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Chemical analysis of white porcelains from the Ding Kiln site, Hebei Province, China

Jianfeng Cui[a], Nigel Wood[b,c], Dashu Qin[a,*], Lijun Zhou[a], Mikyung Ko[a], Xin Li[a]

[a] School of Archaeology and Museology, Peking University, Beijing, 100871, China
[b] University of Westminster, Northwick Park, Harrow, HA1 3TP, UK
[c] Research Laboratory for Archaeology and the History of Art, Dyson Perrins Building, South Parks Road, Oxford OX1 3QY, UK

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A B S T R A C T

The Ding kilns were some of the most famous early kilns of medieval China, producing huge quantities of white and cream-white porcelains of outstanding technical and aesthetic quality. Since 1949 they have been excavated three times, in 1965, in 1987, and in 2009 respectively. In this latest study 69 white porcelain sherds from assured contexts and from the 2009 excavations were analyzed using laser ablation techniques (ICP-AES). The samples date from Five Dynasties, Northern Song and Jin Dynasties respectively (early 10th to early 13th C CE). The results show that Ding wares of different times show different characteristics that can be demonstrated through chemical composition. During the early phase of production the Ding ware bodies consisted largely of high firing kaolinitic clays with predominantly calcareous materials as fluxes. After the early Northern Song Dynasty, some calcareous material was replaced by a more potassic material. The compositions of the glazes show a parallel evolution to the bodies. However, because the glazes are very low in titania it seems unlikely that the main clay ingredients of the bodies could have been used in the glaze recipes. For much of the kiln site's history the glazes appear to have been made mainly from the same siliceous flux-rich materials that had been blended with the main body-clays used to make the Ding ware porcelains, plus some extra calcareous material. The P_2O_5 contents of the glazes suggest that wood ash may have been one source of CaO in the glaze recipes.

1. Introduction

From the 9th to the early 12th centuries the Ding kilns were some of the most famous kilns in China, using kiln-temperatures and porcelain-recipes that were not matched in Europe until the early 18th C at Meissen in Saxony. The wares were made in very large quantities and their appearance and firing technologies were imitated by many other ceramics-centres during the 10th to 13th Cs, such as the Cizhou kilns in north China and the Jingdezhen kilns in south China (Li et al., 2005). The focus of Ding ware manufacture-was located in north China at Jianci and Beizhen villages in Quyang county, Baoding city, Hebei Province, while another important Ding ware kiln site operated in Yanchuan village/Yebei village area, about 8km to the east of Jianci and Beizhen villages.

Before our excavations in 2009, the Ding sites had been excavated twice since 1949. The two earlier studies had shown that a limited number of vessels with black, green and dark brown glazes were made in parallel with the main white porcelain production. The Ding potters also pioneered advanced techniques for stacking porcelain bowls and dishes rim-downwards in the kilns, separated by supporting rings, or by setters with stepped interiors. This practice increased kiln output, and aided production efficiency. However, as a consequence of the technique the mouth-rims of many Ding wares were unglazed, which came to be considered a flaw by Ding ware's more important patrons. To overcome the problem finer examples often had their mouth-rims finished with gold, silver, or copper rings, thereby enhancing the quality of the porcelain and adding to its appeal (Kerr and Wood, 2004:157–162; 543–545).

Over the years a number of scientific analyses have been made of the glazes and the bodies of Ding wares (Zhang, et al, 1983, Li and Guo,1987; Li and Guo,1988; Li and Guo, 1985; Li,1998; Zhang,2000; Kerr and Wood, 2004:157–162;543–545.). The results showed the excellent quality of the Ding ware material, with its high-temperature glaze and its well-matured body consisting of fine white kaolinitic clay. The glaze was of the magnesia-lime type – an

* Corresponding author. Tel.: +86 10 62753245; fax: +86 10 62757493.
E-mail address: qindashu@pku.edu.cn (D. Qin).

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unusual approach to glaze-design, due to its relatively high MgO content in relation to CaO.

2. The new archaeological excavation of Ding Kilns site

In 2009, archaeological excavation at the Ding ware kiln site was conducted by a joint archaeological team from the School of Archaeology and Museology, Peking University and the Hebei Provincial Archaeological Institute. The regions excavated included the Jianci (JC) site, the Jianxi site (JX), (the western Jianci site), the Beizhen (BZ) site and the Yanchuan (YC) site. The former three sites formed the core of Ding ware production from the late Tang Dynasty (9^{th} C.E.) to the Jin Dynasty (1115–1234A.D.) and operated within about a one kilometer square area (see Fig. 1.) These sites are only a few hundred meters from each other. According to historical records, Beizhen and Jianci villages were once part s of the Longquan Township. (Longquan is the ancient name of Beizhen and Jianci villages, and not to be confused with another famous kiln-complex in southern China.) Thus both Jianci site and Beizhen site can be considered as members of one large kiln-group Tons of ceramic sherds and decades of kiln relics from different periods were found during the 2009 excavations

The work also showed that the Ding kilns started producing white porcelains in the late Tang Dynasty(9^{th} C CE and ended in the Yuan Dynasty (1276 - 1368 C.E.). A considerable number of unearthed sherds were carved with the words of '官' ('*guan*', -Government) , '尚食局' ('*shangshiju*-' Imperial Food Bureau), '尚药局' ('*shangyaoju*' -Imperial Medicine Bureau), and '东宫' ('*dong-gong*'- Palace of the Prince), implying that they were made for court or governmental use, and that the Ding kilns were tribute kilns during the Northern Song and Jin Dynasties. At the same time, the excavation has shown that the kilns also produced large quantities of ceramics for ordinary people (Han et al., 2010). In terms of chronology, the new archaeological excavations provided a set of white porcelain samples from the earlier years of Ding ware in the 10^{th} century, from its heyday in the 11^{th} to 12^{th} centuries, and through its decline and closure in the 13th C. Through the use of chemical analysis it has been possible to show the developmental history of the raw materials and the technology of Ding wares, together with the some new phenomena unreported by previous researchers.

3. Samples and analytical methods

In this study, we have analyzed 69 ceramic sherds, all recently excavated from the Ding ware sites. According to analysis and research following the excavation it seems that Ding manufacture was moved over time, with different places having specific importance in different periods. Thus the Beizhen samples all come from the same stratum, which is dated to the Five Dynasties period (FD, 907–960 C.E.). The Jianci samples are all from a stratum dated to the late Northern Song Dynasty (NSD, second half of 11^{th} century to the first quarter of 12^{th} century), while the Jianxi samples are all dated to the late Jin Dynasty (JD, 1115–1234 C.E.). Table 1 is the catalog of the samples, while Fig. 2 shows representative analyses from the three groups.

The samples were quantitatively analyzed for their glazes' and bodies' chemical compositions using Laser Ablation Inductive Coupled Plasma Atomic Emission Spectrometry (LA-ICP-AES). A LEEMAN-Prodigy ICP-AES with a NEW-WAVE laser ablation system was used to carry out the analyses. The operating conditions for the LA-ICP-AES system are as follows: 1) RF generator: 40.82 MHz; 2) RF Power: 1.1 kw; 3) Argon flow rate: Plasma: 1.4 l/min; 4)Auxiliary pressure: 0 psig; Nebuliser pressure: 30 psig; 5) Laser: Nd-YAG; 6) Laser mode: Q-switched; 7) Laser Wavelength: 266 nm; 8) Output energy: 15 ± 1mJ; 9) Facular aperture: 610 μm; 10) Helium flow rate: 1050 ml/min.

Si is used as an internal standard (Ducreux-Zappa and Mermet, 1995), while Corning B and NIST 610 glass standards are used as standard reference materials. In all, fourteen elements were determined, including Al, Fe, Mg, Ca, Na, K, Ti, Mn, Ba, Sr, Cu, Zn, Zr and Sc. The SiO_2 data were calculated by subtracting the sum of all other elements in weight per cent oxides from 100%.The analytical details and calibration method for bodies are presented elsewhere (Cui et al., 2010).

4. Results

4.1. Bodies

Table 2 are the bodies' results.

Table 3 lists the average and std. deviation of major and minor elements (in oxides) of bodies from the different excavated places.

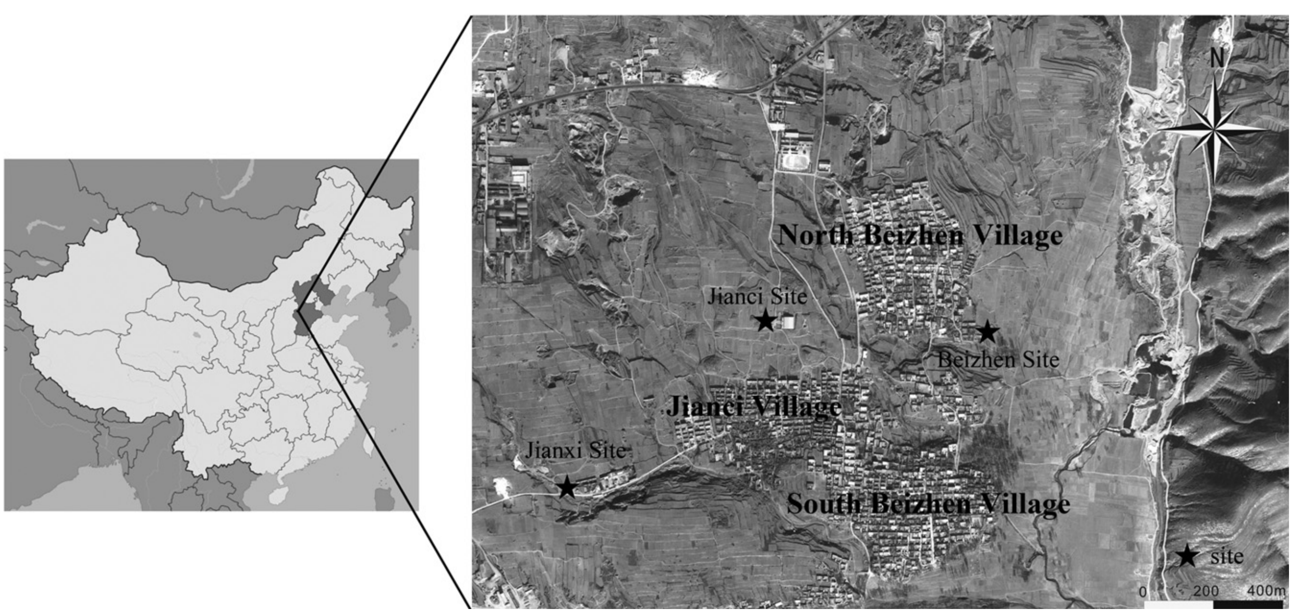

Fig. 1. The location of the Ding Kiln sites archaeologically excavated in 2009.

Table 1
Catalogue of samples.

Prefix of the sample name	Archaeological information	Location	Date	Archaeological Context
BZ-FD (FD Samples)	Excavated from the 4th layer of BZT5 square unit	Beizhen Site	Five Dynasties (907–960 C.E.)	Fine white porcelain
JC-NSD (NSD Samples)	Excavated from the 6th layer of JCBT1 square unit	Jianci Site	North Song Dynasty (960–1127 C.E.)	Fine white porcelain
JX-JD (JD Samples)	Excavated from the 3rd layer of JXT1 square unit	Jianxi (western Jianci) Site	Jin Dynasty (1115–1234 C.E.)	No.1–4 and No.6–17 are black porcelain, No.5 is ring-shaped setter,others are all fine white porcelain.

The results show that all the bodies are made from high-firing clays with alumina levels above 25%. This is characteristic of white porcelain manufacture in north China during the period from the Tang Dynasty until the Yuan Dynasty (Li and Guo, 1988:97–100). There are minor chemical differences among the samples from the three periods, suggesting that, although the samples belong to different times and sites, their raw materials may have been from similar sources. The small differences observed may be due to different recipes, slight variations in raw materials, or to some changes in processing techniques in the different periods.

The chemical data were statistically analyzed using the PCA (principle components analysis) method processed on the 15th version of the SPSS software. The plots of the first three components are shown in Fig. 3. and Table 4 is the component loading matrix derived from the PCA. Selected elements for all samples are illustrated with binary plots in Fig. 4 of the chemical compositions of the bodies

From the above figures and Table 3, we can conclude that the chemical compositions of the bodies of Ding wares from different periods (and from their associated sites) differ slightly. Although the distinctions are small, they can be effectively grouped using multivariate statistics analysis.

4.2. Glazes

Table 5 are the glazes' results.

Table 6 compares the means of all major and minor elements in the glazes of the white wares from the three groups of samples under study. The table shows that the glazes did not change greatly through time. The aluminum oxide contents of the Ding glazes are significantly high, which make them highly refractory, in accordance with the high temperatures needed to mature the bodies (about 1300^{o} C measured using a thermal dilatometer, over 4–6 hours (see Li and Guo, 1988:107)). However, the actual firing times used in small coal burning *mantou* kilns (such as those used for Ding wares) have been established at about 100 hours, with a very slow finish (Shui, 1989: 473) . Since it is known that very slow firings can reduce the finishing firing temperatures needed to mature ceramics substantially, the actual firing temperatures used for Ding wares may have been appreciably lower than the measured ones (Tite and Wood, 2005: 32).

The results also show that Ding wares used a kind of magnesia-lime glaze, with relatively high magnesia-to-calcia ratios. Weight per cent levels of MgO are often more than 2%, which is uncommon with early Chinese ceramic glazes, see Li, 1998:143. Another feature of Ding glazes, already noted elsewhere, is that their RO: R_2O ratios approach 2:1, which supplies certain richness to their fired quality. This feature can also be seen in our results, especially in glazes of the Jin and Northern Song groups.

Next figures (Fig. 5 a-Fig. 5c) are some binary plots of selected elements in glazes.

5. Discussion

5.1. Bodies

The results show that the contents of some major and minor elements, such as Al, Fe, Ti, K, and trace elements such as Sr, Ba,

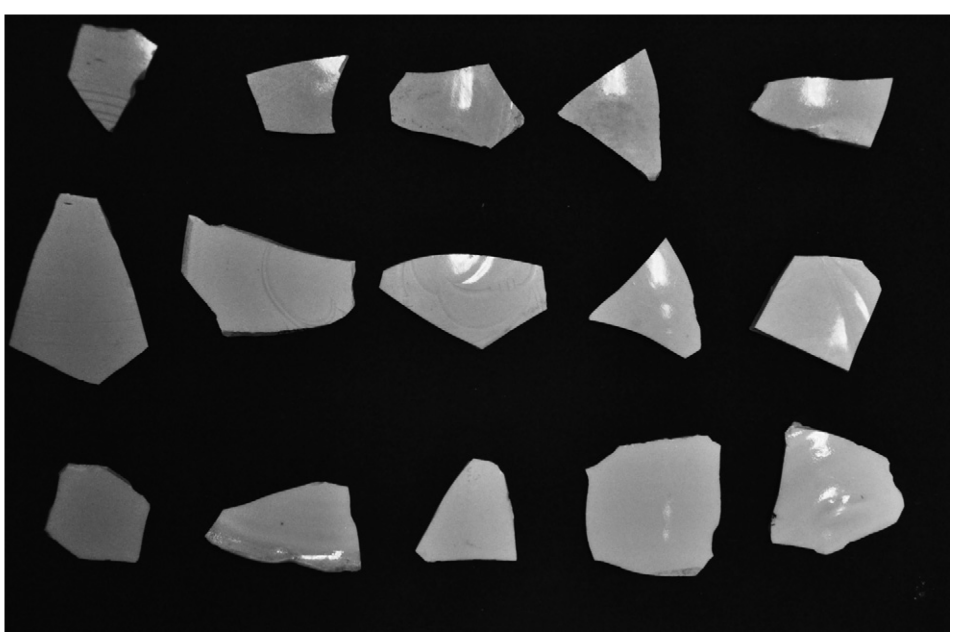

Fig. 2. some representative samples from Ding Kiln sites(Top: JD samples; Middle: NSD samples; Bottom: WD samples).

Table 2
Chemical results of the bodies of the Ding wares (the data from SiO_2 to MnO are in wt%, others in ppm).

Sample ID	SiO_2	Al_2O_3	Fe_2O_3	MgO	Ca O	Na $_2$O	K $_2$O	TiO_2	P_2O_5	MnO	Cu	Zn	Y	Zr	Sr	Ba	Co	Ni	Sc
BZ-FD-01	67.31	28.11	0.84	0.85	0.86	0.60	1.00	0.44	0.04	0.02	22	61	7	121	144	520	22	0	6
BZ-FD-02	68.06	26.93	0.78	0.98	1.29	0.66	0.68	0.62	0.02	0.02	45	94	41	325	124	303	19	35	15
BZ-FD-03	64.94	30.02	0.58	1.01	1.56	0.44	1.17	0.28	0.04	0.03	23	54	5	261	128	418	24	61	5
BZ-FD-04	62.37	32.26	0.73	1.29	1.12	0.62	1.21	0.40	0.02	0.02	18	47	6	111	207	671	11	18	6
BZ-FD-05	65.02	30.17	0.67	1.10	0.78	0.70	1.23	0.34	0.01	0.01	17	28	4	103	218	503	13	14	5
BZ-FD-06	65.99	28.49	0.77	1.19	1.32	0.77	1.07	0.39	0.02	0.02	28	32	11	155	213	902	23	20	9
BZ-FD-07	70.40	25.14	0.60	1.09	0.97	0.48	0.98	0.33	0.03	0.03	17	40	4	132	187	476	13	15	4
BZ-FD-08	64.40	30.63	0.73	0.79	1.00	0.89	1.14	0.42	0.03	0.02	22	50	18	192	138	425	19	27	8
BZ-FD-09	62.03	32.90	0.92	1.09	1.05	0.29	1.37	0.35	0.02	0.01	15	51	11	135	140	1456	14	9	8
BZ-FD-10	68.29	27.16	0.63	1.14	0.83	0.63	1.03	0.29	0.02	0.03	22	21	9	1170	134	899	20	8	5
BZ-FD-11	65.11	27.94	0.61	1.11	3.27	1.00	0.53	0.43	0.07	0.03	30	47	8	155	192	481	18	13	5
BZ-FD-12	63.99	30.80	0.84	1.15	1.12	0.80	0.95	0.35	0.02	0.01	22	29	6	119	242	835	15	6	6
BZ-FD-13	66.25	28.19	0.76	0.96	1.87	0.19	1.38	0.40	0.02	0.03	20	62	3	187	138	416	47	0	5
BZ-FD-14	66.08	29.41	0.59	1.12	0.82	0.60	1.07	0.32	0.04	0.02	25	24	5	218	189	529	11	0	5
BZ-FD-15	67.59	27.93	0.54	0.95	1.35	0.19	1.05	0.39	0.05	0.01	27	76	17	148	109	243	24	39	9
BZ-FD-16	63.99	30.52	0.70	1.53	1.96	0.19	0.66	0.44	0.03	0.02	38	42	19	147	135	682	18	13	9
BZ-FD-17	64.06	29.08	0.66	1.11	3.29	0.89	0.47	0.45	0.04	0.01	44	47	4	77	196	427	33	4	7
BZ-FD-18	63.54	30.04	0.62	1.13	2.55	0.72	1.07	0.35	0.02	0.04	24	66	4	172	144	346	35	22	5
BZ-FD-19	61.93	31.13	0.65	1.08	3.61	0.35	0.74	0.51	0.03	0.02	33	29	22	233	163	530	18	10	18
BZ-FD-20	65.01	30.21	0.69	0.94	1.10	0.28	1.41	0.38	0.02	0.01	15	25	6	136	146	546	8	9	7
JC-NSD-02	61.56	33.35	0.74	1.09	0.63	0.42	1.49	0.72	0.03	0.02	15	29	20	366	89	155	27	25	23
JC-NSD-04	63.37	31.21	0.60	1.13	0.94	0.47	1.64	0.64	0.04	0.03	18	20	16	216	93	277	24	28	17
JC-NSD-05	59.22	35.36	0.74	1.07	1.49	0.15	1.01	0.97	0.03	0.01	23	31	29	585	105	204	31	26	30
JC-NSD-06	63.08	32.26	0.55	0.88	0.78	0.50	1.38	0.58	0.02	0.02	20	0	23	310	90	237	15	9	19
JC-NSD-07	59.12	36.03	0.67	1.30	0.77	0.14	1.23	0.73	0.03	0.02	17	68	29	350	111	183	20	19	19
JC-NSD-08	63.41	30.42	0.60	1.03	2.08	0.26	1.18	1.00	0.03	0.02	24	0	46	372	104	244	30	23	21
JC-NSD-09	63.15	31.81	0.69	1.03	0.62	0.93	1.07	0.70	0.02	0.02	11	26	21	556	91	130	20	43	22
JC-NSD-11	63.95	29.84	0.92	1.64	1.35	0.17	1.53	0.61	0.04	0.03	16	63	23	292	98	114	16	31	15
JC-NSD-12	66.27	28.98	0.61	0.75	0.80	0.48	1.58	0.53	0.03	0.01	17	32	13	157	29	238	1	13	12
JC-NSD-13	61.76	31.89	0.89	1.25	1.93	0.43	1.04	0.81	0.03	0.01	18	11	31	466	108	398	31	19	26
JC-NSD-14	61.01	33.71	0.78	1.33	1.09	0.22	1.14	0.72	0.04	0.01	19	62	18	252	104	229	23	17	14
JC-NSD-16	61.53	33.04	0.97	1.46	0.87	0.22	1.15	0.76	0.03	0.02	10	48	21	321	107	206	30	23	15
JC-NSD-17	62.09	33.26	0.57	0.95	0.68	0.33	1.48	0.63	0.04	0.01	12	9	16	245	89	241	29	21	18
JC-NSD-18	67.34	27.45	0.59	0.90	0.94	0.54	1.56	0.68	0.02	0.03	21	38	18	246	37	268	9	27	20
JC-NSD-19	66.15	28.95	0.61	0.77	0.89	0.50	1.59	0.55	0.03	0.02	31	43	13	171	31	237	4	24	13
JC-NSD-20	58.87	35.64	0.74	1.09	1.52	0.15	1.04	0.95	0.03	0.02	20	46	28	496	106	181	27	26	29
JC-NSD-21	58.39	36.75	0.67	1.09	0.75	0.27	1.30	0.78	0.02	0.03	12	20	18	336	95	210	28	25	21
JC-NSD-22	60.36	34.31	0.73	1.09	0.73	0.38	1.70	0.71	0.03	0.02	15	28	19	356	93	214	21	28	22
JC-NSD-23	66.20	28.47	0.56	0.91	0.98	0.42	1.89	0.58	0.04	0.03	30	50	20	192	34	354	0	25	22
JX-JD-01	65.36	28.34	0.95	1.06	1.19	0.41	2.07	0.62	0.04	0.03	21	45	30	268	68	437	9	41	16
JX-JD-02	62.71	31.51	1.42	0.86	0.87	0.18	1.56	0.88	0.05	0.01	26	82	33	278	93	594	19	37	19
JX-JD-03	65.49	28.11	0.91	1.08	1.26	0.41	2.14	0.59	0.04	0.03	23	51	30	379	67	2110	28	44	17
JX-JD-04	62.79	31.37	1.50	0.89	0.89	0.18	1.51	0.87	0.06	0.01	24	36	27	268	97	619	24	22	18
JX-JD-05	55.60	39.76	0.72	0.82	0.50	0.18	1.57	0.85	0.04	0.02	34	32	30	379	38	138	15	64	22
JX-JD-06	63.37	30.84	1.25	1.02	0.87	0.27	1.58	0.80	0.04	0.02	12	48	24	269	80	559	18	27	17
JX-JD-07	68.46	25.81	0.93	0.90	0.70	0.41	2.06	0.73	0.04	0.02	14	51	27	242	73	350	21	25	17
JX-JD-08	69.15	25.27	0.92	0.93	0.95	0.36	1.74	0.68	0.04	0.02	11	33	26	222	74	342	8	36	17
JX-JD-09	64.60	29.67	1.21	0.80	0.81	0.25	1.77	0.87	0.05	0.01	22	40	31	289	94	438	15	32	21
JX-JD-10	65.44	29.27	1.04	0.73	0.87	0.33	1.43	0.88	0.06	0.01	11	33	38	306	92	401	16	34	22
JX-JD-11	66.63	26.90	1.10	1.23	1.09	0.37	2.06	0.62	0.03	0.03	20	47	34	459	71	811	12	26	17
JX-JD-12	69.33	24.96	0.96	0.95	0.91	0.31	1.75	0.82	0.03	0.02	18	26	27	209	76	329	20	28	16
JX-JD-13	65.60	28.37	1.29	1.02	0.99	0.31	1.64	0.79	0.04	0.02	17	72	31	310	78	861	17	49	16
JX-JD-14	66.18	27.88	1.11	1.02	0.89	0.36	1.74	0.83	0.06	0.02	15	14	25	356	80	947	10	29	18
JX-JD-15	65.12	28.50	1.00	1.12	1.17	0.40	2.01	0.68	0.04	0.03	21	39	36	376	76	426	20	36	18
JX-JD-16	66.30	27.24	1.06	1.21	1.11	0.37	2.10	0.61	0.02	0.03	19	39	28	258	71	508	13	20	16
JX-JD-17	65.49	27.88	0.94	1.06	1.31	0.43	2.29	0.60	0.04	0.03	24	58	29	306	70	315	18	26	18
JX-JD-18	66.93	27.34	1.18	0.99	0.65	0.25	1.89	0.78	0.04	0.02	22	45	29	231	90	461	19	23	18
JX-JD-19	66.64	27.57	1.23	0.92	0.87	0.20	1.76	0.81	0.05	0.01	22	57	31	275	111	942	18	35	19
JX-JD-20	64.36	30.16	1.26	0.87	0.57	0.20	1.67	0.91	0.05	0.01	24	28	31	297	94	529	20	30	22
JX-JD-21	63.69	30.18	1.28	0.94	0.71	0.24	2.07	0.87	0.05	0.02	25	47	33	303	81	566	14	25	22
JX-JD-22	63.74	30.54	1.22	0.88	0.72	0.18	1.81	0.92	0.06	0.01	24	54	33	306	75	413	13	27	23
JX-JD-23	67.30	26.66	1.09	1.01	1.04	0.28	1.89	0.73	0.05	0.02	24	30	27	268	89	564	25	26	19
JX-JD-24	65.62	28.89	1.02	0.83	0.86	0.23	1.76	0.79	0.04	0.02	27	27	32	319	74	394	17	46	18
JX-JD-25	62.99	30.67	1.23	0.99	1.02	0.24	2.00	0.86	0.04	0.01	35	54	31	301	79	537	12	52	21
JX-JD-26	65.92	28.04	1.16	1.14	0.67	0.30	2.01	0.75	0.04	0.02	21	58	31	227	92	508	16	26	20
JX-JD-27	63.60	30.82	1.23	0.87	0.67	0.22	1.65	0.93	0.05	0.01	23	10	29	268	92	511	12	36	23
JX-JD-28	66.26	27.64	1.22	1.09	0.70	0.30	2.12	0.67	0.04	0.02	18	63	24	219	84	485	11	22	17
JX-JD-29	66.37	27.42	1.20	1.22	0.74	0.22	2.03	0.80	0.04	0.02	21	53	25	249	85	571	19	24	19
JX-JD-30	65.50	28.08	1.14	1.05	1.19	0.30	2.00	0.74	0.05	0.02	25	47	31	436	96	661	15	31	19

differ among the three periods, allowing some clear groupings to emerge. This again suggests that the bodies of different periods were made from broadly similar raw materials but with minor differences in proportions, compositions or processing. According to results from chemical analysis, the average alumina values also fluctuated over time: the NSD wares having the highest alumina levels, and the JD samples have the lowest. Conversely, the potters in the Five Dynasties used marginally more flux-rich bodies than

Table 3
Average and standard deviation of major and minor elements of bodies.

Period-Site	Jin-JX(30)		North Song-JC(19)		Five Dynasties –BZ(20)	
Elements	Average	Std.	Average	Std.	Average	Std.
SiO_2	65.22	2.50	61.39	1.84	65.32	2.22
Al_2O_3	28.86	2.70	33.26	2.07	29.35	1.89
Fe_2O_3	1.13	0.17	0.73	0.13	0.70	0.10
MgO	0.98	0.13	1.16	0.20	1.08	0.16
CaO	0.89	0.21	1.08	0.48	1.58	0.90
Na_2O	0.29	0.08	0.34	0.20	0.56	0.25
K_2O	1.86	0.22	1.29	0.23	1.01	0.27
TiO_2	0.78	0.10	0.75	0.13	0.39	0.08
P_2O_5	0.04	40	0.03	26	0.03	64
MnO	0.02	48	0.02	44	0.02	69
Ba	578	342	215	67	580	275
Sr	81	13	99	8	164	38

The data from SiO_2 to MnO are in wt%, others in ppm.

Table 4
Component loading matrix derived from the PCA.

	Factor 1	Factor 2	Factor 3
SiO_2	−.040	.886	−.148
Al_2O_3	−.008	−.913	.048
Fe_2O_3	.773	.346	.235
MgO	−.342	−.149	−.126
CaO	−.587	.047	.509
Na_2O	−.725	.202	−.087
K_2O	.804	.303	−.284
TiO_2	.815	−.334	.281
P_2O_5	.593	.222	.515
MnO	−.041	.199	−.603
Cu	−.263	.173	.743
Zn	.017	.388	.261
Zr	.263	−.304	−.146
Sr	−.852	.114	.112
Ba	.010	.537	−.061
Eigenvalue variance (%)	27.4%	17.8%	12.1%

for the wares of the other two periods although the differences in totaled flux-levels are actually rather small, only 0.5% in total at most (See Fig. 6).

In terms of original body recipes, Zhang et al (1983) and Li & Guo (1985) proposed that the main raw materials were high-firing local clays such as the so called ‘purple ball clay’ (Zimujie Clay) and the ‘Ling-shan refractory clay’. These particular clays are all rich in kaolinite, a mineral with about 46% Al_2O_3 in its fired state, thus they all have high potential refractoriness (Zhang F.K. 2000). Zhang J. et al suggest that some 10–20% of feldspar and quartz, as well as small amounts of calcareous materials were added to these clays as separate ingredients, slightly to lower their maturing temperatures, although this is still not entirely certain.

An interesting phenomenon in this study is that the sample (JX-JD-05) with the highest Al_2O_3 content (>39% is not a porcelain ware but an item of kiln furniture – it is actually a ring-shaped setter with an ‘L’ shaped cross-section to support the rim of a porcelain bowl during firing. It is the only chemically analyzed example of kiln furniture in this study and has a composition very similar to the purple ball clay reported by Kerr and Wood (2004), except for its lower TiO_2 content and higher K_2O content. The reason why the setter contains higher Al_2O_3 than the wares themselves may be that it was used to support the wares during firing so needed to be made from a more refractory clay.

This study also indicates that there is a constant change in the type and the content of the bodies’ fluxes. It is well known that

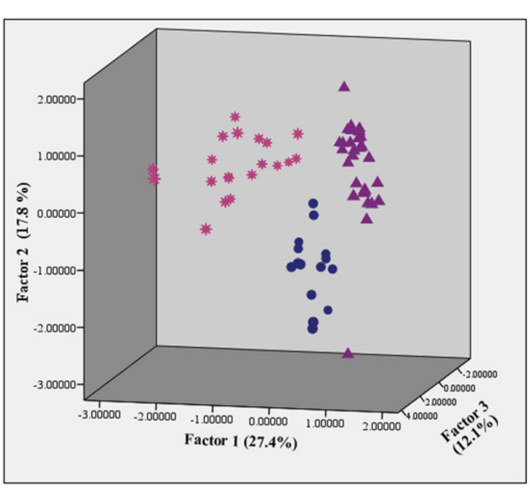

Fig. 3. The first three components plots derived from multivariate statistical analysis (PCA).

raised levels of the alkali earth elements in the bodies are one of the more prominent technical features of Ding ware (Li., 1998). As observed by Zhang et al, (1983), Li & Guo (1985) these elevated contents of alkali earth elements might be due to additions of dolomite and calcite to the bodies’ clays. However, our study suggests that dolomite would have been an unlikely body ingredient in the Northern Song and Jin body-samples tested as their CaO and MgO percentages show higher ratios of MgO to CaO than dolomite itself.

During the Five Dynasties period, the alkali earth oxides’ contents were quite high but not very consistent. Some FD samples contain more than 3% CaO, while others only have about 1%. This means that calcareous materials were operating as fluxes in Ding ware bodies at this time. However, after the Five Dynasties, the CaO levels dropped to less than 1% in the Jin Dynasty, levels similar to those found in modern clays (Kerr and Wood, 2004). Thus it is possible either that smaller amounts of calcareous materials were added to Ding ware bodies at this time, or that the CaO in the Jin Dynasty bodies was associated with major clay ingredients and not added separately.

Correspondingly, the K_2O levels in JD bodies are almost twice as much as in FD bodies, with the K_2O increasing from about 1% in FD to about 1.9% in JD. This means that the main flux-type in the body changed from being a predominantly calcareous material to a mainly potassic material at the Ding ware kiln sites over time.

How this change was managed is still a problem. Most analyses so far published of natural refractory clays associated with the Ding kilns’ region show exceptionally low levels of K_2O – less that 0.35% - which are among the lowest K_2O levels found in Chinese ceramics (Zhang et.al., 1983). It is possible therefore that the K_2O found in the Ding ware bodies represents the addition of potassium-rich raw material(s). Likely candidates for this role might include an igneous rock, a sand containing debris from igneous rock, a crushed feldspathic quartzite, or some kind of botanic ash rich in K_2O. However, Zhang et al (1983) cite a clay raw material local to the Ding sites (Pangjiawa Qingtu, Pangjiawa blue clay) that contains 1.5% K_2O in its fired state. Therefore a further alternative is that a clay, relatively rich in K_2O, may have been mixed with one or more other clay(s) less rich in potassa to create a successful porcelain body. (As the amounts of K_2O involved are so small this would have been a practical approach.)

For the Five Dynasties and Northern Song periods, however there is a very noticeable positive correlation between the sodium and potassium oxide levels in the bodies (see Fig. 4d), and the levels of these same oxides in the glazes used on the same shards (see Fig. 5e). This strongly suggests that the same alkali-bearing

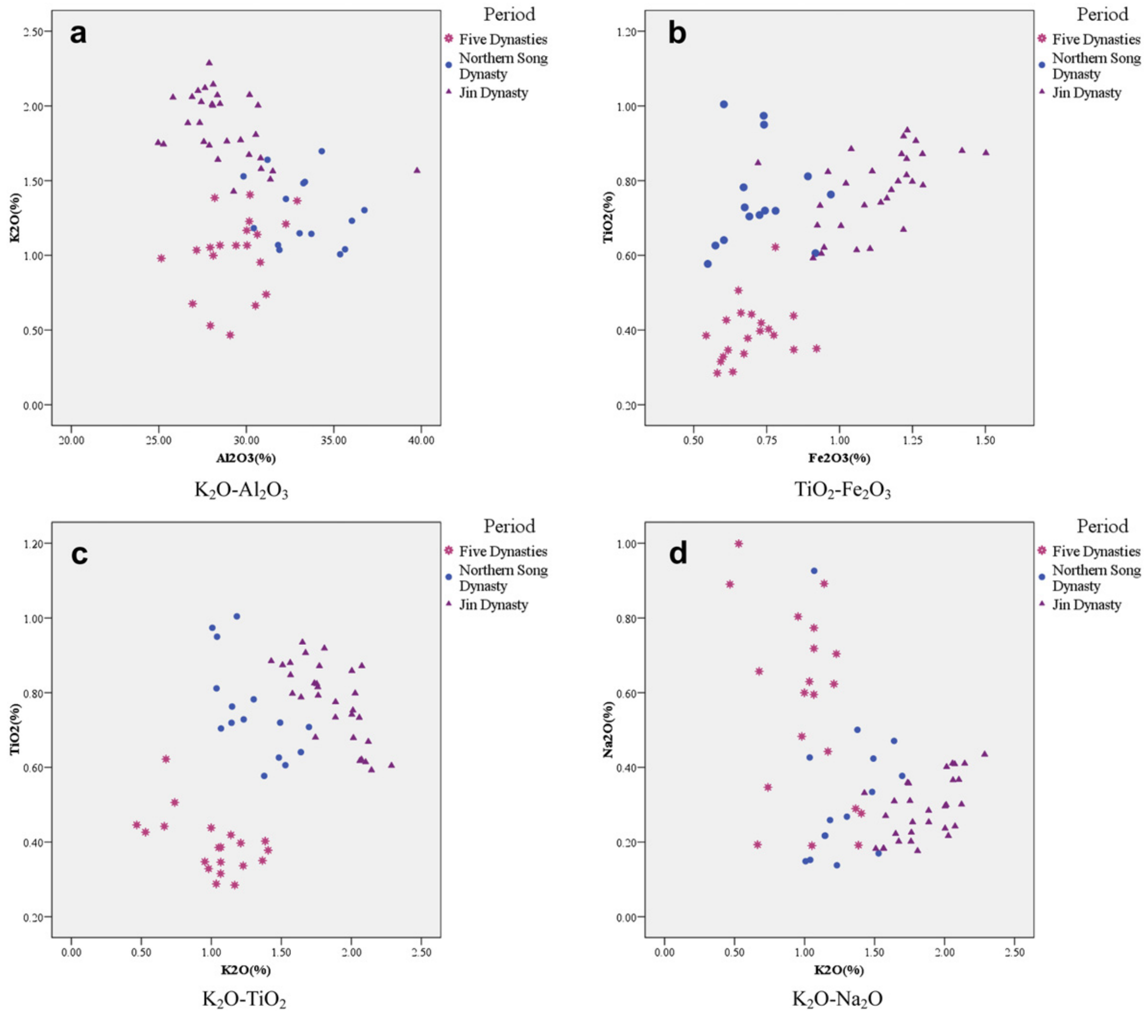

Fig. 4. Bivariate plots corresponding to the concentrations of some elements in bodies as oxides (values expressed in wt %).

powdered rocks were used in both bodies and glazes at these sites and over this period (the principle does not hold in wares analysed from the Jin dynasty). In terms of quantities, and judging from the alkali levels established, it appears that about 50% more rock was used in the glazes than in the bodies. That the material used was rock rather than clay is suggested by the low titania levels in the glazes, compared with the bodies – titania being high in all clays so far analysed from this region.

With regard to lime and magnesia, refractory clays near to the Ding kiln sites often contain CaO up to 1.8% (fired) and MgO up to 0.9% (fired) (Zhang et al.,1983), so a natural explanation for the levels of these fluxes in the Ding ware bodies studied cannot be excluded.

It was also found that the totaled TiO_2 and Fe_2O_3 contents of the bodies have varied over time. The iron and titanium oxides were very low in FD, rose in the NSD, and kept to similar levels during the JD. By contrast the iron oxide alone only rose after NSD

Thus the bodies can be grouped by the TiO_2 and Fe_2O_3 contents (see Fig. 4b). The early Ding wares are much whiter than the later wares, which is partly due to the low levels of TiO_2 and Fe_2O_3 in these earlier sherds. Oxides of Fe and Ti are both coloring materials and make the bodies appear less white after firing. The NSD Ding ware has a warmer tone than FD Ding ware, which is called 'ivory white', and the JD ware looks slightly yellower than NSD. It was thought that using coal as fuel since the middle 11^{th} C was a contributory cause of this phenomenon, as burning coal encourages oxidizing firing conditions (Kerr and Wood, 2004:158). At the same time another possible influence from coal might be iron-sulphur chromospheres forming in the glazes during firing, which can have a strongly yellowing effect on glasses and glazes (See Kerr and Wood, 2004: 590 and Schreurs and Brill 1984). Iron oxide and titania levels in the glazes are also important factors in the fired colours of porcelains. Titania is exceptionally low in most Ding glazes, often below 0.1% in the Five Dynasties period, and less than 0.2% in the Northern Song dynasty. Only in the Jin dynasty do titania percentages rise to the levels where they begin to have a yellowing effect on the glazes (> 0.2% titania). Nonetheless, increasing contents of TiO_2 and Fe_2O_3 in the bodies, combined with oxidizing firings, must be the main reason for the later Ding wares' showing these creamer tones.

It is also thought that the high-firing clays, such as the so called 'purple ball clay' or 'Ling-shan refractory clay', were used as the main raw materials of Ding wares' bodies (Guo, 1985, Guo, 1987). However, both clays are relatively rich in titania, and opinions on whether it is possible to remove titania from natural clays by processing are conflicting. Li & Guo (1985) suggest that this may be possible, while Lawrence (1982: 39) emphasizes the difficulty of the process (with American clays) because much titania tends to be present as the near-colloidal material leucoxene, which is so fine that it passes easily through a 325 mesh sieve. Thus, it is possible

Table 5
Chemical results of the glazes of the Ding wares (the data from SiO_2 to MnO are in wt%, others in ppm).

Sample ID	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cu	Zn	Zr	Sr	Ba	Co	Ni
BZ-FD-01-Y	64.19	22.92	1.19	1.93	6.62	1.08	1.14	0.17	0.55	0.05	44	127	139	224	552	5	31
BZ-FD-02-Y	73.69	17.37	0.98	1.68	3.86	1.12	0.95	0.05	0.14	0.03	31	4	257	111	313	32	61
BZ-FD-04-Y	69.95	16.17	1.09	2.56	7.72	0.79	1.18	0.06	0.27	0.05	20	47	120	256	842	0	38
BZ-FD-05-Y	74.25	15.46	0.57	2.62	4.39	1.00	1.36	0.06	0.16	0.03	15	69	41	294	256	31	40
BZ-FD-06-Y	72.57	19.08	0.76	1.60	2.77	1.26	1.49	0.13	0.15	0.02	36	38	109	221	876	23	51
BZ-FD-07-Y	73.68	17.30	0.71	1.55	4.54	0.67	1.11	0.12	0.13	0.03	11	206	109	277	584	49	66
BZ-FD-08-Y	72.06	16.96	1.34	1.98	4.65	1.31	1.28	0.07	0.20	0.03	26	139	141	168	234	11	84
BZ-FD-09-Y	71.84	18.01	0.92	2.07	4.42	0.73	1.65	0.05	0.17	0.05	24	28	119	133	275	5	39
BZ-FD-09-Y	70.32	14.13	1.21	2.86	8.99	0.41	1.46	0.04	0.31	0.09	35	63	58	170	798	26	39
BZ-FD-10-Y	74.72	16.45	0.89	2.36	3.10	0.89	1.19	0.06	0.15	0.03	27	81	136	132	376	0	83
BZ-FD-11-Y	71.92	19.20	0.35	1.20	4.61	1.55	0.74	0.09	0.18	0.01	21	54	96	181	389	19	56
BZ-FD-12-Y	73.06	18.36	0.89	1.76	2.58	1.41	1.53	0.09	0.14	0.03	84	0	63	268	718	2	56
BZ-FD-13-Y	67.85	18.04	1.29	2.85	7.03	0.36	2.04	0.06	0.29	0.08	26	76	215	173	319	11	34
BZ-FD-14-Y	74.97	14.93	1.05	1.83	5.08	0.74	1.01	0.06	0.14	0.03	14	89	32	238	404	21	87
BZ-FD-15-Y	72.38	18.14	0.64	1.68	5.21	0.28	1.26	0.08	0.15	0.04	23	153	93	131	295	23	53
BZ-FD-16-Y	70.45	20.17	0.71	2.33	4.34	0.43	0.99	0.11	0.29	0.02	60	42	104	137	634	12	31
BZ-FD-17-Y	72.99	15.71	1.27	1.54	6.38	1.06	0.64	0.06	0.22	0.03	18	4	113	180	407	5	95
BZ-FD-18-Y	73.76	16.55	0.79	1.16	4.95	0.94	1.47	0.05	0.17	0.04	16	68	86	115	299	26	52
BZ-FD-19-Y	73.05	17.07	0.58	2.01	5.66	0.46	0.73	0.06	0.26	0.02	32	29	46	120	234	24	66
BZ-FD-20-Y	74.82	15.28	0.72	1.39	4.99	0.42	1.93	0.06	0.14	0.10	13	114	0	142	429	39	46
JC-NSD-04-Y	68.76	19.52	0.69	2.74	4.69	0.80	2.12	0.06	0.44	0.03	39	72	315	86	230	20	50
JC-NSD-05-Y	72.58	18.70	0.68	2.04	3.62	0.31	1.63	0.07	0.26	0.03	25	0	31	86	189	0	78
JC-NSD-06-Y	69.13	19.70	0.66	2.98	4.46	0.84	1.75	0.07	0.27	0.05	41	26	196	90	199	15	16
JC-NSD-07-Y	68.03	21.00	0.77	3.10	4.00	0.34	1.88	0.20	0.49	0.04	20	69	202	147	272	76	65
JC-NSD-08-Y	71.48	18.90	0.66	1.78	4.35	0.46	1.94	0.11	0.20	0.03	34	21	98	82	365	17	53
JC-NSD-09-Y	72.29	18.07	0.67	1.99	3.20	1.75	1.50	0.07	0.26	0.04	19	0	530	75	149	9	72
JC-NSD-11-Y	68.81	20.42	0.78	2.33	4.54	0.30	2.09	0.13	0.40	0.05	33	132	99	92	141	0	72
JC-NSD-12-Y	71.30	19.69	0.80	1.82	2.75	0.88	2.07	0.18	0.33	0.04	15	34	152	72	294	53	81
JC-NSD-13-Y	71.61	19.49	0.90	1.60	3.45	0.77	1.48	0.20	0.24	0.02	13	6	0	81	719	0	275
JC-NSD-14-Y	68.86	20.21	0.85	2.62	4.60	0.45	1.74	0.12	0.40	0.02	28	94	167	110	311	25	50
JC-NSD-15-Y	70.56	18.90	0.63	2.06	4.32	1.39	1.62	0.08	0.33	0.05	9	12	116	70	166	8	36
JC-NSD-16-Y	69.70	20.07	0.95	3.49	3.09	0.52	1.68	0.10	0.22	0.02	13	110	265	107	262	25	70
JC-NSD-17-Y	68.91	20.71	0.61	2.30	3.65	0.69	2.40	0.14	0.43	0.03	23	85	157	82	252	19	29
JC-NSD-18-Y	69.50	18.80	0.76	2.61	5.00	0.93	1.80	0.12	0.32	0.03	23	49	200	110	239	33	36
JC-NSD-19-Y	69.69	20.15	0.80	2.27	3.68	0.85	1.90	0.18	0.33	0.05	22	48	235	85	215	23	44
JC-NSD-20-Y	71.82	19.12	0.68	2.12	3.78	0.35	1.60	0.08	0.28	0.03	23	80	0	89	222	0	89
JC-NSD-21-Y	71.02	17.13	0.84	1.82	6.20	0.43	1.88	0.14	0.39	0.05	15	95	274	115	275	11	53
JC-NSD-22-Y	68.92	16.23	0.82	3.01	7.45	0.60	1.92	0.08	0.69	0.12	41	112	107	158	315	45	21
JC-NSD-23-Y	69.41	19.04	0.70	2.62	4.42	0.65	2.48	0.08	0.39	0.08	42	57	276	99	222	0	0
JX-JD-18-Y	70.21	19.39	1.23	2.71	2.52	0.38	2.71	0.26	0.40	0.02	32	70	154	171	841	13	23
JX-JD-19-Y	69.53	17.96	1.52	3.20	4.64	0.26	1.84	0.14	0.72	0.03	45	97	249	214	560	29	43
JX-JD-20-Y	70.27	19.25	1.43	3.04	2.83	0.30	2.14	0.13	0.45	0.02	36	42	86	155	677	12	40
JX-JD-21-Y	72.59	16.98	1.31	2.15	3.38	0.27	2.41	0.29	0.42	0.03	26	99	123	146	804	29	54
JX-JD-22-Y	65.05	18.66	1.66	4.78	4.93	0.40	3.16	0.20	0.86	0.03	73	187	177	196	1121	26	39
JX-JD-23-Y	71.27	18.52	1.07	2.06	3.57	0.39	2.18	0.26	0.49	0.03	33	76	379	159	558	24	38
JX-JD-24-Y	71.80	18.05	1.01	2.69	3.26	0.33	2.19	0.11	0.33	0.04	49	101	82	146	783	35	40
JX-JD-25-Y	70.15	17.44	1.17	3.24	4.92	0.30	1.87	0.12	0.62	0.02	32	107	74	148	426	21	61
JX-JD-26-Y	70.68	17.47	1.43	2.25	4.93	0.31	2.07	0.21	0.50	0.03	21	77	169	170	574	27	45
JX-JD-27-Y	73.32	17.18	0.95	2.56	2.99	0.33	2.21	0.11	0.21	0.02	39	40	67	160	417	17	25
JX-JD-28-Y	69.28	18.58	1.14	2.82	4.03	0.43	2.62	0.21	0.71	0.03	40	90	153	191	773	12	23
JX-JD-29-Y	69.92	18.33	1.09	2.68	4.65	0.28	2.14	0.17	0.49	0.03	34	46	107	157	1454	18	44
JX-JD-30-Y	70.34	17.91	1.20	2.30	4.03	0.40	2.41	0.46	0.72	0.04	43	69	365	175	647	27	59

Table 6
Average and standard deviation of major and minor elements of glazes.

Period-Site	Jin-JX(13)		North Song-JC(19)		Five Dynasties –BZ(20)	
Elements	Average	Std.	Average	Std.	Average	Std.
SiO_2	70.34	1.98	70.13	1.39	72.13	2.61
Al_2O_3	18.13	0.75	19.25	1.19	17.37	2.02
Fe_2O_3	1.25	0.21	0.75	0.10	0.90	0.27
MgO	2.81	0.70	2.39	0.52	1.95	0.51
CaO	3.90	0.86	4.28	1.10	5.09	1.62
Na_2O	0.34	0.06	0.70	0.38	0.85	0.38
K_2O	2.30	0.36	1.87	0.27	1.26	0.37
TiO_2	0.21	0.10	0.12	0.05	0.08	0.03
P_2O_5	0.53	0.18	0.35	0.12	0.21	0.10
MnO	0.03	0.01	0.04	0.02	0.04	0.02

that the Five Dynasties to Jin raw materials had fewer TiO_2-bearing inclusions than the modern ones.

The FD samples in particular have much lower titania levels than these high-firing clays, so it seems unlikely that their raw materials were the 'purple ball clay' or the 'Ling-shan refractory clay', in the forms described in Li and Guo (1986). The clay of FD wares could either have been local refractory clays rich in lime and magnesia, and low in iron and titanium, as suggested by Kerr and Wood (2004: 161–2), or similar materials with deliberate carbonate additions. However, such high quality materials could have become exhausted after the early North Song Dynasty, according to this study. The titanium dioxide content in the wares' bodies during NSD and JD periods increased to about 0.75%, perhaps indicating that clays with higher titanium dioxide levels had been increasingly used since the later NSD. Even so, the contents of titania are still lower than modern clays – perhaps through careful elutriation of the same clays and/or through use of lower titania raw materials.

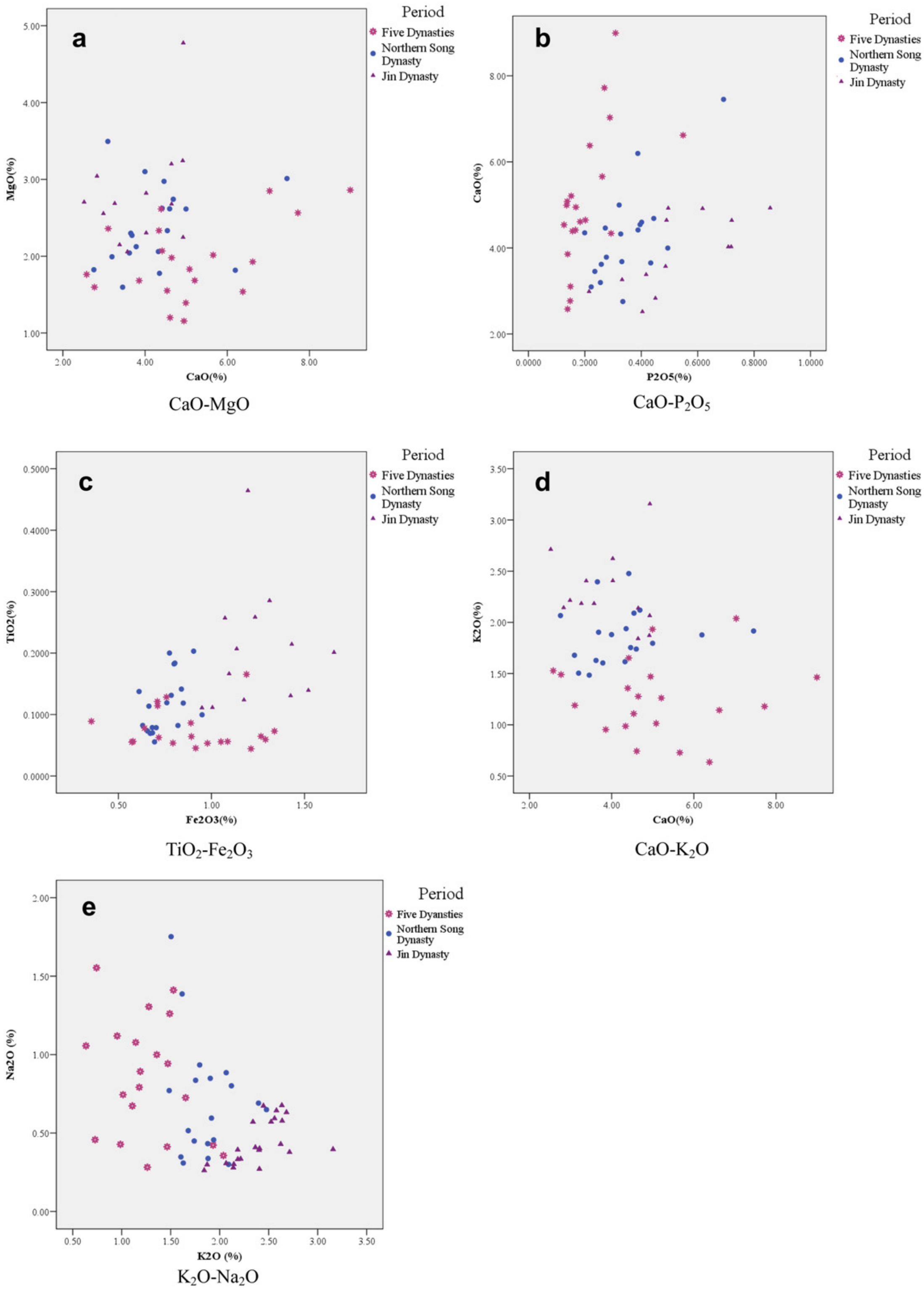

Fig. 5. Bivariate plots corresponding to the concentrations of some elements in glazes as oxides (values expressed in wt%).

It is also interesting that the TiO_2 contents of the bodies have negative correlation with K_2O contents in every group as illustrated by Fig. 4c. This can also be seen in the plot of Al_2O_3 vs. K_2O (Fig. 4a). This means that the K_2O could have an independent source, as suggested above. Whether this source was a lower-titania, higher-potassa clay, or a powdered rock containing potassa is still a question. If the former, then there are precedents in Tang dynasty Yaozhou wares (Rastelli et al, 2002: 181), if the latter, it was reported that Sui (Tang) feldspathic Xing wares used kaolin-feldspathic rock mixtures to achieve their very unusual compositions (Chen et al 1989: 223). In this case Ding ware technology may have been influenced by Xing ware making-practice. According to our recent researches on Ding ware raw materials, we prefer the latter interpretation.

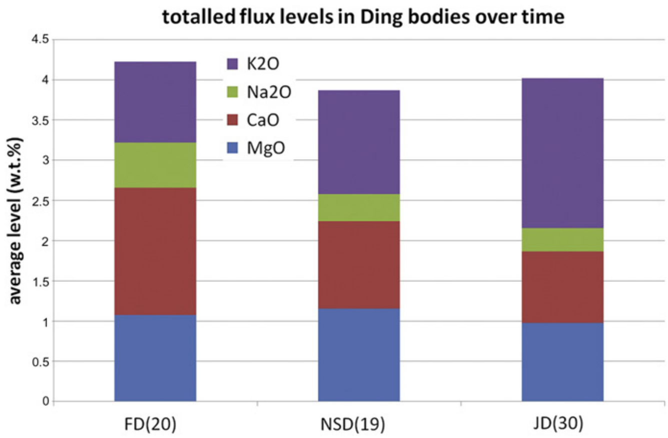

Fig. 6. Totaled flux levels in Ding bodies over time.

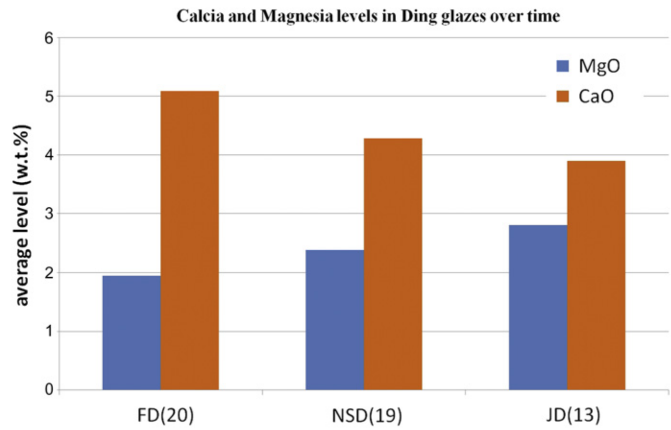

Fig. 7. The average lime and magnesia levels in Ding glazes over time.

5.2. Glazes

It has been proposed that high alumina clays, silica materials, together with lime and magnesia materials. were the main ingredients of Ding glazes (Zhang J. et. al., 1983). Our study, however, indicates that this is only partially true. On the one hand, our results show some similar elemental trends as the bodies (especially regarding Na_2O and and K_2O). On the other hand, there are noticeable differences among the samples of different periods in spite of the fact that the scatters present some superposition in the statistical plot. This suggests that the main sources of raw materials might be similar, while recipes and proportions of the raw materials used could be altered with the passing of time. (The high alumina content in the glaze complements the high refractoriness of the Ding ware bodies, which is a common characteristic of white porcelain from north China.)

Among the samples of these three periods, the FD samples have the highest mean CaO contents and the lowest K_2O contents. The JD samples show a contrasting picture, with lower CaO and higher K_2O. This trend can also be seen in the analysis of Ding bodies. Like the bodies, the CaO contents in glazes of FD samples are not very stable, fluctuating from 2.5% to about 9%.

As with the bodies, the glaze samples of the other two periods are more consistent, especially those of the Jin Dynasty. According to the existing researches, before Five Dynasties the main glaze type of ancient north Chinese white porcelain was the lime glaze, where the CaO contents were relatively high. However, after Five Dynasties, the glaze types changed to lime-alkali or magnesia-lime glazes, causing a fall in the CaO contents to a certain level (often lower than 5%) (Li, 1998; Zhang, 2000). In our study, both lime- and magnesia-lime types can be found in the FD samples, placing Five Dynasties as a transitional and experimental period in the history of Ding ware manufacture.

Most researchers considered dolomite as the most appropriate candidate for sources of lime and magnesia in Ding glazes (see Zhang et.al.,1983;. Li and Guo, 1986). However our work shows that lime and magnesia in these glazes are negatively correlated over time, suggesting that CaO and MgO were probably supplied by different materials in the late Northern Song and Jin periods (see Fig. 7).

In fact the phosphorous oxide contents make wood ash another possible source of lime. This can be seen in Fig. 5b. The CaO contents all have positive relationships with P_2O_5 contents in every stage. Also, one can see that the contents of both P_2O_5 and MnO are positively correlated during every period. This is a common feature of wood ash. Thus it can be proposed that some lime might come from wood ash. This phenomenon was noticed by Kerr and Wood (2004: 543) who pointed out: '……the phosphorous contents found in two of the Ding glazes cannot be ignored. Although at 0.2–0.3% they appear low, they are in glazes where the total flux contents are also low, so their flux–to-phosphorous ratios are still characteristic of wood ash.'

However, the CaO and P_2O_5 are negatively correlated over time. Although the FD glazes have the highest average mean CaO among the sherds of all three periods, its mean P_2O_5 value is the lowest. On the contrary, the CaO lever in JD glazes is the lowest, while the P_2O_5 contents are twice more than in FD glazes. This suggests that the wood ash could not be the sole source of lime during the early phase of the Ding kiln. There could be other materials without P_2O_5 being used as calcic sources, although just what these were has still to be determined.

The glazes show a similar fluctuating trend of iron and titanium contents to the bodies. The TiO_2 contents are all low in FD samples, with a mean value of only 0.08%, ideal for maximizing the whiteness of the porcelain. However, the Fe_2O_3 contents in FD samples are not stable, distributing from 0.3% to 1.4%. The average of titanium oxide in the NSD only increased a little, to about 0.12%. Overall the NSD samples have the most stable and the lowest Fe_2O_3 contents of the three periods. Nonetheless, and despite these obvious parallels between the colouring oxide levels in the Ding bodies and their glazes over various periods, extensive use of body clays in the glaze recipes (typical of south Chinese ceramics at this time) does not seem to have been practiced at the Ding ware kiln sites. This is shown by the very low titania levels in the Ding glazes. These would only allow local-clay contents of below 15% (and often much less) in the Ding glaze recipes.

It is thought that the Northern Song Dynasty was the height of Ding ware manufacture (Han et al., 2010). The appearance of the NSD ware is a little more yellow than FD ware, which is called 'ivory white'. As noted, it was considered that using coal as fuel was a contributory reason for this yellowish white appearance, However, the higher TiO_2 and Fe_2O_3 contents in the glazes can be seen as further important causes for their warm appearances. The Fe_2O_3 contents achieve a mean value of about 1.2% in the JD glazes. Thus the colors of the JD glazes are more yellow than the NSD glazes.

The fact that titania levels are so low in the glazes suggests that the Ding potters chose low-titania raw materials to create them. The local clays all have high titania contents (Zhang et al., 1983; Li and Guo, 1986) making them unsuitable for use in colorless porcelain glazes.

6. Conclusion

In conclusion, the Ding bodies and glazes remained broadly similar through time, although they still show some minor characteristics of their age. Thus Ding wares of different periods can be distinguished by their chemical compositions. In fact, the ability to separate Five Dynasties (BZ site), Northern Song (JC site), and Jin Dynasty (JX site), so effectively by statistical means suggests that the Ding potters moved their main production centres, and slightly changed their body compositions, almost dynasty by dynasty, which is an odd phenomenon in itself.

Our analyses show that the raw materials used for the Ding bodies are mainly high firing clays with some fluxing material, relatively rich in lime during the early phases of the kiln (Five Dynasties and earlier Northern Song). After the early North Song Dynasty, calcareous materials declined somewhat, being substituted by a more potassic material. Magnesia (another minor body-flux) remained fairly constant throughout. In addition, the lower levels of colored elements such as Ti and Fe in the bodies of FD samples suggest that the high quality clays were exploited during the early phase of the Ding kilns and exhausted after the early Northern Song Dynasty. The rising contents of these elements indicate that since the late Northern Song Dynasty impure clays similar to the modern materials began to be used, although these were still somewhat lower in coloring oxides. The increased K_2O content and its negative correlation with Al_2O_3 and TiO_2 suggest that the potassic material was an individual ingredient of body making, although whether this material was a low-titania siliceous clay or a siliceous powdered rock is still uncertain.

The evolution of the Ding glazes is approximate to the bodies, especially in the aspect of the relationship of K_2O and Na_2O which are strongly positively correlated in the Five Dynasties and the Northern Song Dynasty, suggesting use of the same alkali-bearing material in both bodies and glazes during these periods.

The very low TiO_2 contents in the glazes indicate that the clay components of the bodies were not used in the glaze recipes. The main ingredients of the glazes may have been the same siliceous and flux-rich materials that had been mixed with the local clays to make the porcelain bodies, together with a supplementary source of calcia. The P_2O_5 contents in the glazes cannot be ignored, which means that one of the sources of CaO in the glaze-recipes may well have been wood ash.

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