porcelains appear in peal white, ivory white, milk white, goose-down white and shrimp-beard white, etc.; in particular, the last type was called 'China White' by French businessmen. Dehua white porcelain has been a popular ware spread throughout foreign countries over 11 centuries.

The Dehua ware system consists of 238 kiln sites,[2] located in 17 towns and 68 villages. Dehua white ware was mainly distributed in Xunzhong and Gaide towns: in Xunzhong town there were Qudou-Gong ware (DQ) and Biangu-Xi ware (DB), corresponding to the Song-Yuan Dynasty (960–1368 A.D.), and Zulong-Gong ware (DZ), Lingdou ware (DL) and Housuo ware (DH), corresponding to the Ming Dynasty (1368–1644 A.D.), and in Gaide town there were Wanping-Lun ware (DWP) and Wanyang-Keng ware (DWY), corresponding to the Song-Yuan Dynasty. The distance between the two towns is about 30 km.

Qudou-Gong ware (DQ), a representative of the Xunzhong ware system, was discovered in 1976 and distributed over a 45 000 m² area. There was a test pit (57.1 m long and 1.4–2.95 m wide) discovered in 17 kiln chambers and 14 exits, where 800 tools, kiln implements and porcelain objects were excavated. Various styles of the wares were produced with milk white and green–white glaze, the latter so-called 'Yingqing' in China. Qudou-Gong ware was a base for exportation according to historical records.

Wanping-Lun ware (DWP), a representative of the Gaide ware system, was located over a 1500 m² area and unearthed in a test pit of 87 m², where two kiln bases and 1700 porcelain objects and kiln tools were discovered. The glaze colour is green–white and gray–white. The products were also sold to the South-East Asia.

Mulin ware (DM) was located in Meihu town about 65 km from Xunzhong and began to manufacture celadon products during the Tang Dynasty to the Five Dynasty (618–960 A.D.). There was a test pit 22 m long and 2.3 m wide, where tens of celadon and kiln tools were found. This was one of the earliest wares in the Dehua systems.

The energy-dispersive x-ray fluorescence technique was used to analyze the 41 samples from the above three towns of the Dehua porcelain system and to study their relationship with provenance postulations using chemical proxies and principal component analysis.

EXPERIMENTAL

The EDXRF spectrometer used was an International DX-95 with an Mo target and Si(Li) detector. It has a maximum power of 25 kW, a target angle of 45°, a Be window thickness of 12 μm, the distance of 4.5 cm between the sample and the detector, an exposed diameter of 22 mm and an energy resolution of 0.16 kV.

Twelve thick pellets were made as standard samples at a pressure of 25 ton in^{-2}. On the basis of more than 500 published data related to compound concentrations in ancient China porcelain, each pellet contained known amounts of various compounds, in the ranges 0.1–2% of Na$_2$O, 0.05–3% of MgO, 10–29% of Al$_2$O$_3$, 53–75% of SiO$_2$, 0.5–6% of K$_2$O, 0.1–9% of CaO, 0.05–0.8% of MnO, 0.5–8% of Fe$_2$O$_3$ and 0–600 µg g^{-1} of other trace oxides (Cr$_2$O$_3$, NiO, CuO, ZnO, SrO, Y$_2$O$_3$ZrO$_2$, BaO). The pellets were homogeneously mixed in an agate
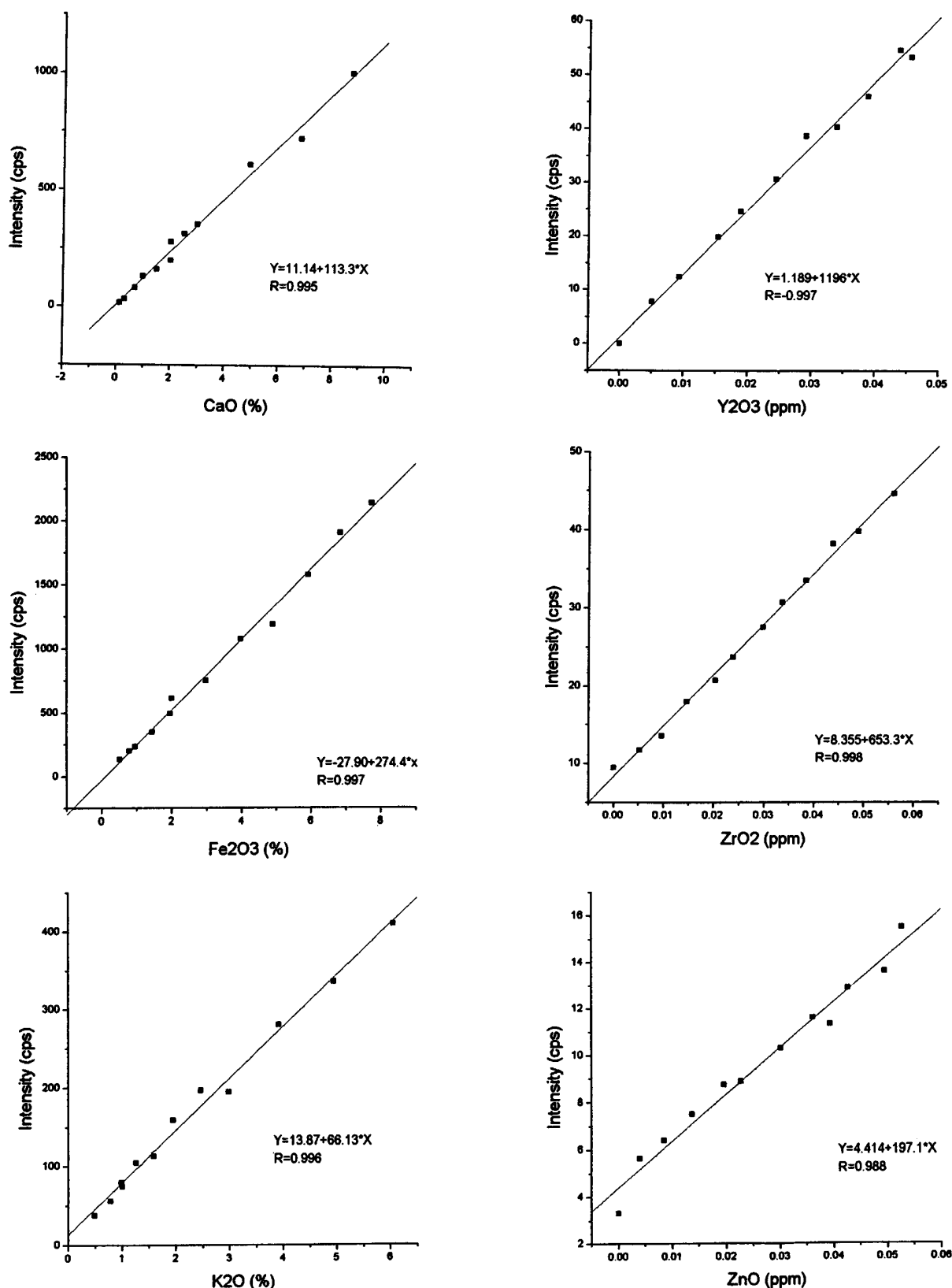

Figure 1. Plots of intensity (cps) against concentration of compounds for some standard pellets.

mortar and pulverized for 8 h. The linear lines between the intensity (counts s^{-1}, cps) and the concentration are partly shown in Fig. 1. Ti and Rb can also be determined using the curve of $\ln(I/C)$ vs $\ln E$, where I = intensity (cps), C = concentration ($\mu g\ g^{-1}$) and E = fluorescence energy (keV). The correlation coefficient between $\ln(I/C)$ and $\ln E$ is 0.99, determined by use of the known parameters for K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Sr and Y compounds.

In order to eliminate the influence of the matrix and the background, DELTA-I software was used for the determination of concentrations. The equation used is $C_i = KI_i[1 + \Sigma(S_j I_j)] + P + \Sigma(B_j I_j)$, where C_i and I_i are the concentration and intensity of compound i, respectively, I_j is the intensity of element j, S and B are the effects of the matrix and background from element $j \neq i$ and K and P are constants. The four parameters can easily be obtained by the iterative method using the known C_j, I_i and I_j from the analysis of standard pellet. After constructing the calibration graph, unknown concentrations of elements in the samples can be calculated. Each porcelain sample was exposed for 500 s at 15 kV and 200 μA for the group Na_2O–ZnO and at 45 kV and 15 μA for Rb_2O–BaO. Based on the measuring conditions, the LLD [lower limit of detection = $3/m(R_b/T_b)^{1/2}$, where m = unit concentration counts, R_b = background counts and T_b = measuring time] corresponds to 0.1% for Na_2O, 0.03% for MgO, 0.03% for Al_2O_3, 0.02% for SiO_2 0.006% for K_2O, 0.003% for CaO, 0.002% for Cr_2O_3, 0.002% for MnO, 0.002% for Fe_2O_3, 0.004% for NiO, 0.001% for CuO, 0.0004% for SrO, 0.0005% for Y_2O_3, 0.0007% for ZrO_2 and 0.0225 for BaO. The RSDs for the major elements were generally in the range 5–10% and those for the trace elements were 10–15%, which are adequate for the purpose of a provenance study of large numbers of ancient Chinese porcelain samples.

RESULTS AND DISCUSSION

Major component analysis

The SiO_2 contents in DQ, DZ, DL, DH and DB, all from Xunzhong, are 72.1–73.7, 71.9–74.2, 72.6–73.6, 72.4–73.0 and 72.4–73.1%, respectively, and the corresponding Al_2O_3 contents are 18.3–20.8, 19.2–21.0, 19.1–20.2, 19.9–20.5 and 20.0–20.6%, respectively. The average values for the above 28 samples are 72.9 ± 0.6% for SiO_2 and 20.0 ± 0.6% for Al_2O_3. The SiO_2 contents in DWP and DWY from Gaide are 70.1–71.8 and 70.1–70.9% and the corresponding Al_2O_3 contents are 20.4–21.8 and 20.8–21.28%. The average values for the Gaide samples are 70.7 ± 0.6% for SiO_2 and 21.2 ± 0.5% for Al_2O_3. The average value of SiO_2 in DM from Meihu is 68.5 ± 0.4% and the corresponding Al_2O_3 content is 22.3 ± 0.3%. It appears that there is a negative correlation between the percentage contents of SiO_2 and Al_2O_3, which is a typical characteristic in porcelain from Southern China. The Fe_2O_3 contents are an important component of the body composition. All of the Fe_2O_3 contents in the Dehua samples are less than 2%. The Fe_2O_3 contents in the samples from Xunzhong are <0.5% and those from Gaide are in the range 0.66–0.92%. However, the samples from Meihu are celadon, which contain slightly higher Fe_2O_3 contents in the range 1.33–1.99%. This is why of the white porcelain produced in Xunzhong and Gaide are of such good quality, because they contain the low Fe_2O_3 contents (<1%).

Based on the porcelain body formula, Table 1 shows the results in terms of [RO_2 (mol)] and [RO (mol) + R_2O (mol)], where [RO_2] consists of SiO_2 + TiO_2 (mol), representative of the body's base, and [RO + R_2O] consists of CaO + MgO (mol) and K_2O + Na_2O (mol), representative of the flux portion. Figure 2(a) shows a plot of
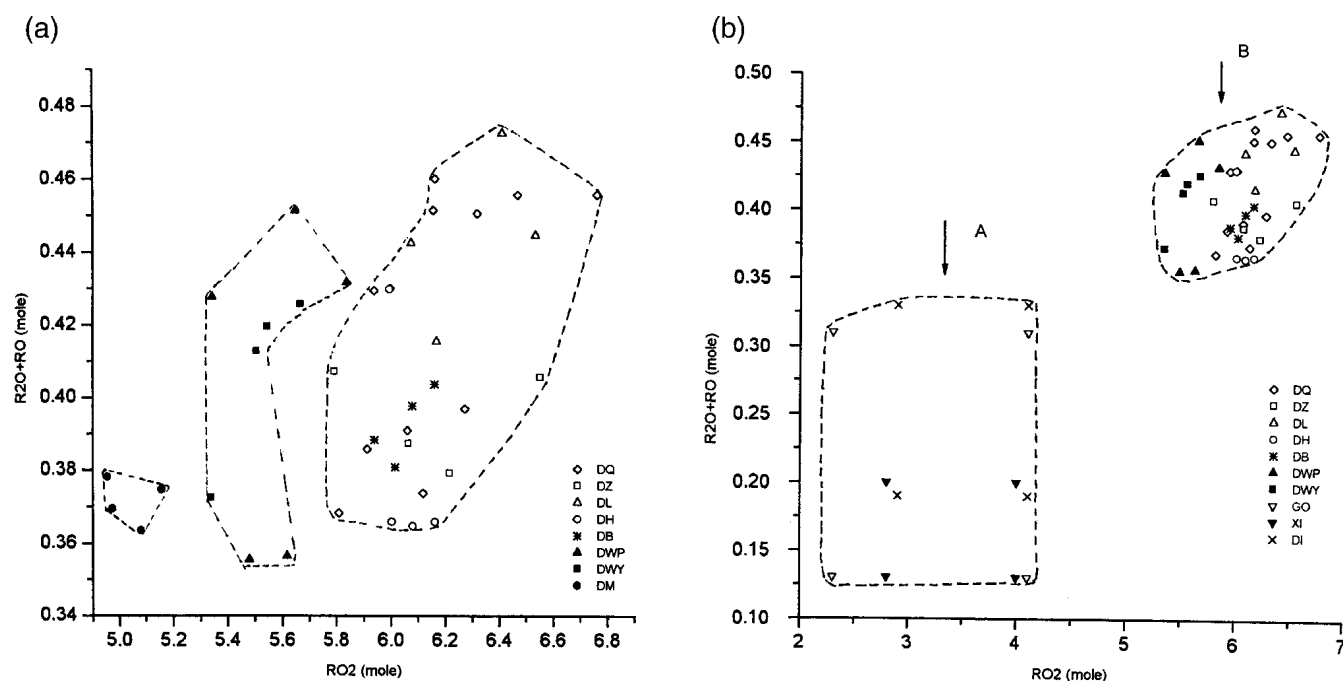
Figure 2. (a) Plot of RO_2 (mol) against RO + R_2O (mol) for Dehua porcelain and (b) plot of RO_2 (mol) against RO + R_2O (mol) in a comparison between southern and northern white porcelains.

Table 1. General description and chemical composition (wt%) of porcelain bodies from Dehua, Fujian, China[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
DQ1	Green–W. P.	Qudou Gong	Song D.	73.09	19.99	0.52	0.05	0.24	0.41	5.18	0.30	0.06	6.12	0.37	−0.67808	0.94157	−0.30077
DQ2	Green–W. P.	Qudou Gong	Song D.	73.66	19.24	0.24	0.09	0.31	0.37	6.30	0.30	0.05	6.46	0.46	−1.17406	1.06545	−0.68616
DQ3	Green–W. P.	Qudou Gong	Song D.	73.41	19.57	0.34	0.13	0.39	0.38	6.19	0.31	0.16	6.32	0.45	−1.86277	3.31528	1.00994
DQ4	Green–W. P.	Qudou Gong	Song D.	72.12	20.39	0.46	0.14	0.31	0.39	6.32	0.28	0.03	5.94	0.43	0.34495	0.89155	−0.54297
DQ5	White P.	Qudou Gong	S.-Yuan D.	72.40	20.44	0.17	0.08	0.44	0.39	6.05	0.30	0.06	6.00	0.43	−0.77736	1.50450	0.10269
DQ6	White P.	Qudou Gong	S.-Yuan D.	72.54	20.00	0.57	0.07	0.34	0.26	5.57	0.38	0.10	6.06	0.39	−1.20317	0.56416	0.36431
DQ7	White P.	Qudou Gong	S.-Yuan D.	72.57	19.78	0.49	0.23	0.47	0.24	6.45	0.37	0.05	6.15	0.45	−0.81857	0.33482	−0.32204
DQ8	White P.	Qudou Gong	S.-Yuan D.	72.55	20.77	0.17	0.10	0.24	0.17	6.14	0.32	0.03	5.91	0.39	−0.33595	−1.30421	−1.28600
DQ9	White P.	Qudou Gong	S.-Yuan D.	72.10	19.64	0.43	0.08	0.32	0.25	6.93	0.27	0.05	6.16	0.46	−0.31163	0.32844	−1.07069
DQ10	White P.	Qudou Gong	S.-Yuan D.	73.53	18.33	0.28	0.06	0.45	0.27	6.04	0.24	0.05	6.76	0.45	−2.28280	0.99489	−1.28730
DQ11	White P.	Qudou Gong	S.-Yuan D.	73.68	19.75	0.36	0.06	0.25	0.21	5.83	0.37	0.04	6.27	0.40	−1.17712	−0.96746	−0.94367
DQ12	White P.	Qudou Gong	S.-Yuan D.	72.31	20.28	1.58	0.57	0.39	0.24	5.41	0.40	0.02	5.81	0.39	1.08535	−0.59195	−0.63402
DZ1	White P.	Zulong	Ming D.	73.38	19.97	0.19	0.09	0.41	0.26	5.02	0.46	0.05	6.22	0.38	−1.94443	−0.51494	0.25994
DZ2	White P.	Zulong	Ming D.	74.22	19.16	0.18	0.08	0.40	0.39	5.07	0.37	0.05	6.55	0.41	−2.17446	0.78695	−0.13390
DZ3	White P.	Zulong	Ming D.	73.46	20.51	0.17	0.11	0.24	0.25	5.88	0.32	0.03	6.06	0.39	−0.61762	−0.68495	−1.16941
DZ4	White P.	Zulong	Ming D.	71.92	21.00	0.23	0.13	0.44	0.31	5.94	0.35	0.09	5.79	0.41	−0.78876	1.34038	0.69678
DL1	White P.	Lingdou	Ming D.	72.82	20.17	0.37	0.07	0.45	0.30	6.29	0.37	0.06	6.07	0.44	−1.01075	0.69902	0.18815
DL2	White P.	Lingdou	Ming D.	73.16	19.20	0.36	0.08	0.36	0.32	6.56	0.37	0.07	6.41	0.47	−1.23653	0.97018	−0.03145
DL3	White P.	Lingdou	Ming D.	73.62	19.07	0.18	0.09	0.47	0.24	5.86	0.44	0.03	6.53	0.44	−2.13882	−0.37697	−0.24597
DL4	White P.	Lingdou	Ming D.	72.86	19.92	0.21	0.12	0.31	0.37	5.57	0.48	0.06	6.17	0.42	−0.99024	0.30362	0.81922
DH1	White P.	Housuo	Ming D.	72.99	20.19	0.38	0.11	0.37	0.14	5.33	0.38	0.05	6.08	0.37	−1.50714	−1.04944	−0.65657
DH2	White P.	Housuo	Ming D.	72.98	19.93	0.36	0.11	0.31	0.23	5.24	0.34	0.07	6.16	0.37	−1.37313	−0.22893	−0.64937
DH3	White P.	Housuo	Ming D.	72.47	20.33	0.39	0.10	0.54	0.37	5.74	0.42	0.02	5.99	0.43	−0.88066	0.48384	0.59498
DH4	White P.	Housuo	Ming D.	72.90	20.51	0.25	0.11	0.17	0.30	5.43	0.37	0.03	6.01	0.37	−0.24538	−1.00521	−0.78860
DB1	White P.	Biangu XI	S.-yuan D.	73.09	20.05	0.23	0.10	0.30	0.38	5.55	0.37	0.05	6.16	0.40	−0.88297	0.49496	−0.02540
DB2	White P.	Biangu XI	S.-yuan D.	72.81	20.46	0.23	0.12	0.32	0.25	5.51	0.40	0.05	6.01	0.38	−1.01010	−0.50791	−0.14114
DB3	White P.	Biangu XI	S.-yuan D.	72.40	20.13	0.21	0.07	0.52	0.39	5.09	0.37	0.08	6.08	0.40	−1.75713	1.59954	0.96845
DB4	White P.	Biangu XI	S.-yuan D.	72.63	20.64	0.26	0.07	0.47	0.30	5.07	0.59	0.09	5.94	0.39	−1.76680	0.09392	2.06517
DWP1	Green–W. P.	Wanping Lun	S.-yuan D.	70.32	20.75	0.83	0.44	0.31	0.32	6.67	0.61	0.06	5.65	0.45	1.50764	−0.14794	1.72077
DWP2	Green–W. P.	Wanping Lun	S.-yuan D.	71.60	21.28	0.67	0.13	0.23	0.33	5.11	0.58	0.05	5.61	0.36	0.38181	−1.12954	1.40295
DWP3	Green–W. P.	Wanping Lun	S.-yuan D.	70.42	21.47	0.66	0.12	0.23	0.23	5.46	0.52	0.05	5.48	0.36	0.79434	−1.64053	0.85521
DWP4	Green–W. P.	Wanping Lun	S.-yuan D.	70.10	21.80	0.86	0.13	0.28	0.37	6.70	0.51	0.02	5.34	0.43	2.18431	−0.56727	1.19991
DWP5	Green–W. P.	Wanping Lun	S.-yuan D.	71.80	20.39	0.87	0.12	0.28	0.28	6.52	0.45	0.02	5.83	0.43	0.77565	−0.91994	0.00209
DWY1	White P.	Wanyang Keng	S.-yuan D.	70.53	21.05	0.92	0.06	0.25	0.28	6.29	0.67	0.02	5.54	0.42	1.27610	−1.98160	1.70748
DWY2	White P.	Wanyang Keng	S.-yuan D.	70.47	21.20	0.92	0.07	0.23	0.34	6.27	0.54	0.02	5.51	0.41	1.58830	−1.20493	1.06455
DWY3	White P.	Wanyang Keng	S.-yuan D.	70.92	20.76	0.85	0.07	0.25	0.24	6.24	0.76	0.03	5.66	0.43	0.77571	−2.54735	2.02710
DWY4	White P.	Wanyang Keng	S.-yuan D.	70.19	21.84	0.86	0.13	0.25	0.38	5.81	0.37	0.06	5.34	0.37	1.60692	0.43091	0.83740
DM1	Celadon	Mulin	Tang D.	68.03	22.67	1.33	1.05	0.17	0.49	6.28	0.20	0.02	4.98	0.37	5.65152	1.68309	−0.66140
DM2	Celadon	Mulin	Tang D.	68.88	22.12	1.34	1.06	0.17	0.42	6.30	0.25	0.02	5.16	0.38	4.97368	1.03826	−0.85628
DM3	Celadon	Mulin	Tang D.	68.46	22.46	1.92	0.82	0.22	0.31	6.90	0.18	0.03	4.96	0.38	5.29085	0.64387	−1.17063
DM4	Celadon	Mulin	Tang D.	68.95	22.02	1.99	0.84	0.22	0.38	6.10	0.29	0.03	5.08	0.36	4.80909	0.61059	−0.38695

[a] W = white; P = porcelain; S = Song; D = Dynasty; RO_2 in mole; $RO + R_2O$ in mole; PRIN 1, PRIN 2 and PRIN 3 = principal components 1, 2 and 3.

RO_2 against $RO + R_2O$, where 41 samples can be divided in to three areas, corresponding to the samples of DQ, DZ, DL, DH and DB from Xunzhong, DWP and DWY from Gaide and DM from Meihu. In a comparison of the Dehua white porcelain with the northern white one porcelain, Fig. 2(b) shows that the northern white porcelains are distributed in the bottom left part of the diagram, whereas the Dehua samples, representative of the southern white porcelain, are the top right part of the diagram. The northern white porcelains consist of Gong ware (GO) from Henan Province and Xing ware (XI) and Ding ware (DI) from Hebei Province. They contain lower values of the RO_2 (mol) and $RO + R_2O$ (mol) than the Dehua samples. The data for the Go, XI and DI porcelain in Fig. 1(b) are taken from Chen and Chen.[4]

Trace component analysis

Table 2 shows the concentrations of trace elements ($Cr_2O_3 - BaO$) and the sum of the total trace elements for DQ–DM ware. The plot of SiO_2 concentration against the total amount of trace elements (see Fig. 3) indicates that the 41 samples from the eight kiln sites are clearly discriminated into three separate areas, corresponding to the samples from Xunzhong, Gaide and Meihu districts. The triangle plot (see Fig. 4) of $ZrO_2\%$, $(TiO_2 10)\%$ and $SrO\%$ (sum $= 100\%$) shows that the samples are basically distributed in three areas, related to their origins of production as mentioned above. However, it is worth noting that sample DQ1 drops into the Gaide group as it contains a higher amount of ZrO_2 and a lower amount of TiO_2 than those in the other samples of the group. Sample DWP1 is far from the Gaide group because it has a higher amount of TiO_2 and lower amount of ZrO_2 than that in the others in the group. Several alternative diagrams relating the trace elements, e.g. $Y_2O_3 - BaO$ ($\mu g\ g^{-1}$), $SrO - Rb_2O$ ($\mu g\ g^{-1}$) and $SrO - ZrO_2 - Rb_2O$ (%) can also be plotted (ellipses here). The results show that most of the samples are discriminated into three areas, but some data points appear with a different dispersion on the basis of the abnormal

Table 2. Trace element compositions ($\mu g\ g^{-1}$) of porcelain bodies from Dehua, Fujian, China

Sample	Cr_2O_3	NiO	CuO	ZnO	Rb_2O	SrO	Y_2O_3	ZrO_2	BaO	Sum	PRIN 1	PRIN 2	PRIN 3
DQ1	159	70	51	60	346	26	121	238	52	1123	−1.61371	0.06455	0.09537
DQ2	42	19	25	64	349	87	148	193	240	1168	1.21523	−0.12289	−0.81378
DQ3	39	94	30	48	335	117	182	229	469	1544	1.26146	0.53006	−0.21814
DQ4	17	79	47	48	350	64	195	225	123	1148	0.14677	1.17817	0.25744
DQ5	74	88	39	33	335	80	150	243	230	1273	−0.13963	0.42903	−0.22581
DQ6	103	96	64	106	305	61	117	235	97	1185	−1.27135	−0.50501	1.01285
DQ7	107	35	38	85	370	55	139	248	159	1236	−0.20653	−0.01199	−0.42387
DQ8	44	58	38	15	374	87	107	210	212	1145	0.63464	0.22994	−0.68956
DQ9	27	99	42	89	346	67	134	215	57	1077	−0.27265	0.23189	0.09379
DQ10	13	91	42	107	349	79	144	204	174	1203	0.42796	0.13439	0.23006
DQ11	102	118	37	22	334	45	187	208	78	1132	−1.00950	1.27081	0.04706
DQ12	34	131	32	75	246	63	55	472	252	1360	−2.16444	−1.48600	−1.37038
DZ1	10	82	32	61	443	102	102	195	305	1332	2.19473	0.57254	−0.41563
DZ2	11	4	30	59	423	94	99	191	331	1242	2.20863	−0.10315	−1.16294
DZ3	10	38	23	33	375	197	125	180	391	1371	2.83911	−0.23882	−0.79139
DZ4	12	52	18	44	388	217	131	189	524	1575	3.32785	−0.19845	−0.84595
DL1	50	91	34	37	401	94	114	209	174	1203	0.47188	0.56502	−0.56865
DL2	119	146	52	65	392	92	106	188	201	1362	−0.48485	0.48481	0.63691
DL3	65	64	52	67	401	121	117	177	256	1321	1.08950	0.15169	0.37204
DL4	46	37	30	49	405	151	127	173	377	1394	2.24812	0.05315	−0.55832
DH1	12	20	13	43	421	131	108	186	582	1517	3.15036	−0.13750	−1.64010
DH2	111	100	40	66	423	138	109	188	553	1728	1.55000	0.14839	0.02960
DH3	54	103	40	11	413	150	141	184	661	1756	2.36291	0.84407	−0.07000
DH4	4	86	149	127	371	162	178	158	400	1635	1.46818	0.61244	4.93819
DB1	150	83	59	37	351	46	181	191	98	1195	−1.01408	1.03224	0.87580
DB2	75	100	43	27	368	47	177	171	96	1103	−0.27151	1.36343	0.19335
DB3	100	60	52	63	217	217	102	139	437	1385	1.39588	−2.10198	1.09519
DB4	67	68	49	61	242	251	116	142	148	1143	1.19373	−1.59531	1.12758
DWP1	56	107	34	27	422	77	111	299	173	1307	−0.27290	0.90913	−0.96240
DWP2	55	41	38	59	289	19	97	328	73	1000	−1.36469	−0.77699	−1.05681
DWP3	45	85	30	37	294	14	106	352	49	1012	−1.79449	−0.20003	−1.34575
DWP4	34	102	46	1	385	58	263	328	70	1286	−0.67185	2.75980	0.05534
DWP5	83	102	56	12	383	58	264	327	64	1349	−1.12969	2.64165	0.57942
DWY1	102	53	52	42	268	24	102	305	34	982	−1.95788	−0.72641	−0.30283
DWY2	45	4	45	56	278	30	104	308	34	903	−0.99661	−0.96287	−0.80944
DWY3	75	47	75	61	266	22	94	276	34	950	−1.74559	−0.86151	0.65335
DWY4	75	109	64	57	389	45	239	287	124	1389	−0.88322	2.19377	1.05336
DM1	192	178	47	72	334	43	57	361	43	1327	−3.48490	−0.39546	−0.16562
DM2	114	161	72	88	318	38	58	368	72	1288	−3.02651	−0.51027	0.66083
DM3	120	131	36	47	325	56	47	342	153	1259	−2.03906	−0.72481	−0.96317
DM4	223	99	52	69	327	52	51	359	174	1406	−2.72374	−1.10577	−0.28644
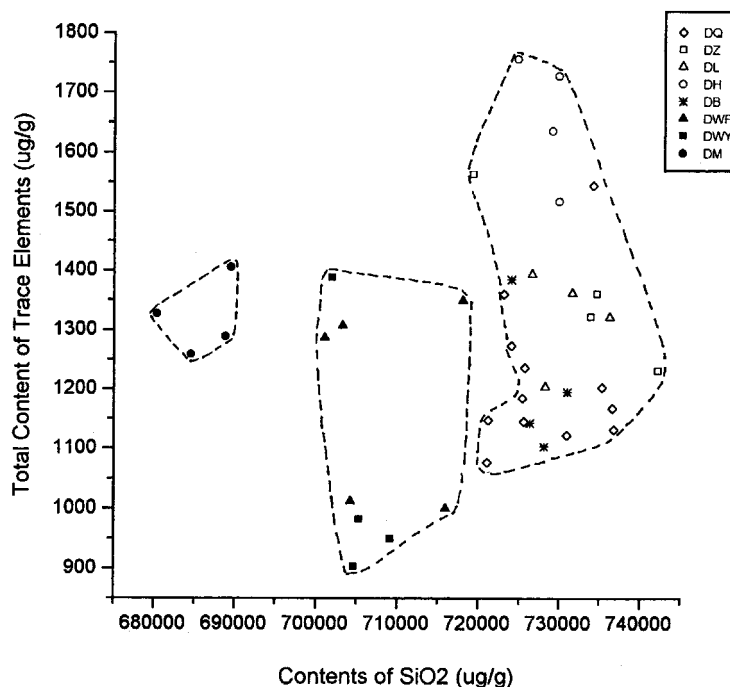
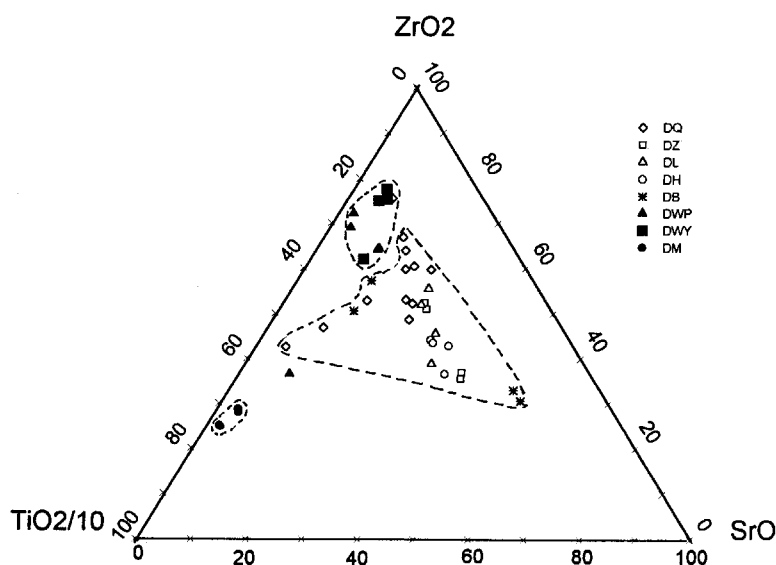**Figure 3.** Plot of SiO$_3$ (μg g^{-1}) against total trace elements from Cr$_2$O$_3$ to BaO (μg g^{-1}).

Figure 4. Triangle diagram for ZrO$_2$% + TiO$_2$10)% + SrO% (sum = 100%).

concentrations of the trace elements in these special samples. This indicates that the varied chemical proxies of the trace elements will apply diverse information for a porcelain provenance study.

Principal component analysis

Statistical mathematics has been used as a potential tool to recognize porcelain proverance.[5] For our study, principal component analysis was performed with the multiple variables made up from major element concentrations (SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$, CaO, MgO, K$_2$O, Na$_2$O and MnO) and trace element concentrations (Cr$_2$O$_3$, NiO, CuO, ZnO, Rb$_2$O, SrO, Y$_2$O$_3$, ZrO$_2$ and BaO). Based on the statistical calculations, the accumulative contributions of the

three resulting principal eigenvalues (PRIN 1, PRIN 2 and PRIN 3) for SiO$_2$–MnO reach 45, 73 and 83%, respectively, which means that the data are well correlated and can be indicated by the three PRIN components. Figure 5 shows the plot of PRIN 1 against PRIN 2, which indicates that the porcelain samples can be divided into three areas, corresponding to the Xunzhong, Gaide and Meihu groups. Principal component analysis applied to the trace element concentrations (Cr$_2$O$_3$–BaO) gives the three principal components (PRIN 1, PRIN 2 and PRIN 3) with cumulative contributions of 49, 63 and 75%, respectively. The distributive pattern of the samples shown in the plot of PRIN 1 against PRIN 3 (Fig. 6) is basically the as same as that in Fig. 5. However, the six samples (DQ1, DQ6, DQ11, DQ12, DH4 and DB1) are far from their
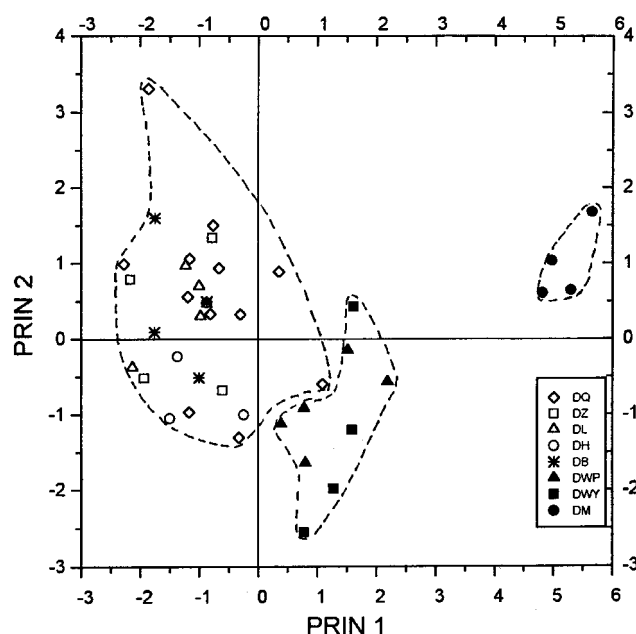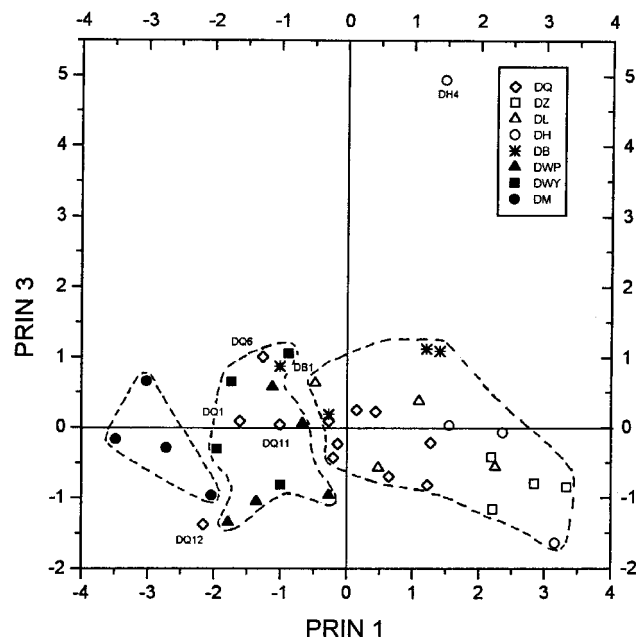
Figure 5. Plot of first two principal components with the concentrations of elements SiO_2–MnO.

Figure 6. Plot of first and third principal components with the concentrations of elements Cr_2O_3–BaO.

group: four of them drop into the Gaide district, one is close to the Gaide and Meihu districts and one is far from the three groups. This is due to the relatively abnormal concentration of a number of trace element compounds (Cr_2O_3, ZnO, Y_2O_3 and ZrO_2) in these special samples (see Table 1). This indicates a high sensitivity of chemical proxy/trace element techniques for discrimination studies.

CONCLUSION

The chemical compositions of major (SiO_2–MnO) and trace (Cr_2O_3–BaO) elements have been used for recognizing the proveniance of Dehua porcelain. Figures 2–4 show that the 41 samples from eight kiln sites are distributed in three areas, corresponding to their original places of production, Xunzhong, Gaide and Meihu towns, respectively. Principal component analysis (PRIN 1, PRIN 2 and

PRIN 3) gives the same results as the chemical proxies. However, the data points with the trace elements in the Fig. 6 are very scattered because some concentration of the trace elements appears in the abnormal values. This means that chemical proxies of the trace elements can be used more sensitively as fingerprints to distinguish among sites of origin. This is not only significant for research into the basic science, production and evolution of porcelain manufacture, but is also beneficial to discriminating between genuine and false ceramics. Therefore, EDXRF is a powerful method for studies in archaeological science.

REFERENCES

1. Management Committee of Dehua County. *Cultural Relic Chronicles of Dehua County, China*. Fujian Geological Press: Fuzhou, 1993; 29–39.
2. Xu BZ, Chen JZ. *Quanzhou Weibol* 1997; **5**: 23–32.
3. Leung PL, Stockes MJ, Li MTW, Peng ZC, Wu SC. *X-Ray Spectrom.* 1998; **27**: 11–16.
4. Chen SP, Chen XQ. *Comprehensive Summary of Chemical Composition of Various Ancient Chinese Pottery and Porcelain*. Shanghai Scientific Technical Publishers: Shanghai, 1984; 31.
5. Yap CT. *App. Spectrosc.* 1991; **45**: 584–587.