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1 **Microscopic Study on Characteristic decorative Black and**
2 **White Porcelain produced in Shanxi province, Jin and Yuan**
3 **dynasties (1115-1368 AD), China**

4
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14 Abstract: Black and white porcelain plays a critical role in Chinese decorative
15 porcelain history. It is famous for its decorative styles and techniques, which create a
16 strong black and white color contrast in its appearance. In this study, representative
17 black and white porcelains produced in Shanxi province were analyzed by X-ray
18 fluorescence, Raman spectroscopy and SEM-EDS. The results show that both Ca-rich
19 (~5.33 wt%) and Ca-poor (~1.99 wt%) glazes were used leading to quite different
20 microstructures. The pigment particles of Ca-rich glazes are characterized by small
21 size ($\leq 2 \mu\text{m}$), wide distribution, and tightly wrapped by anorthite. In contrast, they are
22 larger ($\geq 2 \mu\text{m}$) and tightly cumulated together in Ca-poor glazes. Hematite is the
23 major crystal in pigment, double-substituted by Al and Ti. The Al/Fe ratios are
24 similar, but Ti/Fe ratios are quite different: they do not exceed 0.03% in Ca-poor
25 glazes, whereas they reach 0.12% in Ca-rich glazes, suggesting that the origin of the
26 pigments must be different. Al-rich mineral such as kaolin was added to the pigment
27 preparation in Ca-rich glazes. The color of the pattern is mainly influenced by the
28 size, quantity and concentration of brown Ti-doping hematite, as well as the thickness
29 of the glaze layer and other crystals and Fe ions. The fired atmosphere of Ca-rich
30 glaze type seems less oxidizing than for Ca-poor glaze type. Overall, the results
31 confirm that black and white porcelain has a variety of production techniques, which
32 is attributed to the craftsman adjusting the techniques according to the composition of
33 raw materials.

34 Keywords: Black and white porcelain; multilayered structure; hematite ($\alpha\text{-Fe}_2\text{O}_3$);
35 Raman spectroscopy; SEM-EDS

36 1 Introduction

37 Black and white porcelain, a kind of decorative ware popular in the Jin and Yuan
38 Dynasties (1115-1368 AD),^[1] was invented by craftsmen who perfectly incorporated
39 paintings and calligraphy as decorative motifs on white supports.^[2] Black and white

1 porcelain is presently considered as the most typical and characteristic product of
2 decorative Chinese porcelain, with its vivid and realistic design, based on a strong
3 folk style.^[3] The development of black and white porcelain reached its peak during the
4 Jin Dynasty with the manufacturing of many exquisite works for foreign markets.
5 More importantly, it is believed that the implementation of new decoration processes
6 influenced the development of other decorated porcelains such as red and green
7 porcelains or blue and white porcelain to some extent.^[4,5]

8 The production of black and white porcelain is a crucial stage in the development
9 of Chinese decorated porcelain. It is because it inherited the decorative techniques of
10 black and white porcelain figurines from the Sui Dynasty (581-619 AD). On this
11 basis, it developed a unique decorative style and exquisite craftsmanship, which
12 greatly influenced the creation and development of blue and white porcelain in the
13 Yuan dynasty (1271-1368 AD) and beyond. The development of black and white
14 porcelain stimulated the emergence of a rich array of decorative techniques and
15 thematic motifs, to a certain extent, encapsulating the prevailing socio-economic and
16 cultural milieu of that era. Black and white porcelain has a rich variety of decorative
17 techniques, it is usually categorized into three types depending on the location of the
18 decoration,^[6] as shown in Fig. S1, (a) over-glazed decoration: glaze is applied to the
19 body/slip, paint decoration is applied on top of it; (b) under-glazed decoration:
20 decoration is applied directly to the body/slip, then transparent glaze is applied on top
21 of it; (c) inter-layer decoration: glaze is applied to the body/slip, then paint decoration
22 is applied to the body/slip and transparent glaze is applied on top of it after it dries.
23 Brushes are the most common tool used for decoration. Besides, more complex
24 techniques are applied to it, such as carving and inlay, to obtain more elaborate
25 designs.^[7]

26 This key role played by black and white porcelain in the development of
27 decorative techniques has received increasing attention in recent years from
28 researchers. Leung *et al.*^[7] characterized the chemical composition of the bodies and
29 glazes, revealing that Fe_2O_3 is the colorant and flux of colored glaze. Jiang *et al.*^[4]
30 investigated the chemical formulation and microstructure of black decoration in red
31 and green porcelain, indicating that they are high-temperature underglazes and
32 revealing the evolution of the technology. D. Ma *et al.*^[8] performed technical analyses
33 on black and white inlay porcelain, subsequently elucidating the interplay of
34 technologies in Southeast Asia. Moreover, Some archaeologists have pointed out that
35 black and white porcelain to some extent influenced the development of blue and
36 white porcelain in the Yuan and Ming dynasties (1271-1644 AD).^[6] However, a
37 comprehensive understanding of the complex structure of black and white porcelain
38 and of the structure and composition of the fugitive crystals in black decoration
39 continues to be explored.

40 In this study, we combined Raman spectroscopy and scanning electron
41 microscopy to investigate in-depth the microstructure and color-imparting crystals of
42 the black decorations produced in Shanxi province. The samples are categorized into
43 Ca-rich glazes from the Hejin^[9] and Xiangning^[10] kilns and Ca-poor glazes from the
44 Huozhou^[11] kilns based on the Ca concentration in glazes.

1 2 Materials and Methods

2 2.1 Sample description and preparation

3 A preliminary study on 21 black and white porcelain sherds collected from
4 archaeological strata of the Jin-Yuan period (AD 1115-1368) from Hejin, Xiangning,
5 and Huozhou regions has shown that the main differences between the samples are the
6 Ca content and the microstructure. Taking these features into account, 4 sherds were
7 selected for this study: 2 sherds with high Ca content GZ-BD01 (Fig.1a) and TGD-
8 BD06 (Fig. 1b) and 2 sherds with low Ca content HZ-BD01 (Fig. 1c) and HZ-BD02
9 (Fig.1d). The patterns of these fragments are all black according to visual observation.
10 Optical microscopy images of the surfaces under each picture of sherds (Figs.1e-h)
11 show that the patterns are not pure black. GZ-BD01, TGD-BD06 and HZ-BD01 are
12 black-brown (Figs. 1e,1f and 1g, respectively), while HZ-BD02 has the darkest colour
13 (Fig. 1h). More detailed characterization of the samples is described in Table S1.

14 SEM and Raman spectroscopy measurements were carried out on polished cross-
15 sections. The cross-sections were made by cutting the fragments into small pieces
16 using a diamond cutter, then fixing them in epoxy resin. They were then ground with
17 silicon carbide paper (1200-4000 grit) and polished with micro-diamond paste down
18 to 1 μm . As the samples were not electrically conductive, they were coated with
19 carbon before being examined under a scanning electron microscope.

20 2.2 Analytical techniques

21 2.2.1 X-ray fluorescence spectroscopy (XRF)

22 Elemental composition was measured using the micro-XRF analyzer (Horiba,
23 XGT-7200, Japan). Spectral collection and analysis are performed by the XGT-7200
24 software equipped with the instrument. The analysis was performed with x-ray tube
25 voltage of 50 kV and a current of 1 A. **Calibration with Corning Glass prior to**
26 **measurement.** The incident X-ray beam diameter was 1.2 mm and the acquisition time
27 for each spectrum was set to 120 s. The measurements were carried out on surface and
28 at least three spectra were recorded for each zone in order to minimize heterogeneous
29 effects. Mappings were performed on ceramic surfaces (19*19 mm²) with also a beam
30 diameter of 1.2 mm. All measurement processes were carried out under vacuum
31 conditions.

32 2.2.2 Scanning electron microscopy and energy dispersive spectrometry (SEM- 33 EDS)

34 The investigations were performed in Thermo Fisher Helios NanoLab 600i with
35 an acceleration voltage of 15 kV and 18 kV, the current is 0.69 μA , and the working
36 distance between 6~7 mm, the chamber pressure range from 3.12×10^{-4} Pa to 5.05×10^{-4}
37 Pa. An Oxford instruments EDS detector was used to record the elemental content and
38 distribution, the diameter of the EDS probes is about 0.2 μm , the process time is 4.
39 The data obtained were recorded and processed using AZtec software.

40 2.2.3 Micro-Raman spectroscopy

41 The study was performed by Xplora MV 2000 (Horiba Jobin-Yvon) micro-
42 Raman spectroscopy equipped with 532 nm excitation provided by a solid-state laser
43 was performed to analyze the crystals in cross section of the glaze at room

1 temperature. The laser was focused and scattered light was collected under a 100x
2 objective. The spatial resolution is 1 μm and the laser power is about 1.3 mW. The
3 optimal spectral curve was obtained by the minimum smoothing method. Igor Pro
4 software was used for data fitting.

5 3 Results

6 3.1 Elemental composition

7 The elemental compositions obtained by XRF are given in Table 1, in oxide mass
8 equivalence. For the body, Al_2O_3 (24.35-30.25 wt%) and SiO_2 (59.38-67.15 wt%) are
9 in accordance with the ones the productions of the northern regions. High Fe
10 concentration (~ 4.46 wt%) is the source of gray/brown bodies. Since the XRF
11 analysis of black decorations and white background was measured from the surface of
12 the fragments and only a fraction of the X-rays penetrated the glaze to reach the
13 pigmented area due to the effect of the upper glassy matrix, so the chemical
14 composition of the black decorations cannot be taken as an accurate composition of
15 the pigment. The major difference between the black decoration and the white
16 background is the Fe content. As the concentrations of Al, Si, K and Ca are very
17 similar, this means that Fe is the main colouring element in the black decoration. An
18 obvious result is that the CaO content in GZ-BD01 (5.13-6.31 wt%) and TGD-BD06
19 (4.56-5.32 wt%) is significantly higher than in HZ-BD01 (1.42-1.72 wt%) and HZ-
20 BD02 (2.26-2.57 wt%). The Fe_2O_3 content of the HZ-BD02 black decoration is much
21 higher, 19.00 wt%, which can be explained by the fact that the pigment zone is closer
22 to the surface than in the other samples.

23 As shown in Fig. S2, the XRF mapping images better visualize the elemental
24 distribution on the surface. The distribution of iron elements is consistent with the
25 black pattern. The traces of using brushes can be observed on TGD-BD06, HZ-BD01
26 and HZ-BD02. In addition, Ti concentration is high in the pattern of TGD-BD06, and
27 almost absent in HZ-BD01 and HZ-BD02.

28 3.2 Morphological analysis

29 Fig. 2 shows the multilayer structure of the cross-section of samples as well as
30 the microscopic images of the pigmented areas. The microstructures of black
31 decorations exhibit significant differences. In GZ-BD01, glaze on the top and the
32 pigment area below, with a white reaction layer at their junction (Fig. 2a). In the
33 enlarged image of the pigmented area, the white reaction layer comprises a large
34 number of well-developed needle-like crystals. Beneath it, a substantial gathering of
35 plate-like crystals and irregular particles can be observed (Fig. 2b). In TGD-BD06, a
36 white slip lies between the body and pigment (Fig. 2c). A considerable portion of the
37 glaze layer is occupied by numerous plate-like crystals and irregular particles (Fig.
38 2d). The glaze of HZ-BD01 and HZ-BD02 is very thin (Fig. 2e and 2g, respectively),
39 with a large number of tightly packed large irregular crystals in the pigment area (Fig.
40 2f and 2h, respectively). Needle- and plate-like crystals are not observed in the
41 pigment of either HZ-BD01 or HZ-BD02. In addition, large crystals with melted
42 edges were observed in the glazes of TGD-BD06, HZ-BD01, and HZ-BD02 (crystals
43 marked with yellow circles in Figs. 2d, 2f, and 2h, respectively). Interestingly, HZ-

1 BD01 and HZ-BD02 feature a thin layer of approximately 25 μm between the
2 pigment layer and the white slip.

3 The crystallization zones of the samples exhibit some similarities. Specifically,
4 the crystallization zones of GZ-BD01 and TGD-BD06 feature small and dispersed
5 crystals surrounded by plate-like crystals, while the crystallization zones of HZ-BD01
6 and HZ-BD02 share similarities in crystal size and morphology. Consequently, we
7 chose to further investigate the crystallization regions of TGD-BD06 and HZ-BD01,
8 as shown in Fig. 3. In TGD-BD06 (Fig. 3a), plate-like crystals are well developed,
9 and elemental mapping suggests that they are rich in Al (Fig. 3c) and Ca (Fig. 3d).
10 Besides, a large aggregation of needle-like crystals contains Al (Fig. 3c). An
11 enlargement image is shown Fig. S3a. EDS analysis of individual crystals revealed
12 that the Al concentration is about 26.5 wt% (Fig. S3b). Fig. 3e and 3f show that these
13 irregular crystals contain high Fe concentration and low Ti concentration. In HZ-
14 BD01 (Fig. 3g), there is no plate-like crystals rich in Al (Fig. 3i) and Ca (Fig. 3j)
15 formation other than irregular-shaped crystals (2-8 μm) at the interface between the
16 white slip and the glaze layer. However, as shown in Fig. 3g, a high concentration of
17 Al is below the pigment layer (corresponding to the thin layer between the pigment
18 and makeup clay in Fig. 2e). Upon image magnification, it is found that this area
19 consists of many needle-like crystals (Fig. S3c), and the EDS results show that the Al
20 content of the crystal is approximately 25.3 wt% (Fig. 2d). Fig. 3k and 3l show that
21 these crystals are also Fe-rich and contain a low Ti concentration.

22 These irregular crystals were analyzed by EDS to obtain their chemical
23 composition. In order to avoid the influence of glassy matrix, only large-sized
24 particles ($\geq 2 \mu\text{m}$) were measured. The results are expressed in atomic percent (Table
25 2). Whatever the sample, Fe concentration is similar in all crystals, range from 26.97-
26 33.35 atom%, but the concentration of Ti in the particles from zone 1 (1.32-2.28 atom
27 %) is significantly higher than that of zone 2 (0.22-0.23 atom%).

28 The microstructure of the cross-section at the interface between black decoration
29 and white glaze is investigated, as shown in Fig. 4. In GZ-BD01, numerous needle-
30 like and plate-like crystals were observed both in black decoration and white glaze,
31 but there is no white slip in the black decoration area (Fig. 4a). For the three other
32 samples, there is a clear difference in the distribution and number of crystals at the
33 junction of the black decoration and the white glaze. In TGD-BD06 black decoration
34 (Fig. 4b), a large number of needle-like crystals and iron particles occupy most of the
35 area in the glaze, whereas in the white background, only needle-like particles are
36 formed at the interface between the glaze and the slip. In HZ-BD01 (Fig. 4c) and HZ-
37 BD02 (Fig. 4d), we observe irregular particles in black decoration but no needle-like
38 crystals: only a small number of plate-like crystals are observed at the interface in the
39 white background area.

40 3.3 Micro-Raman spectroscopy analysis

41 We investigated the structure of the upper glazes in black decorations, as
42 illustrated in Fig. S4, and their Raman spectra exhibit two broad bands at $\sim 480 \text{ cm}^{-1}$
43 and $\sim 1000 \text{ cm}^{-1}$, corresponding to the bending and stretching vibrations of the SiO_4
44 tetrahedra, respectively. These characteristics align with the Raman spectral features

1 of the silicate glass phases found in ancient porcelain glazes.^[12] A noticeable
2 difference is the relative intensities and areas (A500/A1000) of the bending and
3 stretching modes in the spectra of GZ-BD01 and TGD-BD06, which are significantly
4 higher than those of HZ-BD01 and HZ-BD02. This difference may be attributed to the
5 high concentration of Ca in the GZ-BD01 and TGD-BD06 glazes.^[13]

6 Crystallographic identification of the crystals labeled in Figs. 3a and 3g (pt01 to
7 pt07) resulted in the characteristic bands of the 7 crystals shown in Figs. 3b and 3h.
8 Fig. 3b shows that the Raman bands of pt01, pt02 and pt03 in zone 1 are located at
9 about 223, 295, 414, 618, 668 and 1333 cm^{-1} , which are the typical Raman bands for
10 hematite^[16]. It has been checked that hematite has not been generated from oxides by
11 thermal effect by using a lower power for the Raman experiment: the spectra have
12 also been recorded with a lower power of 0.08 mW, it exhibits the same bands, but
13 less defined and much noisier (Fig. S5). Crystal pt04 is identified as anorthite because
14 of the 189, 280, 482, 505 and 558 cm^{-1} bands. Fig. 4h also shows that pt05, pt06, and
15 pt07 are hematite crystals, but there is no anorthite formation. As shown in Fig. 5, in
16 addition to the large amount of hematite in zone 1, spinel and pseudobrookite crystals
17 are also formed in other black-decorated areas of TGD-BD06.

18 To investigate the effect of ion doping on the crystal structure of hematite, the
19 elemental compositions and corresponding Raman spectra of hematite crystals were
20 measured in different areas of the Ca-rich glaze GZ-BD01, TGD-BD06 and the Ca-
21 poor glaze HZ-BD01, HZ-BD02, respectively. The deconvolution calculation of the
22 Raman spectra was performed to get the displacement and half-height widths of the
23 strong spectral bands at about 670 cm^{-1} . It should be noted that the measured hematite
24 crystals are larger than 5 μm in size, thus minimizing the influence of the glass matrix
25 on the measurements. As shown in Fig. 6, a double substitution of Ti and Al ions is
26 formed in the hematite structure. Fig. 6a and 6b show the trend of Ti and Al doping on
27 the position of the 670 cm^{-1} band, respectively. Fig. 6a shows that Ca-rich glazes GZ-
28 BD01 and TGD-BD06 have slightly higher Ti-doping in hematite than Ca-poor glazes
29 HZ-BD01 and HZ-BD02. This band also shifts towards lower wavenumber with
30 increasing Ti-doping, whereas it tends to shift to higher wavenumber with increasing
31 Al-doping (Fig. 6b). In Fig. 6c, it is shown that with an increase in the Ti-doping
32 concentration, the FWHM (full width at half maximum) of the band exhibits a nearly
33 linear trend of augmentation. In Fig. 6d, the Al doping concentration appears to
34 exhibit no pronounced correlation with the broadening of the 670 cm^{-1} band. Under
35 equivalent levels of Al-doping, the spectral band broadening of GZ-BD01 and TGD-
36 BD02 exceeds that of HZ-BD01 and HZ-BD02.

37 4 Discussion

38 As observed in the results section, Ca-rich glaze and Ca-poor glaze samples
39 exhibit numerous differences not only in micro-structure but also in the chemical
40 composition related to elements other than Ca. These discrepancies can be attributed
41 to disparities in raw materials and the manufacturing processes employed.

1 Considering the positioning of the black pigment layer, GZ-BD01 and TGD-
2 BD06 are both under-glazed decorations because their pigments are between the
3 body/slip and the transparent glaze. The process involves covering the raw body with
4 a variable thickness layer of white slip, waiting for it to dry, then painting with
5 brushes dipped in black pigment and covering it with a layer of transparent glaze
6 before firing at high temperature. GZ-BD01 has a more complex process involves
7 carving the design into the white slip and filling it with pigment before glazing it,
8 resulting in a sharper effect.

9 The pigment layer of HZ-BD01 and HZ-BD02 is also underneath the transparent
10 glaze, but seems to have a more complex structure. It is noteworthy that there is a ~25
11 μm layer between the pigment and white slip. The elemental distribution shows that
12 this layer is enriched in aluminum as well as small amounts of calcium and potassium
13 compared to the transparent glaze, while the silicon concentration is significantly
14 lower (Fig. S6). The composition of the glass matrix encapsulating the iron particles is
15 very similar to that of the upper transparent glaze (Table S2), which implies that a
16 glaze liquid may have been added to the pigments. Enlargement image shows that only
17 a large number of mullite particles are observed below the pigment (Fig. S3c and
18 S3d). Its formation is facilitated by the melting of pigments at high temperatures
19 accompanied by diffusion of iron ions into the white slip, while aluminum ions
20 migrate from white slip along the concentration, thus promoting the growth of mullite
21 at the interface. The layer is therefore most likely formed by the reaction between the
22 pigment and the white slip during the firing stage, its thickness are related to the firing
23 temperature and duration.

24 The high Ca concentration in the GZ-BD01 and TGD-BD06 glazes (4.56-6.31 wt
25 %) provides sufficient material conditions for the formation of anorthite. Ca^{2+} readily
26 reacts with Al^{3+} to form a dense layer of anorthite crystals at the body/slip-glaze
27 interface. Therefore, large amounts of well-developed anorthite crystals in the
28 pigment are formed in-situ. Moreover, glazes with a high Ca concentration are less
29 viscous and easier to flow at high temperatures, which leads to pigment diffusing into
30 the glassy matrix. Therefore, Al-rich minerals or the addition of kaolin to black
31 pigments are applied to prevent the diffusion of pigment. This technique is similar to
32 that used for cobalt blue pigments of blue and white porcelain produced during the
33 Ming and Qing dynasties.^[17]

34 Although the high concentration of Ca in the upper glaze facilitates the flow of
35 the glassy phase, the high concentration of Al in the pigment increases its viscosity at
36 high temperatures,^[18,19] making it less likely to flow with the glaze, leading to the
37 formation of a large number of anorthite crystals in the pigmented areas. This explains
38 the significant difference in the distribution of anorthite between the regions of the
39 white background and the black decoration. On the contrary, the Ca contents in HZ-
40 BD01 and HZ-BD02 are lower than that of GZ-BD01 and TGD-BD06, and there is a
41 slight decrease in the concentrations of MgO and Na_2O , while K_2O content does not
42 change. Theoretically, the reduction of fluxes such as CaO and MgO leads to an
43 increase in glaze viscosity.^[1,20] Therefore, there is no need to use aluminum-rich
44 pigments in Ca-poor glazes to ensure the sharpness of the patterns. Moreover, Ca is a

1 modifier of the glass network, breaking the Si-O bonds and altering the degree of
2 polymerization. Consequently, the higher Ca concentration results in lower relative
3 intensities (A500/A1000) of the Si-O bending and stretching modes,^[14,15] this explains
4 the difference in Raman spectra of black decorations of Ca-rich and Ca-poor glazes
5 (Fig. S4). It can be inferred that the craftsmen in Shanxi Province were able to select
6 different pigment sources and to adjust their processes according to the composition
7 of the glazes to their composition.

8 In the black decoration of the Ca-rich glaze samples, although the presence of
9 numerous hematite crystals indicates that they were mainly fired in an oxidizing
10 atmosphere. Spinel phase is also detected (Fig. 5), the EDS results indicate Fe content
11 is 15.78 atom%, Ti content is 1.23 atom%, and Al content is 6.88 atom% (Table S3).
12 Consequently, the crystal in question may be identified as an iron spinel, with the
13 possibility of some Fe atoms being substituted by Al and Ti. Given that magnetite can
14 form from hematite in a reducing atmosphere, we can assume that the atmosphere was
15 not totally oxidizing, or at least unstable. During this transformation, the color of the
16 initial hematite changes to earthy brown or even black, probably due to elemental
17 substitution.^[21] The abundance of pseudobrookite in the pigment area of GZ-BD01
18 and TGD-BD06 could be attributed to the formation of high concentrations of Fe and
19 Ti in the raw material at elevated temperatures, as suggested in the references.^[22,23] It
20 is also observed in ancient Roman Terra Sigillata^[24] and Chinese oil spotted glaze,^[25]
21 Alternatively, it's possible that pseudobrookite is inherently present in the raw
22 material itself, as it is known to be highly stable and does not completely decompose
23 until temperatures as high as 1300 °C.^[26] Therefore, the large stable pseudobrookite
24 crystals in the pigment area suggest that the porcelain may have been fired at
25 temperatures lower than 1300 °C. Furthermore, the crystal types in Ca-poor glazes
26 HZ-BD01 and HZ-BD02 are relatively simple, consisting primarily of hematite and
27 unmelted particles, identified as quartz crystals (Fig. S7). The large amount of
28 hematite crystals suggests that the atmosphere up to the glaze vitrification was
29 oxidizing.

30 The hematite crystals in this study are substituted with Al and Ti. The strong
31 band around 670 cm⁻¹ observed in Raman spectroscopy is not present of pure
32 hematite.^[27] It can be attributed to (i) the superimposition effect of magnetite,^[28,29] (ii)
33 the breaking of lattice symmetry caused by Al^[27,30] and Ti^[31] doping, thermal treatment,
34 weathering, etc; (iii) finite-size effects in nanocrystalline hematite.^[16,29] Previous
35 studies have shown that Al-doping will lead to the appearance of the 670 cm⁻¹ band,
36 but its intensity is low.^[30,32] Therefore, we speculate that this band is most likely
37 produced by the substitution of Al ions and Ti ions, these ions change the color of
38 hematite. Al-doping lightens the color of hematite^[33,34] but Ti-doping may change
39 hematite crystals to brownish red color.^[25]

40 Scatter plots of Ti and Al doping versus the around 670 cm⁻¹ band (Fig. 6)
41 illustrate that the relationship between the amount of ion doping and the shift of the
42 peak position is complex and is not determined by a single ion doping. However,
43 there is a clear relationship between Ti-doping and the FWHM of this band, rather
44 than Al. Since the radius of Ti⁴⁺ (0.61 Å) is slightly smaller than the radius of Fe³⁺

1 (0.65 Å), Fe³⁺ in the hematite lattice is easily replaced by Ti⁴⁺, forming a highly
2 polarizable Ti-O bond.^[35,36] But in order to maintain the charge balance inside the
3 hematite crystal, another Fe³⁺ must be converted into Fe²⁺. The more Ti-doping, the
4 more hematite structure disordered, which is consistent with the result that the
5 FWHM of the band increases with the increase of Ti-doping concentration.

6 Based on the positioning of the black pigment within the glaze layer, both Ca-
7 rich glaze and Ca-poor glaze samples fall under the category of under-glazed
8 decoration. A delicate white slip covers dark and rough objects to enhance the contrast
9 between black and white colors. Additionally, Al-rich pigments are used in the
10 decoration of Ca-rich glazes, while higher purity iron ores are used for decoration in
11 Ca-poor glazes.

12 The color of black decorations is affected by the categories, size, and quantities
13 of crystals, as well as the valence and concentration of the color-imparting ions in the
14 glass phase. We find that the pattern is darker in areas where the pigment layer is
15 thicker. Hematite, the major color-imparting crystal, changes from red to brown due to
16 Ti doping. Hematite is small in size and quantity, the glaze is thicker and has a large
17 number of anorthite crystals, and a large number of magnetite particles are formed,
18 deepening the patterned color of the Ca-rich glaze. In contrast, the hematite crystals in
19 the Ca-poor glaze are larger and more numerous, some of the crystals are exposed on
20 the surface. After the light passes through the extremely thin glaze layer and reaches
21 the densely arranged hematite, it is diffusely reflected, thus deepening the color of the
22 pattern and making it dark brown.

23 5 Conclusions

24 The multilayered structure of the black and white porcelains investigated in this
25 study is consistent with the characteristics of underglaze-decorated porcelain,
26 including body, white slip, black pigment and top transparent glaze. Both Ca-poor and
27 Ca-rich glazes were used leading to significant differences in the microstructure. In
28 Ca-rich glazes, large quantities of well-developed anorthite surround iron particles,
29 which is in agreement with a deliberate addition of kaolin into the pigment. The
30 majority of crystal iron oxides found in black decoration are substituted (Ti, Al)
31 hematite. Besides, the categories, size, and distribution of iron particles, as well as
32 different Ti/Fe ratios in the hematite, reveal that different sources of black pigments
33 were certainly applied. Their rather large crystal size and Ti substitution could be the
34 origin of the dark color of the decorations. The presence of Ti in the hematite
35 structure increases the charge transfer between cations and anions leading to an
36 increase in absorption in the visible range, so that the patterns observed by the naked
37 eye is dark brown in color, and the shade of the color is related to the size and number
38 of iron particles in the pigment. A large number of tiny magnetite particles was also
39 observed but only in Ca-rich glaze samples.

40 Acknowledgments

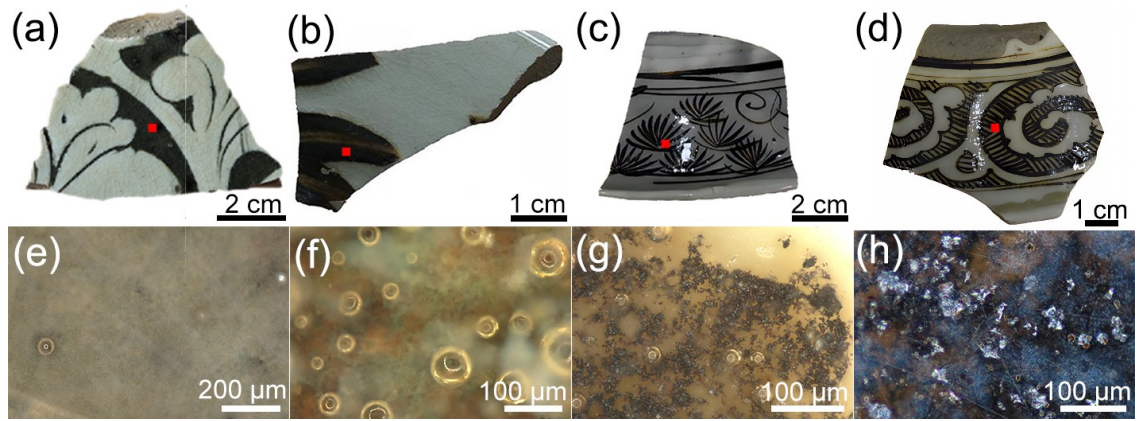
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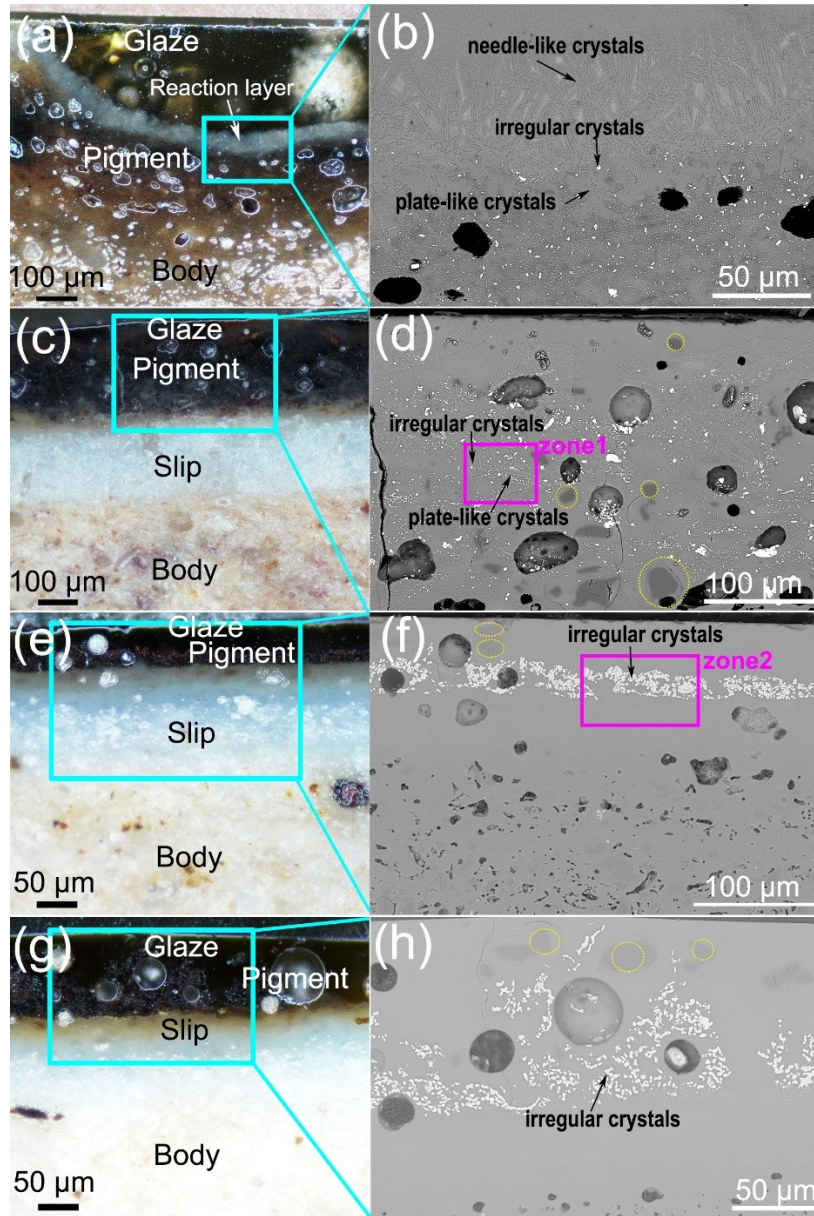
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3 Figure 1 Photographs of four black and white porcelain fragments (a) GZ-BD01;(b) TGD-BD06;
4 (c) HZ-BD01; (d) HZ-BD02 excavated in the southwestern region of Shanxi province and
5 produced in the Jin and Yuan dynasties (1115-1368 AD). The images below each sample
6 correspond to optical microscopy imaging of the surface (labeled as red spots) respectively.



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2 Figure 2 Optical images of the cross-section and SEM images of the corresponding pigment zones
 3 of (a and b) GZ-BD01; (c and d) TGD-BD06; (e and f) HZ-BD01; (g and h) HZ-BD02.

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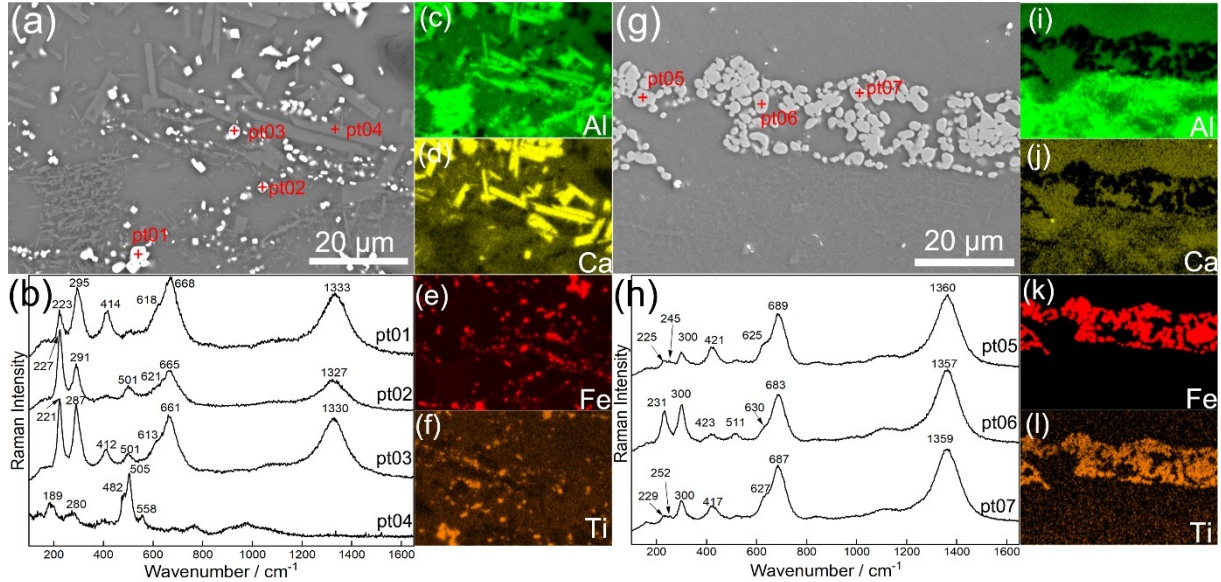
Table 1 Analytical results (wt %) obtained by X-ray fluorescence of the four samples.

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No.	Component	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
GZ-BD01	Black decoration	1.22	1.85	16.10	69.53	3.50	5.13	0.21	2.45
	White glaze	0.71	1.59	16.55	70.49	3.15	6.31	0.16	1.05
	Body	0.42	0.38	30.25	59.38	1.94	0.60	1.59	5.44
TGD-BD06	Black decoration	1.18	1.45	15.89	68.51	4.17	4.56	0.27	3.96
	White glaze	1.26	0.82	15.85	72.14	3.65	5.32	0.13	0.83
	Body	0.12	0.28	25.24	65.45	1.39	0.63	1.27	5.61
HZ-BD01	Black decoration	0.71	0.59	15.96	69.83	4.38	1.42	0.17	6.93
	White glaze	0.74	1.05	17.32	73.24	4.39	1.72	0.19	1.35
	Body	0.61	0.45	24.35	67.15	2.31	0.30	1.03	3.80
HZ-BD02	Black decoration	0.28	0.82	14.03	60.07	3.15	2.26	0.31	19.06
	White glaze	0.79	1.31	16.60	72.67	3.83	2.57	0.25	1.99
	Body	0.84	0.53	25.26	66.93	1.84	0.47	1.14	3.00

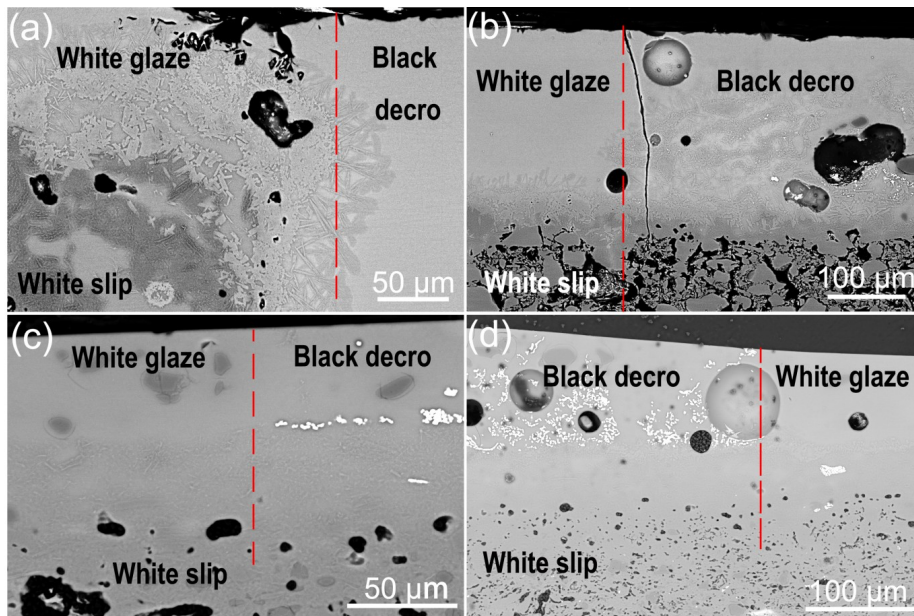
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Figure 3 Enlargement SEM images of (a) zone1 in TGD-BD06 and (g) zone2 in HZ-BD01 (magenta rectangles in Figure 2); element mapping of zone1 (c: Al, d: Ca; e: Fe, f: Ti) and (b) Raman spectra recorded on crystals (pt01, pt02 and pt03: hematite, pt04: anorthite) of zone 1; element mapping of zone2 (i: Al, j: Ca; k: Fe, l: Ti) and (h) Raman spectra recorded on crystals (pt05, pt06 and pt07: hematite) of zone 2

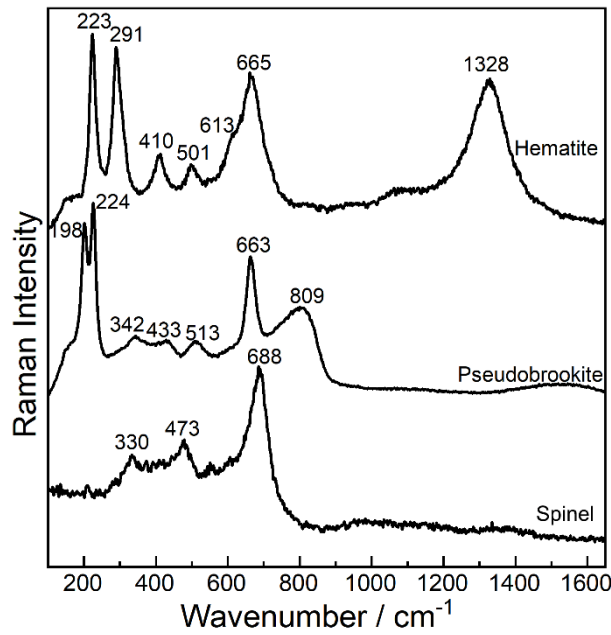


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Figure 4 SEM images of the intersection of white glaze and black decoration in cross-section of (a) GZ-BD01; (b) TGD-BD06; (c) HZ-BD01; (d) HZ-BD02

Table 2 EDS spectrum analysis results (atom%) of labeled crystals in Figure 3

	O	Mg	Al	Si	K	Ca	Ti	Fe	Ti/Fe
pt01	59.39	1.20	5.47	1.29	0.31	-	1.32	31.03	0.043
pt02	58.50	0.35	3.99	1.56	-	0.03	2.21	33.35	0.066
pt03	61.58	-	5.69	2.89	0.30	0.28	2.28	26.97	0.085
pt04	62.67	-	15.60	16.05	0.15	5.32	0.20	-	-
pt05	60.58	-	6.00	3.67	0.38	-	0.23	29.00	0.008
pt06	60.78	-	5.69	0.35	-	-	0.23	32.95	0.007
pt07	60.65	-	5.99	0.24	-	-	0.22	32.90	0.007

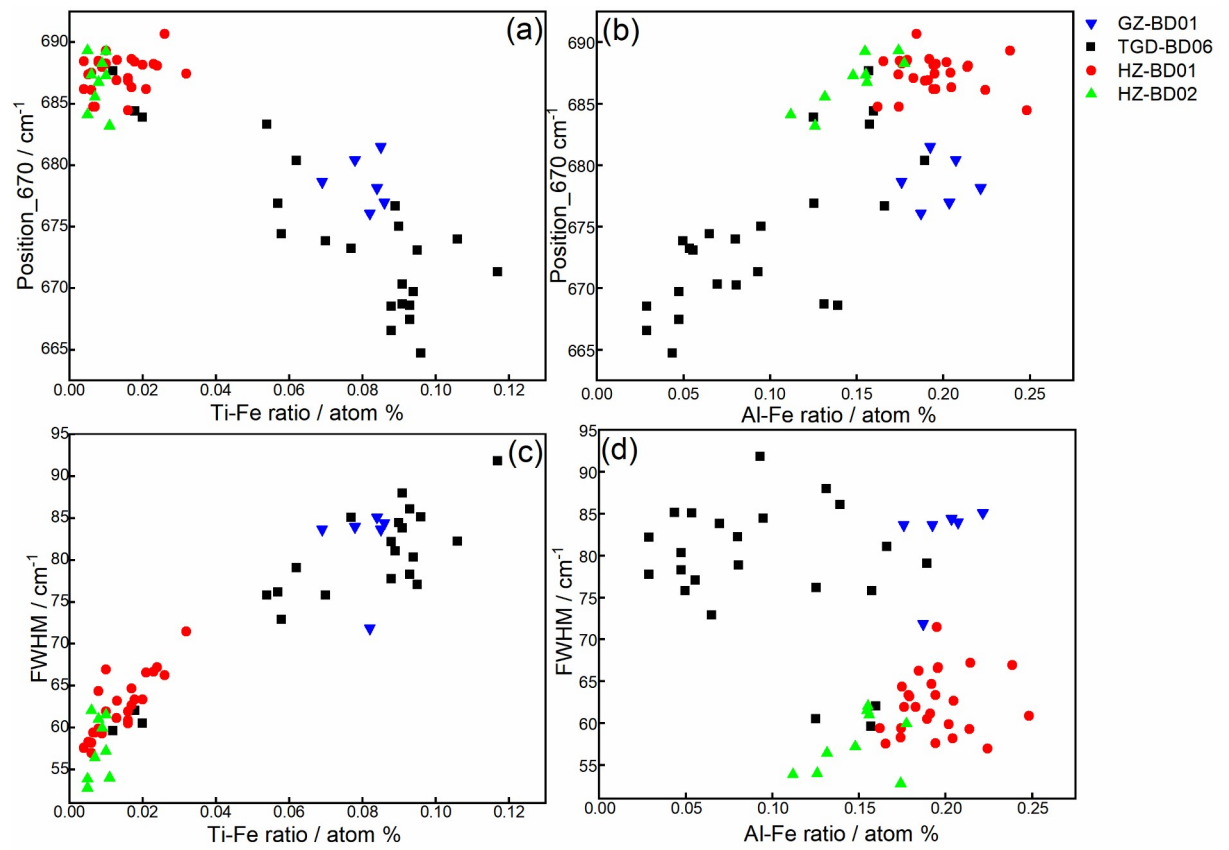


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Figure 5 Raman spectra of iron particles collected in the black decorations of Ca-rich glaze TGD-BD06

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2 Figure 6 Scatter plots of the 670 cm⁻¹ band position in hematite versus (a) Ti/Fe ratio (b) and Al/Fe
 3 ratio; Scatter plot of the FWHM (full width at half maximum) of the 670 cm⁻¹ band versus (c)
 4 Ti/Fe ratio and (d) Al/Fe ratio