

Article

An Archaeometric Study of Chinese Porcelain Sherds Found at the Santana Convent in Lisbon—Part 2: A Comparison with Coeval Chinese Samples of Well-Known Provenance

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Highlights

- Sherds from the Santana Convent in Lisbon were compared with 17th-to-19th c. Chinese porcelains
- A multi-analytical approach (XPS, GSDR, micro-Raman, XRD, XRF, SM) was used.
- Results point to different forms of cobalt ions and emplacements in the surface glassy structure.
- Implications:
- XPS, GSDR and SM studies established clear differences between the dark- and light-blue glazes.
- For sample 15, in light-blue zones, cobalt ions exhibit a XPS lower-intensity multiplet structure than in dark zones.
- The 18th c. samples from the Santana Convent were most probably from the Dehua kilns (Quanzhou, Fujian)

Abstract

This study presents an archaeometric characterization of fifteen blue-and-white Chinese porcelain sherds (17th–19th centuries) from the Jingdezhen, Anxi, and Dehua kiln systems, compared with fragments recovered from the Santana Convent (Lisbon), particularly eighteenth-century materials. A combination of non-invasive, minimally invasive and micro-destructive techniques, including Ground-State Diffuse Reflectance Spectroscopy (GSDR), X-ray Photoelectron Spectroscopy (XPS), micro-Raman spectroscopy, X-ray Fluorescence (XRF), X-ray diffraction (XRD), and stereomicroscopy, was employed to investigate cobalt pigments, glaze composition, firing conditions, and provenance indicators. The results reveal systematic differences between dark- and light-blue glazes, reflecting distinct pigment-processing technologies or simple concentration effects inducing different cobalt coordination environments and/or oxidation states. Raman spectroscopy confirms that cobalt occurs mainly as Co²⁺ ions dissolved in the amorphous silicate glaze matrix. No Raman-detectable crystalline cobalt silicate or cobalt aluminate phases were identified. XRF and XPS analyses show elevated Mn/Co and Fe/Co ratios combined with extremely low



Academic Editor: Lucia Toniolo

Received: 18 May 2026

Revised: 24 June 2026

Accepted: 25 June 2026

Published: 27 June 2026

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arsenic contents, suggesting the predominant use of domestic Chinese cobalt sources. XRD analyses identified quartz, mullite, and minor anorthite, consistent with traditional high-fired hard-paste porcelain technology. Dark-blue radiating star-shaped colored radiating features, particularly frequent in Dehua porcelains, were also identified in selected Santana Convent samples, suggesting their attribution to Dehua kiln production and demonstrating the value of glaze defects as complementary provenance markers.

Keywords: Chinese porcelains; Santana Convent; blue and white glazes; micro-Raman; XPS; GSDR; XRD; XRF; SM

1. Introduction

This work is the part 2 of a previous publication [1]. When, in 1498, Vasco da Gama arrived in Calicut (Kozhikode), on the Malabar Coast in the Indian Subcontinent, he was presented by the raja Samorim (Samuthiri) with 13 Chinese porcelain vessels. The Portuguese captain would go on to acquire, at the Chinese trading factory established there, a collection of porcelain to present his queen. From that time onwards, porcelain reached Europe via the maritime route that enabled clear commercial, technique, and cultural interaction with the East.

Following the establishment of a permanent Portuguese trading post or factory in Macau in 1557, an intense maritime commercial network was developed between China and Portugal. Through this route, large quantities of porcelain; silk; spices; ivory; pearly, precious stones; and many other luxury goods reached Lisbon, from where many were redistributed throughout Europe. During the sixteenth and seventeenth centuries, Lisbon became one of the most important cosmopolitan commercial centers in Europe [2,3].

Several large Portuguese vessels belonging to the “Carreira das Índias” were wrecked along the African coastlines during this period. Chinese porcelain fragments recovered from these shipwrecks, collected off the South African or West African coasts, have provided valuable archaeometric information regarding export porcelains from the Ming and Qing dynasties [4,5]. However, most previous studies were based on relatively limited numbers of samples.

The catastrophic earthquake of 1755, which devastated much of Lisbon and its outskirts, also created exceptional archaeological contexts where many more sherds and sometimes almost complete vessels of Chinese porcelains could later be recovered from palaces, convents, and monasteries, or in rich houses, domestic refuse deposits, wells, and garbage pits [6,7].

The Santana Convent in Lisbon was constructed between 1561 and 1564, under the patronage of King John III and of his wife, Queen D. Catarina. It was a women’s religious house and remained operative until 1884, 50 years after the 1834 law, which abolished the religious orders and closed all convents and monasteries in Portugal.

Excavations directed by two of the co-authors (RVG and MVG) in the area it once occupied, that took place in 2002–2003 and 2009–2010, led to the identification of many of its subterranean structures, as well as a vast assemblage of finds. Among these, around 1800 pieces, either complete or fragmentary, corresponding to 500 Chinese vessels were recovered in wells or garbage pits. They were mainly produced in the late 16th century and the following century, and a few in the 18th century, used as tableware or for decorative purposes [7].

Porcelain richly painted in cobalt blue on a white background predominates and was produced in the kilns of Jingdezhen during the reigns of Jiajing and Wanli. Polychrome

and gilded examples (kinrande and wucai) were also identified, as well as some bearing imperial symbolism and intended for the Chinese court.

In the present work, fifteen blue-and-white porcelain sherds of well-documented Chinese provenance were selected for comparative archaeometric characterization against the Lisbon fragments previously described in Part 1 [1].

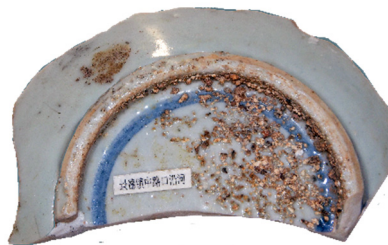
The Fifteen Chinese Sherds Under Study

In Figure 1, we present all sherds under study in this work. The N1 to N15 samples are porcelain sherds of archaeological Chinese provenance.

The dating of these reference specimens strictly adheres to the typological methods of ceramic archaeology. The chronological attribution was made through a comprehensive assessment of period-specific features, including decorative motifs, body and glaze characteristics, underglaze blue coloration, and firing techniques. These evaluations were strictly cross-referenced against artifacts excavated from kiln sites and dated standard wares recovered from shipwrecks [8].



N1—Jingdezhen kiln (Jingdezhen, Jiangxi), 17th c.
Bowl internal face



Bowl external face, with ring foot



N2—Jingdezhen kiln (Jingdezhen, Jiangxi), 17th c.
Bowl internal face



Bowl external face, with ring foot



N3—Anxi kiln (Quanzhou, Fujian): Zhuta Village
kiln site, late 17th c.
Dish front face



Dish back face, with ring foot

Figure 1. *Cont.*



Bowl internal face



Bowl external face

N4—Anxi kiln (Quanzhou, Fujian): Zhuta Village kiln site,
late 17th c.



Bowl internal face



Bowl external face

N5—Anxi kiln (Quanzhou, Fujian): Zhuta Village,
Huoshaoban kiln site, late 17th c.

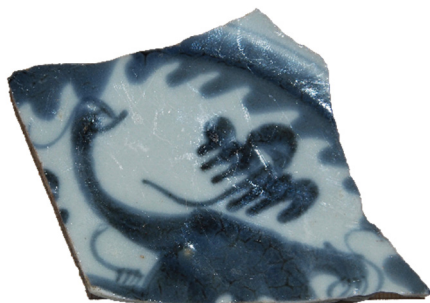


Dish front face



Dish back face, with ring foot

N6—Dehua kiln (Quanzhou, Fujian): Neiban kiln site,
late 17th c.–18th c.



Dish front face



Dish back face, with ring foot

N7—Dehua kiln (Quanzhou, Fujian): Dalongkou
kiln site, 18th c.

Figure 1. *Cont.*



Bowl internal face



Bowl external face

N8—Dehua kiln (Quanzhou, Fujian): Dalongkou
kiln site, 18th c.



Bowl internal face



Bowl external face, with ring foot

N9—Dehua kiln (Quanzhou, Fujian): Dalongkou
kiln site, 18th c.



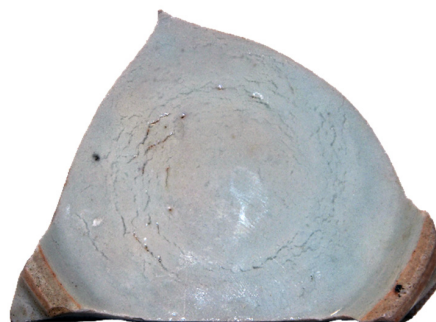
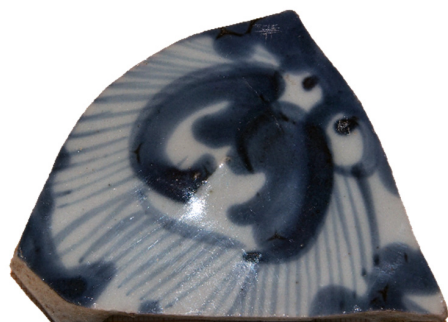
Bowl internal face



Bowl external face, with ring foot

N10—Dehua kiln (Quanzhou, Fujian): Dalongkou
kiln site, 18th c.

Figure 1. *Cont.*



N11—Dehua kiln (Quanzhou, Fujian):
Dalongkou kiln site, 18th c.

Dish front face

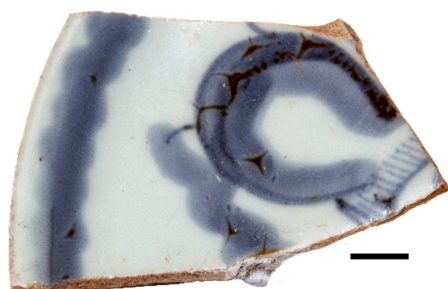
Dish back face, with remains of ring foot



N12—Dehua kiln (Quanzhou, Fujian): Dalongkou
kiln site, 18th c.

Bowl internal face

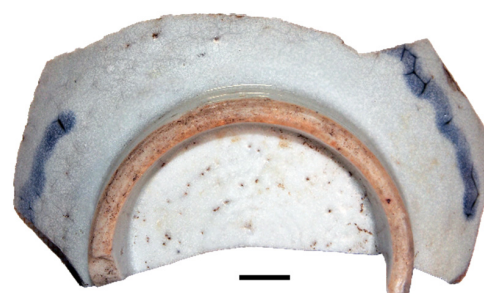
Bowl external face, with ring foot



N13—Dehua kiln (Quanzhou, Fujian): Dalongkou
kiln site, 18th c.

Bowl internal face

Bowl external face, with ring foot



N14—Dehua kiln (Quanzhou, Fujian): Dalongkou
kiln site, 18th c.

Bowl internal face

Bowl external face, with ring foot

Figure 1. *Cont.*



N15—Dehua kiln (Quanzhou, Fujian): Housno
kiln site, late 18th c.–19th c.

Bowl internal face

Bowl external face, with ring foot

Figure 1. Chinese porcelain sherds N1–N15 were provided by the co-author (SL) as reliable reference specimens for comparison with the sherds excavated from the Santana Convent in Lisbon. These specimens, currently housed in the Sun Yat-sen University Museum, were all collected in situ with well-documented kiln site contexts. Based on typological comparison, their dates range from the 17th to the 19th century. Scale bar—1 cm.

All samples studied here, in Part 2, are from the Qing Dynasty, and dated the 17th and 18th century, although sample N15 is dated late 18th century–19th century.

N1 and N2 are blue-and-white samples from the Jingdezhen kilns in Jiangxi Province, representing typical products of that region in the 17th century.

Samples N3, N4, and N5 originate from the Anxi kilns. Anxi County is located in the southeast of Fujian Province, on the upper reaches of the West Stream of the Jin River, and is administratively under Quanzhou City. The blue-and-white porcelain of the Anxi kilns was significantly influenced by Dehua kilns in firing technology, yet still possesses distinct local characteristics. Its products generally exhibit coarser forms and a higher ring foot; the body is mostly grayish-white or gray with relatively many impurities; the glaze color is white with a slight bluish or grayish tinge; and the underglaze blue decoration tends to be relatively simple and roughly executed.

Samples N6 to N15 come from the Dehua kilns. In a broad sense, “Dehua kilns” refers to the extensive kiln industry system distributed within the administrative boundaries of Dehua County, Fujian Province. To date, archaeological surveys have identified over 200 kiln sites in this county, among which approximately 160 Qing dynasty sites are recorded as having produced blue-and-white and white porcelains for export. These kilns are mostly named after specific localities (such as villages or hills). The kiln sites referred to in this study as “Dalongkou”, “Neiban”, and “Housno” are relatively independent production units with their own characteristics within the Dehua kiln system. In terms of product features, Dehua blue-and-white porcelain pieces inherit the deep-rooted ceramic traditions of the area. Their forms are regular and finely crafted; the body is white and dense; the glaze surface is smooth and lustrous, mostly pure white or white with a slight bluish tinge; the underglaze blue decoration is rich in subject matter, executed with skilled and stable brushwork that flows freely and generously, and the patterns have a strong sense of layering.

A large portion of the blue-and-white fragments excavated from the Santana Convent was primarily attributed to Jingdezhen, 16th and 17th centuries. Many sherds studied in Part 1 were from the 17th century, Ming dynasty, and some of them from the Wanli reign. Only samples S11 and S12 (from Part 1) were dated to the 18th century.

2. Experimental Section

GSDR experiments were conducted employing a home-built diffuse reflectance set-up, using an ICCD as detector and a W-Hal lamp as an excitation source. Three standards, Spectralon white disk, magnesium oxide and barium sulphate powder, were used to obtain reflectance data. Each spectrum was acquired at least three times. As a first step of this technique, the reflectance R is determined as a function of the wavelength in the 250-to-750 nm range (UV, Vis and NIR spectral regions), and with the use of R and the Kubelka Munk equation, the Remission Function (absorption spectra) is calculated.

X-ray Photoelectron Spectroscopy (XPS) was employed to investigate possible chemical differences between strongly pigmented dark-blue regions and weakly pigmented light-blue regions, particularly regarding cobalt and manganese. Two representative samples were analyzed, N2 and N15, each of them in two different regions, one exhibiting intense dark-blue decoration and another showing light-blue pigmentation. Due to the shallow analytical depth of XPS (typically below 10 nm), superficial glaze layers were carefully scratched in selected areas to expose the pigment-rich regions. The scratched pieces were mounted onto the sample holder using double-sided conductive tape. Spectra were acquired using a Kratos XSAM800 dual-anode spectrometer operating with Al $K\alpha$ radiation ($h\nu = 1486.6$ eV).

The power was set to 120 W. Samples were analyzed in an ultrahigh-vacuum (UHV) chamber ($\approx 10^{-7}$ Pa) at room temperature, with an analysis angle of approximately 0° relative to the surface normal. Spectra, collected with a 0.1 eV step size using Vision 2 for Windows software (Version 2.2.9, KRATOS). Data treatment and peak fitting were performed with XPSPeak 4.1 software using Shirley or linear (Co 2p and Mn 2p) background corrections and Gaussian–Lorentzian peak shapes.

No flood gun was used for neutralizing charge accumulation. Charging effects were corrected by setting the C 1s component of adventitious carbon to 285.0 eV [9,10]. Under these conditions, the Si 2p_{3/2} peak remained constant at 103.0 eV in all the samples.

For quantification purposes, the sensitivity factors (SFs) used were those furnished by the equipment library: 0.278 for C 1s, 0.78 for O 1s, 0.477 for N 1s, 2.393 for Co 2p_{3/2}, 0.328 for Si 2p, 0.193 for Al 2p and 2.659 for Mn 2p.

Micro-Raman spectroscopy proved to be particularly effective for identifying pigments, assessing glaze structure, and characterizing crystalline phases present in both the glaze and the ceramic body. Raman spectra were acquired directly on glazed surfaces using a confocal micro-Raman system under low laser power to avoid thermal alteration—Renishaw InVia Confocal Raman equipment in a back-scattering micro-configuration. A powerful 300 mW, 532 nm laser excitation (Cobolt, Samba model, Solna, Sweden) used 100 $\times$, 50 $\times$, 20 $\times$, and 10 $\times$ objectives in a Leica microscope. Most spectral collections were made with the use of a 20 $\times$ or 10 $\times$ long-working-distance objective. The spectral resolution of the Raman spectrometer was ~ 1 cm^{−1}. The laser power for the sample lies in the 1-to-15 mW range, depending on the sample under study.

The Renishaw equipment has accurate confocal capabilities, enabling in-depth studies from the surface to about 150 μ m. All Raman spectra were recorded at least in 5 different spots for each sample, and all spectra presented in this paper are representative of the samples under study. For the micro-Raman investigations, the analyzed spot had a diameter of approximately 10 μ m. Data acquisition was performed with the Renishaw software Wire 4, and data processing, namely, the baseline correction, was performed, when needed, with the Wire 4 software or with the LabSpec software (v5.25) from Jobin Yvon.

The technique provided information regarding the silicate network organization of the glaze, as well as the occurrence of crystalline inclusions.

X-ray fluorescence (XRF) was used here to determine the chemical composition of the porcelain sherds, as it was used before for studies of ancient Portuguese pottery of our group, although it only allows for the determination of the elemental compositions of elements heavier than sodium. The chemical composition of the pastes was accurately determined by X-ray fluorescence with the use of a Niton XL3T GOLDD from Thermo Scientific (Waltham, MA, USA) spectrometer, with an X-ray generator of 50 kV/200 μ A, equipped with a CCD for image location (3 mm spot diameter) and storage. The benchtop XRF-EDS system was used in an air atmosphere. This equipment was used at the laboratory level in a bench mode, but it also can be used as a portable/hand-held XRF instrument. Apart from the internal calibration, the equipment was also calibrated with standards IRRM-BCR-126A—Lead Crystal Glass, and BAM-S005B—Multi-element Glass for XRF Analysis. Analyses were made for sherds and not for powders. All the analyses were performed at least in three spots, but in some cases, in five spots for each sample. The estimated error for major elements (Si and Al) was $\leq 3\%$, for minor elements (K, Ca) $\leq 4\%$ and for trace elements $\leq 8\%$.

Table containing XRF data presents these data, expressed as the weight % of the indicated oxides for major, minor or trace elements.

To study the mineralogical and phase composition of the ceramic bodies and glazes of the porcelain sherds, XRD experiments of the powder crystalline phases were carried out by using an X-ray diffractometer (Panalytical X'PERT PRO model, Almelo, The Netherlands), with CuK α radiation. Powdered samples were used only for the XRD experiments (about 10 mg per sample).

In the stereomicroscopy (SM) experiments, sherd features were directly examined using a Nikon SMZ645 stereomicroscope after gentle surface cleaning with ethanol to remove the paste patina and reveal the original microstructural characteristics. Representative images were acquired using a Moticam 10.0 MP digital camera.

Further details regarding all these techniques were described in previous papers from our group [11].

3. Results

3.1. GSDR Spectra Glazes and Ceramic Bodies

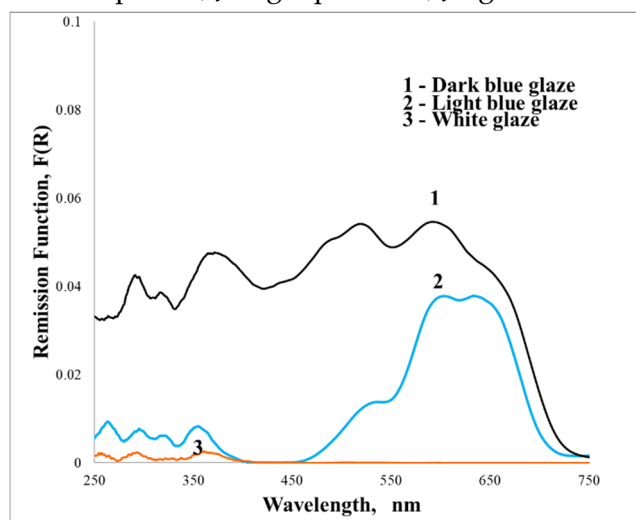
From the reflectance curves (R_s) and using the Kubelka Munk function $F(R) = (1 - R)^2/2R$, the UV–Vis–NIR absorption spectra of the sherds were obtained for all cases. The GSDR absorption spectra obtained for samples N2, N4, N6, N10, and N15 are representative of the entire group of studied porcelains and are presented in Figure 2.

Sample N2 GSDR absorption spectra are similar to those obtained for the sherd N1. The N4 GSDR absorption spectra are representative of the three Anxi kiln samples, while N10 spectra are like all Dehua, Dalongkou kiln ones. The GSDR spectra of N15, Dehua, Housno kiln, are also quite similar to those of Dalongkou kilns. The exception is the N6 GSDR absorption spectra.

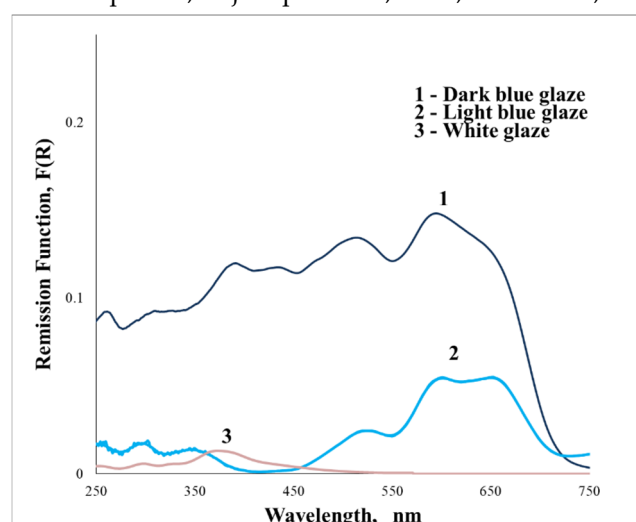
Clearly, in the porcelains N1 to N5, the dark-blue and light-blue pigments seem to be obtained with pigments of a different cobalt origin, except for sample N6, where only one type of blue pigment seemed to have been applied, obviously in high or lower loadings.

The GSDR absorption spectra for the dark-blue glaze of all samples presented in Figure 2 (except the N6 case) are similar to the ones published for a 16th-century Seville faience in a previous paper from our group [11], and to several dark-blue glazes reported in [1]. When comparing with the light-blue glaze, the reduced absorption in the 400–450 nm region, or even the 250–450 nm region, exhibits now large absorptions, pointing to either a different cobalt species responsible for the absorption or even to a different pigment.

GSDR spectra for sample N2, Jiangxi province, Jingdezhen kiln, 17th century.



GSDR spectra for sample N4, Fujian province, Anxi, Zhuta kiln, late 17th century.



GSDR spectra for sample N6, Fujian province, Dehua, Neiban kiln, late 17th–early 18th century.

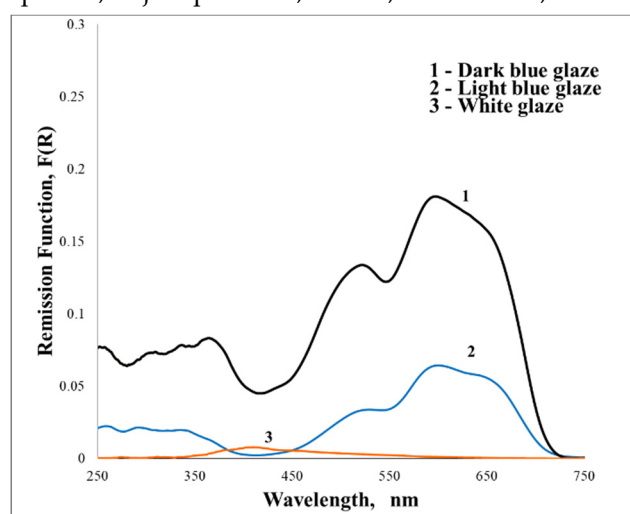
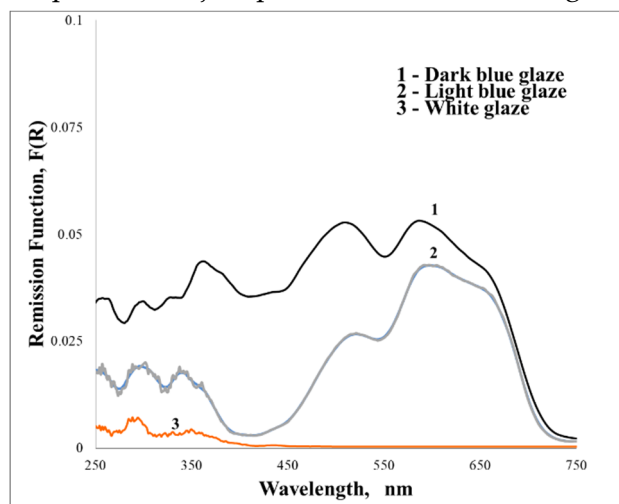


Figure 2. Cont.

GSDR spectra for sample N10, Fujian province, Dehua, Dalongkou kiln, 18th century.



GSDR spectra for sample N15 Fujian province, Dehua, Housno kiln, late 18th–early 19th century.

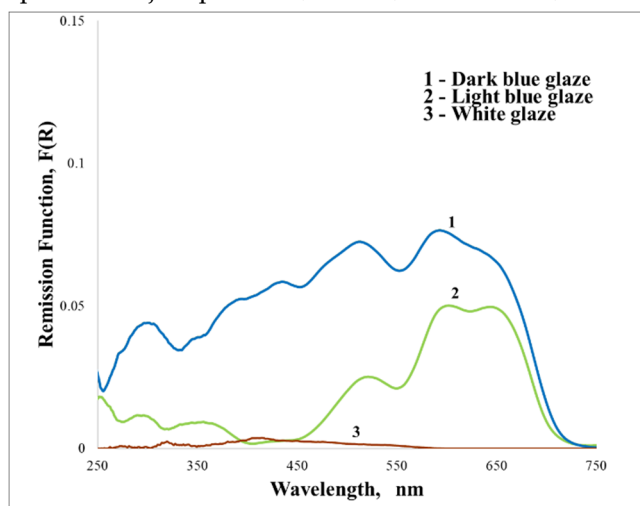


Figure 2. GSDR absorption spectra of Samples N2, N4, N6, N10 and N15: (1) Dark-blue glaze, (2) Light-blue glaze, and (3) White glaze.

The light-blue glaze, for all the samples, exhibits three different absorption bands, located at about 524, 596 and 650 nm, which are characteristic of Co^{2+} in a tetrahedral environment. This is also the case for sample N6 in the dark-blue glaze.

These absorption bands derive from spin, and symmetry allowed electronic d-d transitions of Co^{2+} from the $^4\text{A}_2(\text{F})$ ground state to the $^4\text{T}_1(\text{P})$ excited state and from the $^4\text{A}_2(\text{F})$ to the $^4\text{T}_1(\text{F})$, and respective splittings [12,13]. Differences between the bands' relative intensities observed on different samples were ascribed to some variation in the glass matrix composition where the Co^{2+} ions are embedded [12–15].

For dark-blue zones, new bands appear on the ~250 to 450 nm region [12,15,16].

Figure 4 from Part 1 (reference [1]) presents the GSDR absorption spectra for sample S11 (similar data were observed for S12). S11 and S12 are 18th-century productions. At this stage, these observations suggest the GSDR absorption spectra of dark blue, or to different oxidized forms of cobalt, Co^{2+} in different structural environments, or to different specific pigments of different origins.

Summarizing, the spectra suggest differences in cobalt coordination and/or glaze matrix effects between dark- and light-blue regions. The use of distinct cobalt-bearing raw materials remains possible, but it is not uniquely demonstrated by the use of GSDR data alone.

The use of X-Ray Photoelectron Spectroscopy as a surface analysis of the dark- and light-blue glazes provided us new information on these issues.

3.2. XPS Spectra for Dark-Blue and Light-Blue Glazes for Sample N15 and Sample N2

XPS, through the photoelectrons coming from the core, allows the detection and quantification of all the elements but He and H. A fine analysis of a specific photoelectron peak can also provide information about the oxidation state and/or about its atomic neighborhood, as well as, for transition elements, about the existence of unpaired electrons. However, as stated above, due to the extremely limited depth of analysis in XPS (less than 10 nm, depending on the photoelectron energy), an entirely non-destructive analysis of the pigment is impossible: the surficial glaze layer must be removed in order to have the pigment in the first surficial atomic layers. This operation was performed using a diamond pen. Two samples were submitted to this procedure: sample 2 and sample 15. For the latter one, the scratching yielded two dull surfaces, keeping the color difference existing before the scratching, while for sample 2, the color difference almost vanished.

Figure 3 displays the Co 2p and Mn 2p photoelectron regions for sample 15 in the dark- and light-blue zones. A typical Co 2p region presents a doublet, each component corresponding to a different spin–orbit coupling, characterized by a total angular momentum quantum number $j = 3/2$ at a lower binding energy (BE), and $j = 1/2$ at higher BE, the spin–orbit split being ~ 14.9 eV. For the ionic form Co^{2+} , the most intense component, Co 2p_{3/2}, presents BE values in the literature ranging from 780.0 to 781.6 eV, when under the form of CoO. For the mixture of Co^{2+} and Co^{3+} , as in Co_3O_4 , BE ranges from 779.3 to 780.7 eV [17–19]. In sample 15, both for the light- and dark-blue zones, a Co 2p typical spectrum could be obtained. The position of the Co 2p_{3/2} component is different in the two zones studied, as shown in Table 1.

Spectra obtained for sample 2 in the binding energy range corresponding to Co 2p were impossible to treat adequately, and therefore, they will not be shown in the following discussion.

For manganese, also the 2p region was chosen since it is the most intense. As a transition element, the Mn 2p region also presents two components, Mn 2p_{3/2}, and Mn 2p_{1/2} with an intensity ratio around 2. The Mn 2p_{3/2} component is located at 641.9 ± 0.1 eV, whereas the component Mn 2p_{1/2} is at 653.7 ± 0.1 eV. The position of the Mn 2p_{3/2} component and the spin–orbit split (11.8 eV) identify the Mn as the Mn^{3+} species [18].

Table 1 shows the details of the BE, FWHM and atomic % for the chosen elements.

The lower BE value of the C 1s region, due to adventitious carbon, was taken as a reference to correct the charge accumulation in the sample and set to 285 eV. This criterion yielded a value for Si 2p_{3/2} identical (103.0 eV) in both dark- and light-blue regions which reinforces the correctness of the choice. The Oxygen O 1s region was fittable with a single, wide peak coming mainly from the aluminosilicate component of the sample. Al 2p and Si 2p were fit with single doublets, as shown in Figure 3 and Table 1, and easily assignable to Al and Si in an aluminosilicate.

Mn 2p and, especially, Co 2p regions were acquired for a long time to improve the signal-to-noise ratio which, due to the very low relative amounts, was rather poor.

Concerning the Co 2p region, the fitting region was extended to the end of the photoelectron Co 2p_{1/2} peak to clearly show that the distance between the main features present corresponded well to the spin–orbit split expected in XPS Co 2p: 14.8 ± 0.1 eV. However, since the fitting of the entire sub-region Co 2p_{1/2} (including also the multiplet structure) was difficult, just the Co 2p_{3/2} region components were used for quantitative purposes.

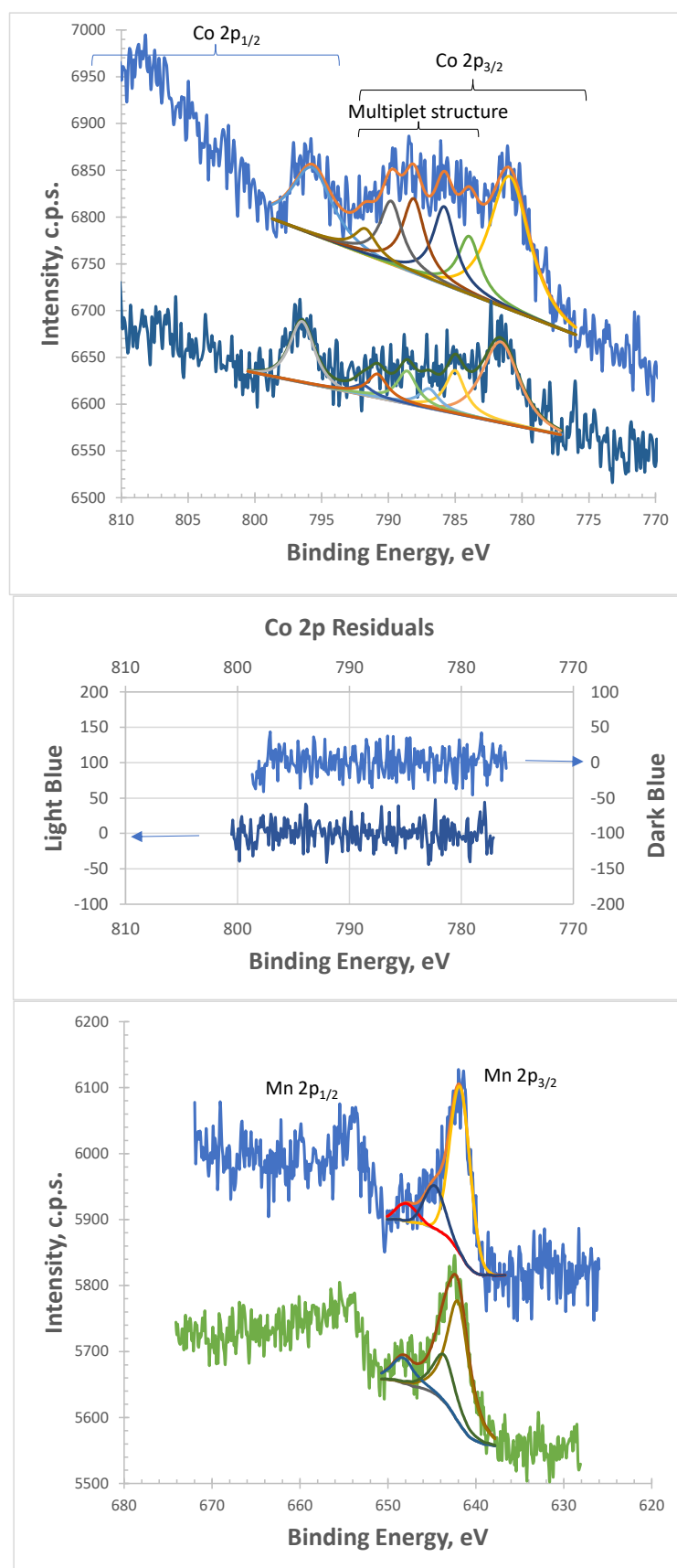


Figure 3. XPS Co 2p, respective residuals, and Mn 2p spectra for sample N15. From bottom to top, light blue and dark blue.

Table 1. XPS binding energies and FWHM, in eV, and atomic percentages for the main elements detected in sample N15 together with Co and Mn. Also, the total atomic percentages and atomic ratios are presented at the end of the table.

	Dark Blue			Light Blue			Assignments
	BE	FWHM	At. %	BE	FWHM	At. %	
C 1s 1	285.0	1.8	22.6	285.0	2.3	46.6	C-C, C-H sp ³ adventitious carbon C-O C=O
C 1s 2	286.7	1.8	5.7				
C 1s 3	288.7	1.8	2.4	288.2	2.3	4.4	
O 1s	532.3	2.4	51.9	532.4	2.6	37.2	
Al 2p _{3/2}	74.5	1.8	1.7	74.8	2.1	1.4	Al ³⁺
Al 2p _{1/2}	74.9	1.8	0.9	75.2	2.1	0.7	
Si 2p _{3/2}	103.0	2.0	9.3	103.0	2.1	6.1	silica
Si 2p _{1/2}	103.6	2.0	4.6	103.6	2.4	3.0	
Co 2p _{3/2}	780.9	3.5	0.18	781.6	3.3	0.098	
Co multipl.	784.0	2.0	0.052	785.0	1.8	0.037	
Co multipl.	785.8	2.0	0.071	787.0	1.8	0.017	
Co multipl.	788.1	2.0	0.067	788.6	1.8	0.028	
Co multipl.	789.8	2.0	0.057	790.8	1.8	0.020	
Co multipl.	791.7	2.0	0.023	791.9	1.8	0.009	
Mn 2p _{3/2} 1	641.8	2.7	0.296	642.0	3.0	0.261	
Mn 2p _{3/2} 2	644.7	2.7	0.077	643.6	3.0	0.102	
Mn 2p _{3/2} 3	647.9	2.7	0.031	648.3	3.0	0.055	
Total Quantifications							
C			30.7			51.1	
O			51.9			37.2	
Al			2.6			2.1	
Si			13.9			9.1	
Co			0.45			0.21	
Mn			0.40			0.42	
Si/Al			5.3			4.4	
Mn/Co			0.90			2.00	
Co Multipl/total			0.60			0.53	
Co/Si			0.032			0.023	

The striking difference observed between the two samples resides in the multiplet structure: in the dark zone, its relative importance is higher than in the light zone. Since the multiplet structure is due to the existence of unpaired electrons in the atomic species, this means that, at least on average, the cobalt presents a higher multiplet structure intensity in the dark-blue zone than in the light-blue zone. Another difference between the two samples is the average BE of the main Co 2p_{3/2} photoelectron peak, which is lower in the dark zone (780.9 ± 0.2 eV) than in the light zone (781.6 ± 0.2 eV). The first difference may be compatible with a larger fraction of high-spin Co ions than in the light zone, where lower-spin Co species may prevail. The difference, at least partly, may be due to the existence of some high-spin Co³⁺ in the dark zone, absent or less abundant in the light zone. The larger Co³⁺ existence in the dark region can be explained through a concentration effect: its high-spin, by their occupancy of the low field, distorted cavities [20].

Summarizing, the XPS data for N15 suggest differences in the cobalt chemical environment between dark- and light-blue regions. However, the precise assignment of the oxidation state and coordination geometry requires further confirmation from additional samples and reference materials.

3.3. Micro-Raman Spectra for Glazes and Ceramic Bodies

Raman micro-spectrometry can be used to obtain information regarding the crystalline or glassy structures [5], which are built from covalent bonds between the SiO_4 tetrahedra in different modes.

The first observation is that in sample N2 (or N1), one cannot detect the Raman signatures of cobalt silicate Co_2SiO_4 or cobalt aluminate CoAl_2O_4 as the ones published in references [5,11,21]. The same happens in all the other samples, N3 to N15. According to reference [5], this suggests that the Co^{2+} concentration is low in all cases, and the Co^{2+} ions are simply dissolved in the glaze matrix, without formation of crystalline cobalt silicate or aluminate phases, and showing no specific Raman signature as reported in other cases for Chinese porcelains [5].

In the dark-blue spectra for samples N2, N4, N10 and N15, one can only observe the bending and the stretching bands of SiO_4 , with maxima at about 483 and 1041 cm^{-1} , respectively, and also, a small band at 793 cm^{-1} from the isolated tetrahedra (Q_0) [22]. For the light-blue and white glazes, however, the Raman signature of crystalline quartz is superimposed on the bending and stretching envelopes of quartz, as Figure 4 consistently indicates. The light-blue pigment is not so deep and strong as in the dark-blue pigment, and the crystalline quartz peaks becomes relevant.

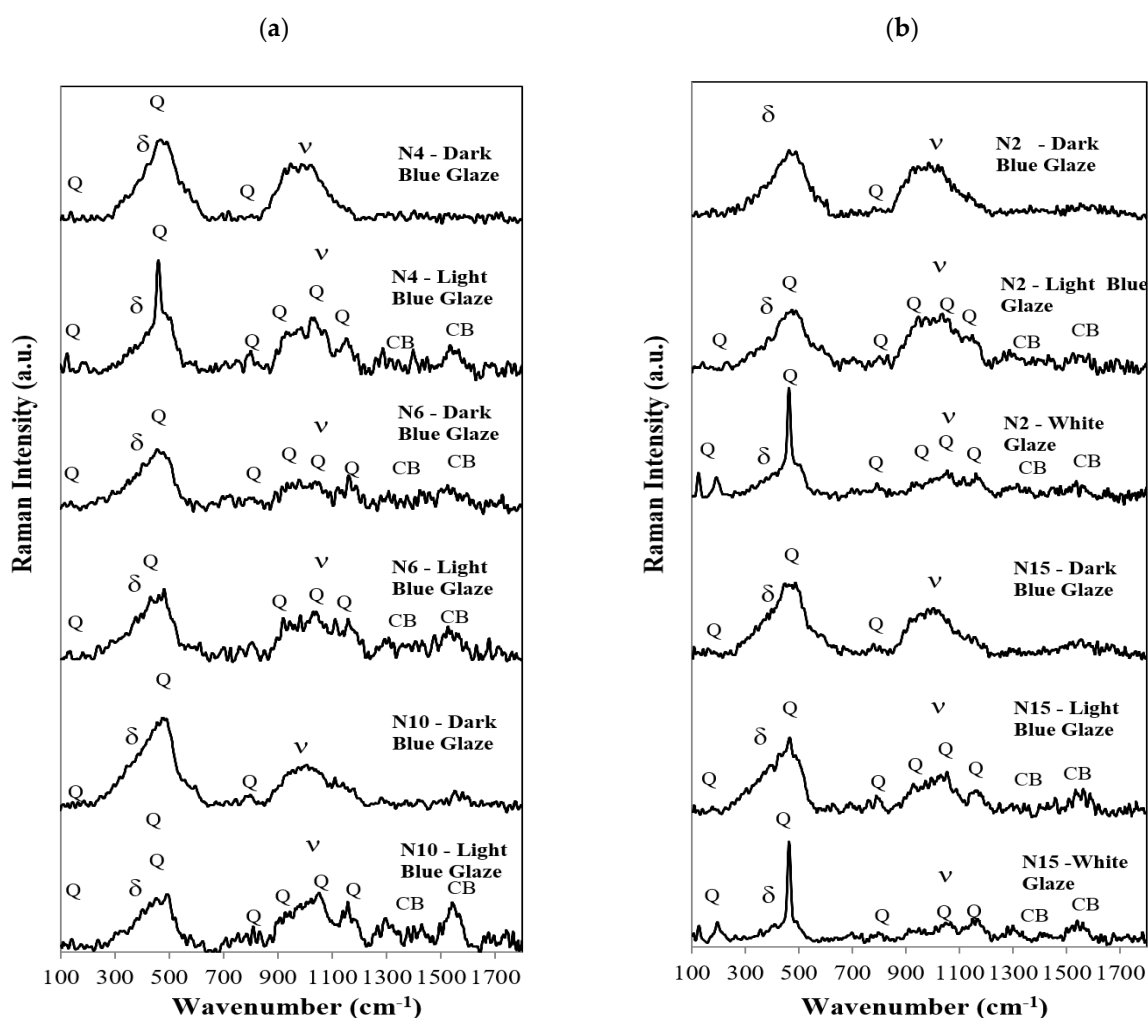


Figure 4. Micro-Raman glaze spectra: (a) N2 and N15 for the dark-blue, light-blue and white glazes; (b) N4, N6 and N10 for the dark-blue glaze and light-blue glazes. Q—Quartz, CB—Carbon Black, ν —stretching and δ —bending Raman envelopes of SiO_2 .

In the case of the white glaze, the Raman spectrum is dominated by the crystalline signature of crystalline quartz, although mullite is also a strong presence, as we will show later in the corresponding diffraction patterns (powder XRD technique). In Figure 4a,b, we do not label the small peaks at 505 cm^{-1} (and very rarely the 513 cm^{-1} peaks), but they exist and correspond to anorthite formations respectively, as again, the diffraction patterns will clearly show, later in the text.

Carbon black is also present in many Raman spectra of the 15 porcelain sherds under study here, but no calcium carbonate, gypsum or anatase could be detected in our samples.

3.4. Glaze and Body Microstructural Observations

Cross-sections and oblique sections of samples N1–N15 were examined using stereomicroscopy, providing valuable information on glaze thickness, pigment distribution, and microstructural features (Figure 5). The observed surfaces correspond to naturally exposed fracture planes that were only cleaned to remove the surface patina, without polishing or further preparation. Although such observations do not provide the spatial and chemical resolution of polished SEM sections, they enable direct visualization of the color distribution and relative pigment concentrations along the glaze profile. Attention was paid to the distribution and size of cobalt-blue pigment particles [23].

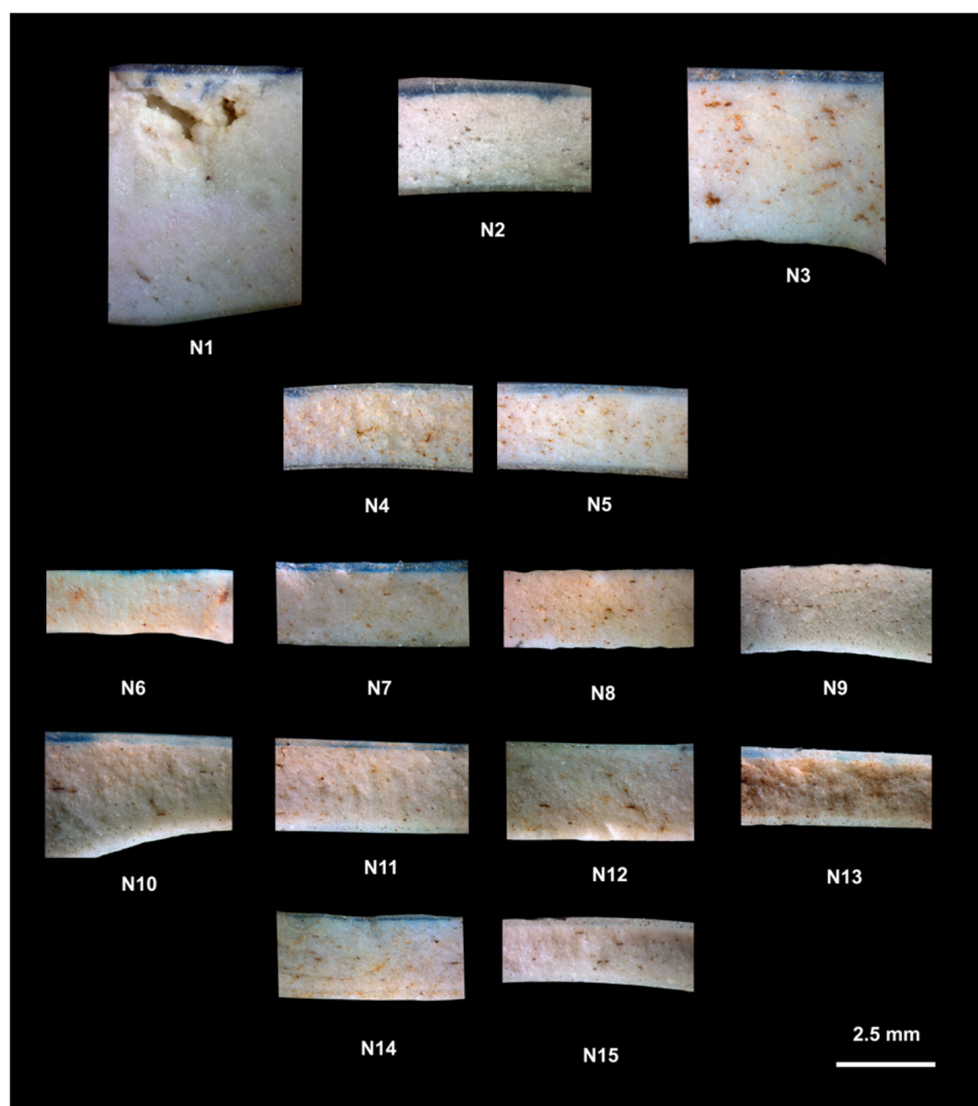


Figure 5. Cross sections and interfaces of samples N1 to N15.

Sherd thickness ranges from approximately 3–5 mm at vessel walls, and rims to 7–10 mm at the base regions. The glaze layer generally varies between 200 and 400 μm in thickness. Stereomicroscopic observations allowed identification of the ceramic body/glaze interface, the outer glaze surface, and the spatial distribution of cobalt-blue pigments across the glaze section.

In all analyzed samples, cobalt-bearing blue pigments are observed within the glaze layer, although their distribution varies among specimens. In most cases, the pigments appear dispersed throughout the superficial glaze region, whereas in some samples, particularly N2, N11, and N14, localized pigment enrichment is observed near the glaze–body interface. These observations are consistent with variability in pigment incorporation and distribution during manufacture.

In a few sections, apparent layering or pigment concentration gradients can be visually identified. However, stereomicroscopy alone does not provide sufficient resolution to determine unequivocally whether these features reflect pigment segregation during firing, diffusion processes, or the application of distinct decorative layers such as underglaze or overglaze decoration. Consequently, the present observations should be regarded as descriptive optical evidence of pigment distribution rather than definitive proof of specific decoration techniques or glaze stratigraphy. Further investigation using polished cross-sections, SEM-BSE imaging, and elemental mapping would be required to establish decoration mechanisms, diffusion pathways, and the detailed stratigraphic organization of the glaze.

Several technological defects were also documented. Sample N1 exhibits large irregular pores, whereas sample N2 shows triangular shrinkage-related paste deformation structures. Samples N3 to N5 contain small rounded or irregular pores, while samples N6 to N15 commonly display elongated pores preferentially oriented parallel to the external surface.

These microstructural features likely reflect differences in paste preparation, firing atmosphere, firing temperature, and glaze viscosity during production.

3.5. Star-Shaped Features and Glaze Defects

Radiating star-shaped blue features are predominantly observed in eighteenth-century Dehua porcelains (N7, N10–N14), particularly in samples associated with the Dalongkou kiln site (Figure 6). Some of these features appear to be preferentially located at the junctions between polygonal domains, whereas others occur as isolated structures within the glaze. Higher-magnification observations (Figure 7) reveal a complex internal zoning characterized by a transition from the surrounding bluish glaze matrix to a pale halo, followed by a brownish rim and, in some cases, distinct metallic or dendritic domains resembling the black spots described above.

The first two images in Figure 7 were acquired in transmitted-light mode, with illumination passing through the sherd, whereas the remaining images were obtained under reflected-light illumination. The use of these complementary observation modes highlights variations in transparency and microstructural organization within the star-shaped features.

Sample N2 additionally presents star-shaped shrinkage structures developed within the ceramic body and amplified within both the white and blue glaze regions (Figure 8), frequently associated with a central cavity, and also craquelée. Black spots containing large dendritic structures and crystalline aggregates were also observed at the center of the bowl.

Radiating blue features are observed in several Dehua/Dalongkou sherds and in selected Santana Convent samples. Their morphology suggests a relationship with glaze heterogeneities and firing/cooling defects, but chemical mapping is required to confirm whether these features are cobalt-enriched features. These features are compatible with a Dehua/Dalongkou attribution and may represent a promising complementary indicator, but their provenance value requires further confirmation.

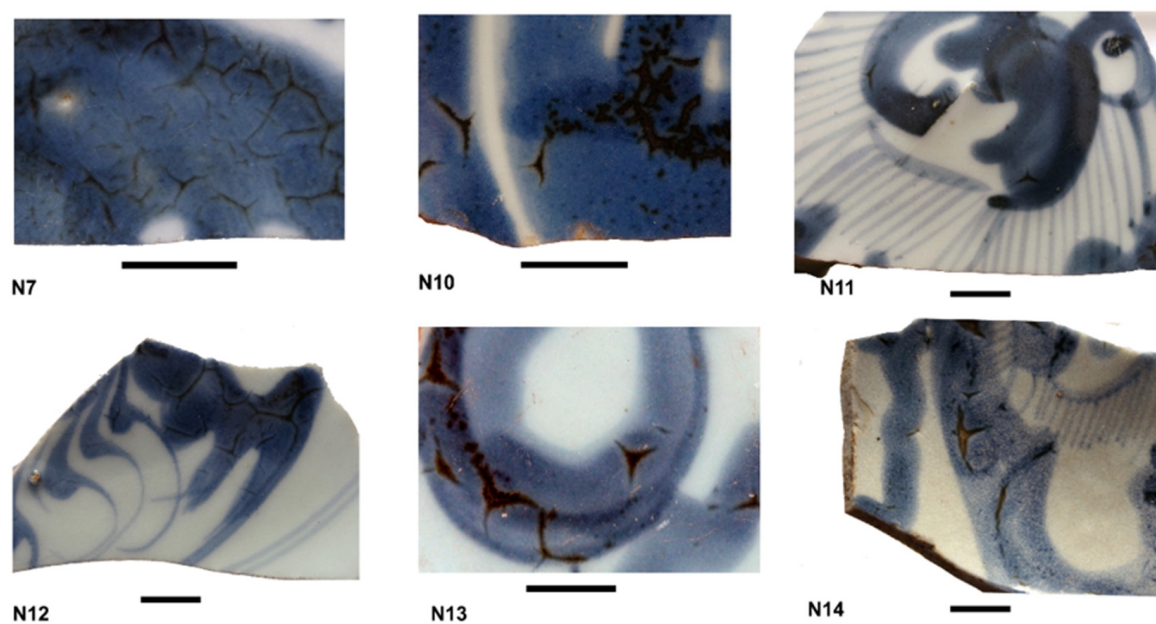


Figure 6. Star-shaped features in Dehua Dalongkou porcelains. Scale bar—10 mm.

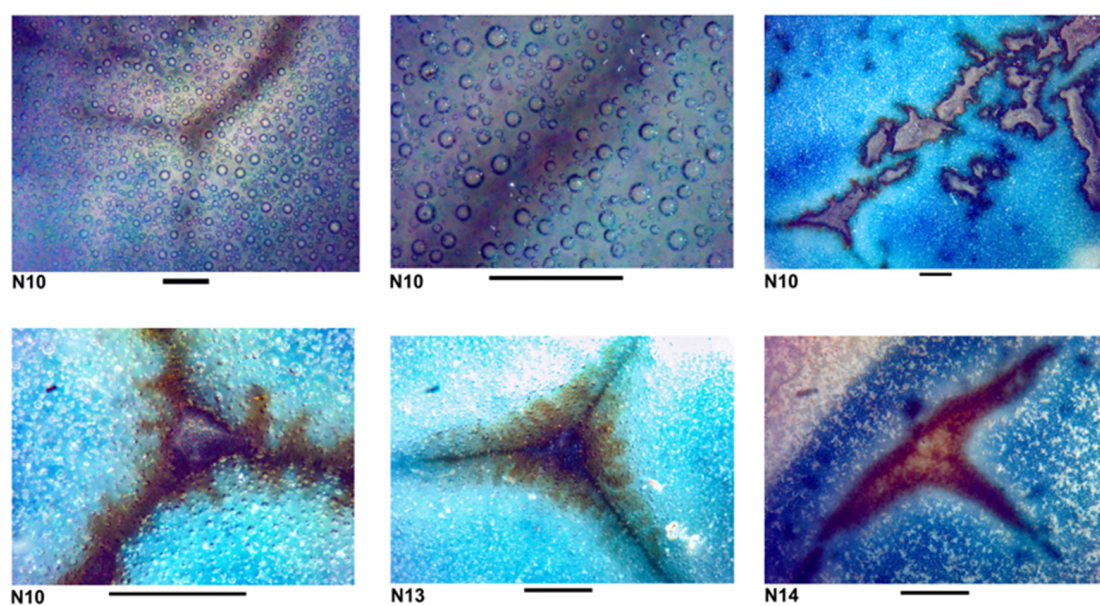


Figure 7. Stereomicroscope images of star-shaped dark-blue features in Dehua porcelains from the Dalongkou kiln site, showing examples with and without dendritic metallic segregations in their central regions (black spots). Scale bar—1 mm.

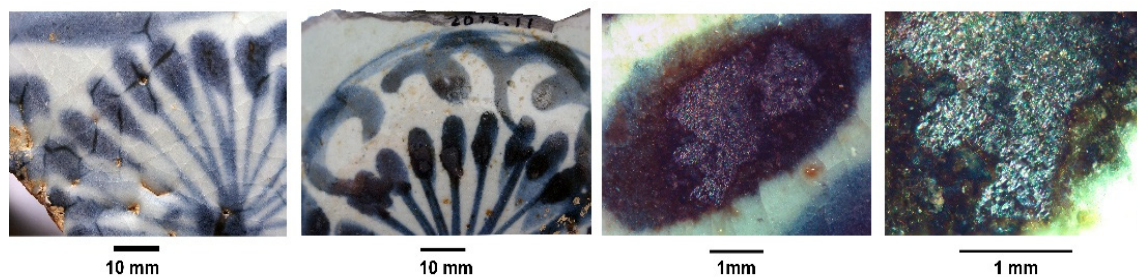


Figure 8. Star-shaped features and black spots inside dark-blue glaze (N2 sample), presenting different color halos and dendritic metallic inclusions.

3.6. XRD Data for Ceramic Bodies

Ceramic bodies and glazes from all 15 samples listed in Figure 1 underwent comprehensive analysis using X-ray diffraction (XRD powder method), which provided information on the mineralogical and phase compositions of each sherd. Figure 9 shows a clear resemblance among diffractograms of all ceramic bodies.

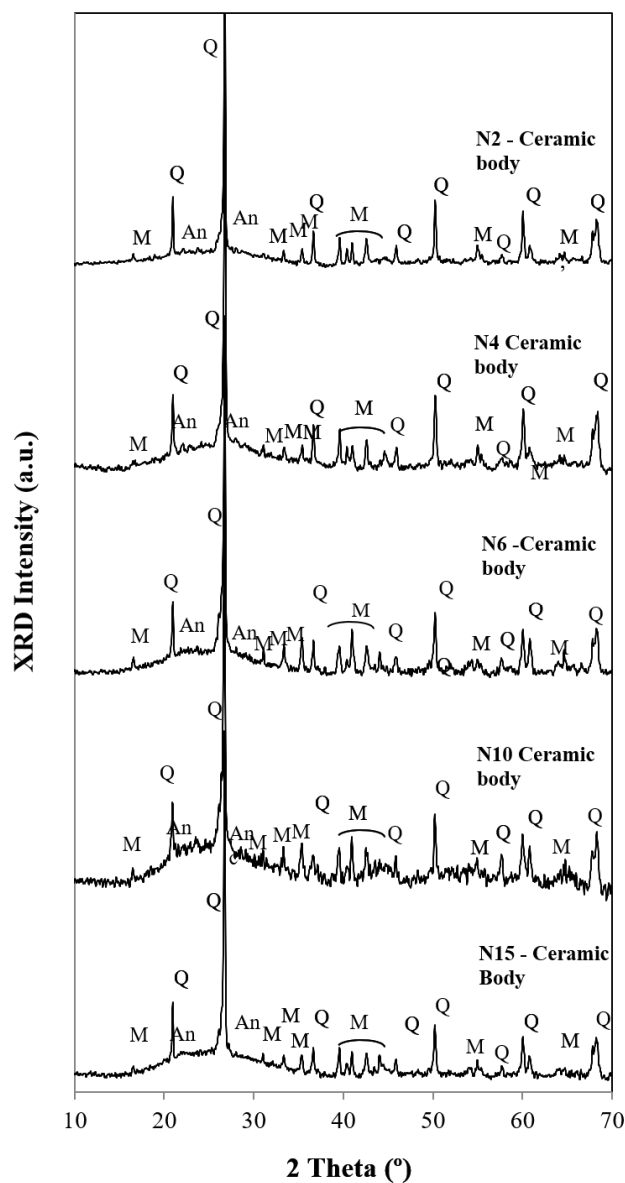


Figure 9. Diffractograms for ceramic bodies of samples N2, N4, N6, N10 and N15. Q—Quartz, M—Mullite, An—Anorthite.

In the evaluation of the diffractograms presented in Figure 9, it should be noted that X-ray diffraction (XRD) analyses were performed on powder samples (~10–15 mg per measurement) obtained by mechanical drilling with a mini-drill. Minor amounts of surficial glaze may have been inadvertently collected during sampling, and therefore, the analyzed powders may not be fully representative of a single layer. Furthermore, the XRD data were used primarily for phase identification rather than for a quantitative determination of the relative proportions of crystalline and amorphous phases. Estimating crystalline-to-amorphous ratios from conventional powder XRD patterns is inherently limited, particularly in heterogeneous archaeological materials and in the absence of ded-

icated quantitative approaches. Nevertheless, all samples were collected and prepared following the same protocol, ensuring consistency in sample preparation. Therefore, while the assessment of phase proportions should be considered qualitative or semi-quantitative, the significant differences observed among samples processed in the same manner remain meaningful for comparative purposes.

The phase composition of the 15 ceramic bodies under study is relatively homogeneous. Quartz (SiO_2), mullite ($\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$, $x \sim 0.4$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) are the only crystalline phases identified in the diffractograms (Figure 9 and Table 2). Quartz is the dominant phase, with its characteristic diffraction peaks clearly visible in all samples. The persistence of quartz reflects the incomplete dissolution of silica grains during vitrification, a common feature of traditional hard-paste porcelains.

Table 2. XRD main peaks used to identify the minerals in the diffractograms for ceramic bodies and glazes.

Quartz—Q, SiO_2 , $2\theta = 21.0, 26.7, 36.7, 46.0, 50.2, 60.0, 64.1, 68.2$
Mullite—M, $(\text{Al}_2\text{O}_3)_3(\text{SiO}_2)_2$, $2\theta = 16.5, 26.4, 33.3, 35.4, 39.4, 40.8, 42.7, 49.6, 64.8$
Anorthite—An, $\text{CaAl}_2\text{Si}_2\text{O}_8$, $2\theta = 22.0, 27.5, 27.9, 30.3, 32.0, 38.0$

Mullite was identified in all ceramic bodies and constitutes an important mineralogical marker of high-temperature porcelain production. Its formation is associated with the transformation of alumina-rich clay minerals during firing and reflects both the elevated alumina content of the raw materials and the firing temperatures employed. According to the literature, firing temperatures of approximately 1250 °C are typical for porcelains with calcium-rich glazes, whereas temperatures close to 1350 °C are generally associated with porcelains containing calcium-poor glazes [5].

Anorthite occurs as a minor crystalline phase in most samples, indicating the presence of calcium-bearing components within the ceramic bodies and/or glaze formulations. Although less abundant than quartz and mullite, its recurrent presence suggests the systematic use of calcium fluxes during porcelain manufacture.

In the range between approximately 15° and 35° 2θ , all diffractograms exhibit a broad diffuse band that is consistent with the presence of an amorphous and/or nano-crystalline vitreous phase formed during high-temperature firing. Variations in the intensity of this diffuse contribution are observed among the samples. As cited previously, although conventional powder XRD does not allow a quantitative determination of crystalline-to-amorphous ratios, the samples were collected and prepared following the same protocol. Therefore, the observed differences can be interpreted comparatively: sample N10 exhibits the most pronounced diffuse contribution, suggesting a higher degree of vitrification, whereas sample N2 shows the least pronounced diffuse band and a relatively more crystalline character. The remaining samples display intermediate behavior.

Overall, the coexistence of quartz, mullite, anorthite, and a significant vitreous phase is fully consistent with traditional Chinese hard-paste porcelain technology based on kaolin-rich raw materials and high-temperature kiln firing conditions.

3.7. XRF for the Dark-Blue, Light-Blue and White Glazes

XRF spectroscopy provided the elemental compositions of both white and blue glazes. The results obtained are in Table 3 and were obtained by irradiating the glazed surfaces of each sherd since this is a non-destructive technique.

Table 3. Chemical composition of the dark-blue, light-blue and white glazes, obtained by XRF. (nd: not detected; nq: not quantified).

Samples		MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	CoO	NiO	CuO	ZnO	As ₂ O ₃	Rb ₂ O	BaO	Mn/Co	Fe/Co
N1 17 th c.	Dark-blue glaze	nd/nq	8.34	73.66	2.80	12.24	0.05	1.49	1.11	0.15	0.06	0.01	0.01	0.01	0.01	0.03	10.49	6.94
	Light-blue glaze	nd/nq	6.83	73.24	3.09	15.51	0.06	0.20	0.97	nd/nq	nd/nq	0.01	0.01	nd/nq	0.02	0.04		
	White glaze	nd/nq	7.61	74.33	2.94	14.04	0.06	0.06	0.89	nd/nq	nd/nq	0.01	0.01	nd/nq	0.02	0.03		
N2 17 th c.	Dark-blue glaze	nd/nq	9.49	72.01	3.15	11.34	0.07	1.69	1.82	0.30	0.05	0.01	0.01	nd/nq	0.01	0.02	5.95	5.69
	Light-blue glaze	nd/nq	7.86	72.23	3.57	14.80	0.07	0.16	1.21	0.03	nd/nq	0.00	0.01	nd/nq	0.01	0.03	5.63	37.85
	White glaze	nd/nq	8.99	73.28	3.40	13.26	0.06	nd/nq	0.94	nd/nq	nd/nq	0.01	0.01	nd/nq	0.01	0.02		
N3 Late 17 th c.	Dark-blue glaze	nd/nq	8.67	73.53	2.99	12.25	0.02	1.11	1.18	0.10	nd/nq	0.01	0.01	nd/nq	0.01	0.09	11.73	11.07
	Light-blue glaze	nd/nq	8.34	74.89	3.15	12.14	0.03	0.49	0.81	0.04	nd/nq	0.01	0.01	nd/nq	0.01	0.06	12.94	19.00
	White glaze	nd/nq	8.73	74.75	3.49	12.33	0.04	nd/nq	0.58	nd/nq	nd/nq	nd/nq	0.01	nd/nq	0.01	0.03		
N4 Late 17 th c.	Dark-blue glaze	nd/nq	9.60	70.02	2.52	12.56	nd/nq	3.45	1.30	0.41	0.03	0.01	nd/nq	nd/nq	0.01	0.05	8.89	2.98
	Light-blue glaze	nd/nq	8.57	73.39	2.83	13.30	0.04	0.80	0.92	0.09	nd/nq	nd/nq	nd/nq	nd/nq	0.01	0.02	9.39	9.59
	White glaze	1.01	8.52	72.59	2.88	14.15	0.03	nd/nq	0.78	nd/nq	nd/nq	nd/nq	nd/nq	nd/nq	0.01	nd/nq		
N5 Late 17 th c.	Dark-blue glaze	1.01	11.05	72.00	2.65	8.98	nd/nq	2.85	1.06	0.33	0.01	nd/nq	nd/nq	nd/nq	0.01	0.04	9.12	3.01
	Light-blue glaze	nd/nq	11.45	73.42	2.72	10.66	0.03	0.65	0.95	0.07	nd/nq	nd/nq	nd/nq	nd/nq	0.01	0.01	9.81	12.74
	White glaze	nd/nq	10.77	74.38	2.79	11.07	0.03	0.06	0.86	nd/nq	nd/nq	nd/nq	nd/nq	nd/nq	0.01	0.01		
N6 Late 17 th –18 th c.	Dark-blue glaze	nd/nq	7.74	75.40	4.78	9.26	0.06	1.66	0.73	0.29	nd/nq	0.01	0.01	nd/nq	0.01	0.02	6.05	2.36
	Light-blue glaze	nd/nq	8.80	76.18	4.35	7.93	0.04	0.88	0.65	0.13	nd/nq	nd/nq	0.01	nd/nq	0.01	0.01	7.15	4.69
	White glaze	nd/nq	7.65	76.92	5.06	9.54	0.05	0.09	0.64	nd/nq	nd/nq	0.01	0.01	nd/nq	0.01	nd/nq		
N7 18 th c.	Dark-blue glaze	nd/nq	8.21	71.53	6.44	6.59	nd/nq	5.63	0.96	0.41	nd/nq	0.02	0.02	nd/nq	0.01	0.11	14.51	2.20
	Light-blue glaze	nd/nq	8.45	73.92	6.47	6.68	0.06	3.13	0.87	0.23	nd/nq	0.01	0.01	nd/nq	0.01	0.08	14.38	3.55
	White glaze	0.00	7.96	75.76	6.40	8.81	0.07	0.11	0.71	nd/nq	nd/nq	0.01	0.01	nd/nq	0.01	0.09		
N8 18 th c.	White glaze	nd/nq	8.04	78.09	6.82	6.33	0.05	0.09	0.45	nd/nq	nd/nq	nd/nq	nd/nq	nd/nq	0.01	0.07		
N9 18 th c.	White glaze	1.48	5.98	77.88	7.05	6.66	0.04	0.37	0.42	nd/nq	nd/nq	nd/nq	nd/nq	nd/nq	0.02	0.05		
N10 18 th c.	Dark-blue glaze	nd/nq	6.77	73.04	5.70	7.51	nd/nq	4.43	1.72	0.39	0.14	0.04	0.01	nd/nq	0.01	0.14	12.00	4.14
	Light-blue glaze	nd/nq	5.66	77.55	6.31	8.45	0.07	0.53	1.08	0.07	0.05	0.03	0.01	nd/nq	0.01	0.07	8.00	14.48
	White glaze	nd/nq	7.94	79.25	5.20	6.61	0.06	0.05	0.79	nd/nq	nd/nq	0.02	0.01	nd/nq	0.01	0.05		

Table 3. Cont.

Samples		MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	CoO	NiO	CuO	ZnO	As ₂ O ₃	Rb ₂ O	BaO	Mn/Co	Fe/Co
N11 18 th c.	Dark-blue glaze	nd/nq	7.60	72.89	4.34	12.12	0.05	1.66	0.95	0.15	0.05	0.03	0.01	nd/nq	0.01	0.11	11.69	5.94
	Light-blue glaze	nd/nq	7.87	74.56	4.45	11.25	0.04	0.82	0.76	0.06	0.01	0.03	0.01	nd/nq	0.01	0.09	14.44	11.89
	White glaze	nd/nq	8.34	74.45	4.83	11.32	0.06	0.13	0.76	nd/nq	nd/nq	0.02	0.01	nd/nq	0.01	0.05		
N12 18 th c.	Dark-blue glaze	nd/nq	9.05	70.19	5.63	9.38	0.05	4.04	0.97	0.36	0.06	0.03	0.01	nd/nq	0.01	0.14	11.85	2.53
	Light-blue glaze	nd/nq	9.61	72.87	5.58	9.90	0.06	0.93	0.77	0.08	0.02	0.02	0.01	nd/nq	0.01	0.09	12.28	9.03
	White glaze	nd/nq	8.51	73.30	6.03	11.29	0.08	nd/nq	0.65	nd/nq	nd/nq	0.02	0.01	nd/nq	0.01	0.06		
N13 18 th c.	Dark-blue glaze	nd/nq	6.70	75.91	4.61	8.84	nd/nq	2.31	1.26	0.19	nd/nq	nd/nq	nd/nq	nd/nq	0.01	0.02	12.84	6.22
	Light-blue glaze	nd/nq	8.13	78.87	4.28	7.46	0.07	0.26	0.80	nd/nq	nd/nq	0.01	0.01	nd/nq	0.01	0.11		
	White glaze	nd/nq	7.94	78.61	4.56	7.98	0.06	0.04	0.73	nd/nq	nd/nq	0.01	0.01	nd/nq	0.01	0.02		
N14 18 th c.	Dark-blue glaze	nd/nq	4.81	74.89	5.61	11.88	0.07	1.50	0.91	0.09	nd/nq	nd/nq	0.01	nd/nq	0.01	0.17	17.61	9.49
	Light-blue glaze	nd/nq	8.37	77.10	4.27	9.50	0.05	0.11	0.48	nd/nq	nd/nq	0.01	0.01	nd/nq	0.01	0.07		
	White glaze	nd/nq	7.40	77.83	4.62	9.53	0.05	0.00	0.46	nd/nq	nd/nq	0.01	0.01	nd/nq	0.01	0.05		
N15 Late 18 th –Early 19 th c.	Dark-blue glaze	1.4	8.28	71.87	3.95	7.46	nd/nq	5.55	0.96	0.32	0.03	0.01	0.01	nd/nq	0.01	0.09	18.32	2.82
	Light-blue glaze	nd/nq	8.52	73.16	3.90	7.62	nd/nq	5.38	0.94	0.30	0.02	0.01	0.01	nd/nq	0.01	0.09	18.94	2.94
	White glaze	nd/nq	7.95	77.65	4.36	9.19	0.07	0.09	nd/nq	nd/nq	nd/nq	0.01	0.01	nd/nq	0.01	0.04		

Data in Table 3 are presented as wt.% (nd: not detected; nq: not quantified). The estimated error for major elements (Si and Al) was $\leq 3\%$, for minor elements (K, Ca, and Fe) $\leq 4\%$, and for trace elements $\leq 8\%$. Please note that values for CuO, ZnO, As₂O₃ and Rb₂O stay below wt. 0.05%. Mn/Co and Fe/Co are atomic ratios.

A global analysis of the results shows that, in general, the glazes with a bluish color are slightly less siliceous and calcic, and, as would be expected, are more cobaltic, to which Fe and Ni are added. The white pastes do not contain Co and Ni and have very little Mn, which reveals that the pigment, in addition to Co, is enriched in Mn and Fe.

In the Dehua samples, the average values of Al₂O₃ and CaO, both in the colored and white glazes, are lower than the average of the full set of samples, respectively, 8.22% and 4.4%. Conversely, the values of K₂O, MnO, FeO, CoO and NiO are higher than the average of the set. Trace elements such as Cu, Zn, Pb, and Sn are present in very low concentrations or below detection limits.

Arsenic was absent in 14 of the 15 samples under study.

4. Discussion

The GSDR results show systematic differences between dark- and light-blue glazes. In the latter ones, the presence of three well-defined absorption bands at approximately 524, 596, and 650 nm in light-blue regions is characteristic of Co²⁺ ions in tetrahedral coordination. In contrast, dark-blue glazes exhibit further absorption features previously described, suggesting differences in the cobalt coordination environment and/or a different oxidation state. These differences are consistent across most samples and can be explained by pigment concentration effects. The use of different pigments cannot be discarded. The spectra obtained for Dehua, Jingdezhen, and Anxi productions suggest the use of different pigment application technologies or even distinct cobalt sources [12–16].

The XPS results reinforce the interpretation derived from the GSDR data. In sample N15, the Co 2p_{3/2} binding energy is lower in the dark-blue region (780.9 eV) than in the light-blue region (781.6 eV), and the multiplet structure is more pronounced in the darker glaze. These observations may be compatible with a greater contribution of high-spin cobalt species and consequent differences in the cobalt coordination geometry, or even in the oxidation state, between dark- and light-blue regions [18].

Micro-Raman spectroscopy confirms that cobalt is not present as a crystalline phase but rather as dissolved Co ions within the amorphous silicate glaze matrix. No Raman signatures corresponding to cobalt silicate or cobalt aluminate crystalline phases were detected in any of the analyzed samples, consistent with efficient incorporation of cobalt into the vitreous network during high-temperature firing [21–23]. The Raman spectra are dominated by the characteristic silicate bending and stretching envelopes around ~ 500 and ~ 1000 cm^{−1}, consistent with highly vitrified glazes. In the light-blue and white glazes, the increased visibility of quartz Raman peaks reflects lower pigment concentrations and greater optical transparency. The absence of crystalline cobalt compounds is fully compatible with previous studies of Chinese blue-and-white porcelains, where cobalt generally behaves as a network modifier dissolved in the glaze structure [21–23].

The microstructural observations obtained by stereomicroscopy reveal important technological differences between the studied porcelains. Several glaze and body defects were identified, including rounded and elongated pores, shrinkage-related cavities, pigment accumulations, and irregular deformation structures. These features reflect variations in paste preparation, glaze viscosity, firing atmosphere, firing temperature, and cooling dynamics. In some samples, particularly N2, N11, and N14, cobalt enrichment near the glaze–body interface suggests underglaze application followed by glaze coating and partial cobalt migration during firing.

The XRD analyses indicate a relatively homogeneous mineralogical composition among all the studied porcelain bodies. Quartz and mullite are the dominant crystalline phases, while anorthite appears as a minor component. Mullite formation confirms firing temperatures characteristic of traditional Chinese hard-paste porcelain technology, typically above 1250 °C [24]. The recurrent presence of anorthite suggests the use of calcium-rich components or fluxes in ceramic formulations.

The XRF analyses complement these observations by showing that blue glazes are systematically enriched in Co, Mn, Fe, and Ni, whereas white glazes contain only residual amounts of these elements. Dehua samples exhibit relatively higher concentrations of transition metals when compared with Jingdezhen and Anxi productions, suggesting distinct raw material procurement strategies and pigment preparation methods within the regional kiln systems. These compositional differences reinforce the evidence for technological variability among Chinese export porcelain production centers.

The transition-metal impurity signatures identified by XRF and some by XPS provide important archaeometric information regarding cobalt provenance. In historical blue-and-white porcelains, Persian cobalt sources are typically characterized by elevated arsenic and nickel contents combined with relatively low manganese concentrations, whereas Chinese domestic cobalt ores commonly exhibit low arsenic and comparatively higher Mn/Co and Fe/Co ratios [25,26]. The very low arsenic contents observed in the present samples (<0.05 wt.% As_2O_3), together with the relatively elevated manganese concentrations and Mn/Co ratios, strongly suggest the predominance of domestic Chinese cobalt sources rather than imported Persian cobalt. These observations are fully compatible with Qing period cobalt exploitation and pigment preparation technologies associated with Fujian and Dehua kiln systems. The compositional variability observed between dark- and light-blue regions further suggests the use of heterogeneous cobalt-bearing raw materials and/or different pigment-processing strategies during glaze preparation.

Particularly significant are the radiating triangular or star-shaped blue features identified predominantly in the Dehua porcelains, especially those associated with the Dalongkou kiln site. To the best of our knowledge, these structures represent a previously underreported class of glaze heterogeneities in Chinese export porcelains. Rather than corresponding to intentional decorative motifs, they are interpreted as the result of localized physicochemical processes occurring during glaze melting, vitrification, and cooling.

The occurrence of these features within a shallow region of the glaze, together with the absence of an evident fracture network, suggests that they are unlikely to represent true microfractures. Instead, their morphology is more consistent with localized segregation and possible phase evolution of coloring agents and impurity-bearing phases during glaze development. The occurrence of dendritic metallic domains in the central regions of certain radiating star-shaped features suggests a genetic relationship with the isolated black spots identified in several sherds. The shared presence of metallic dendrites indicates that both features may originate from similar processes of impurity accumulation, phase segregation, and localized crystallization within the glaze during firing and cooling (Figure 7). Similar segregation phenomena have been reported in viscous silicate melts, oxide ceramics, and glasses, where interfacial regions and compositional heterogeneities can act as preferential sites for solute accumulation, phase separation, and crystallization [27–31].

In sample N2, the exceptional occurrence of shrinkage-related star-shaped structures extending from the ceramic body into the glaze suggests that at least part of the defect formation originated during body contraction and was subsequently modified or amplified during glaze cooling. The frequent presence of a central cavity further supports the interpretation that trapped gases or localized heterogeneities acted as nucleation centers for feature development. The associated black spots containing dendritic metallic structures

and white crystalline aggregates additionally indicate complex interactions among impurity segregation, localized crystallization, and glaze evolution.

From a technological perspective, the formation of these glaze features is fully compatible with the production context of the Dehua kiln system during the Qing dynasty. Historical and archaeometric studies emphasize the decentralized nature of porcelain manufacture in Fujian province, involving numerous kiln sites operating with varying control over raw materials, glaze formulations, firing temperatures, kiln atmospheres, and cooling rates [24,32,33]. Such variability directly affects critical parameters including glaze viscosity, gas release, thermal expansion mismatch between glaze and body, and cooling dynamics, all of which strongly influence glaze stability and the development of heterogeneities.

The present observations therefore contribute new evidence regarding the microstructural complexity of Dehua glazes and provide insights into the interplay among raw materials, firing conditions, and glaze evolution.

Importantly, the presence of similar features in selected Santana Convent porcelains, particularly in samples S11 and S12, together with the spectroscopic, compositional, and mineralogical similarities identified in this study, suggests the attribution of these Lisbon fragments to Dehua kiln production. These observations also reinforce the evidence for the circulation of Dehua export porcelains through the maritime trade networks connecting Fujian, Macau, Lisbon, and broader European markets during the seventeenth and eighteenth centuries [2].

From a broader heritage and archaeometric perspective, these results demonstrate that glaze defects and microstructural imperfections, often regarded merely as secondary technological artefacts, can provide highly relevant information for provenance studies. When integrated with spectroscopic, compositional, mineralogical, and microstructural analyses, these features significantly strengthen the archaeometric characterization of eighteenth-century Chinese export porcelains and contribute to a better understanding of technological variability associated with intensified export-oriented production during the Qing dynasty.

All the combined evidence is consistent with a Dehua assignment for S11 and S12 from Part 1, but a larger reference dataset and quantitative multivariate comparison are required before a definitive provenance attribution can be made.

5. Conclusions

The results obtained in this study demonstrate that the integration of spectroscopic, compositional, mineralogical, and microstructural analyses provides a robust framework for the characterization and provenance assessment of Chinese blue-and-white porcelains, particularly within the context of archaeological assemblages from Santana Convent.

GSDR, XRF and XPS analyses reveal systematic differences between dark- and light-blue glazes, reflecting variations in the cobalt coordination environment and chemical composition rather than simple concentration effects. These results indicate different cobalt in glaze environments or the use of distinct preparation methods or even pigments, consistent with the coexistence of multiple technological traditions associated with major Chinese production centers such as Jingdezhen and Dehua. The available evidence does not allow a definitive demonstration of distinct cobalt sources.

Raman spectroscopy confirms that cobalt is predominantly present as Co^{2+} ions dissolved in the amorphous glaze matrix, while XRD results show a consistent mineralogical composition dominated by quartz and mullite, indicative of high firing temperatures typical of Chinese hard-paste porcelain. The presence of anorthite further reflects the use of calcium-based fluxes. XRF data highlight compositional differences between glaze types and show that Dehua samples are characterized by relatively higher concentrations of tran-

sition metals (Co, Mn, Fe, Ni), suggesting distinct raw material selection and technological practices within regional kiln systems. The very low arsenic contents (<0.05 wt.% As_2O_3), combined with relatively high manganese concentrations and Mn/Co ratios, indicate that the cobalt used in the present samples was predominantly derived from domestic Chinese sources rather than imported Persian cobalt.

Microstructural analyses demonstrate that glaze defects provide valuable technological information. In particular, the identification of radiating star-shaped and polygonal features constitutes a significant finding. These features are interpreted as cooling-induced defects associated with gas entrapment, stress development, and cobalt redistribution within the glaze. Their occurrence is systematic in Dehua porcelains, especially those attributed to the Dalongkou kiln site. The presence of similar features in some of the Santana Convent samples, together with the spectroscopic, compositional, mineralogical, and microstructural evidence obtained in this study, supports a probable attribution of selected fragments to Dehua kiln production. This interpretation is further consistent with the documented circulation of Chinese porcelains through the trade networks that linked China and Lisbon during the early modern period, particularly in the context of Portuguese maritime expansion and patterns of consumption. Nevertheless, a larger reference dataset and quantitative multivariate analyses will be required before a definitive provenance attribution can be established.

From a broader heritage perspective, this study highlights the importance of integrating multiple analytical approaches to improve the reliability of provenance assessment and to better understand technological variability in Chinese porcelain production. To our knowledge, XPS is not usually employed in archaeometric studies of the type reported here. However, its application to one of the samples (N15) proved to be a highly promising complementary technique to the more conventional methods. In particular, it enabled the assignment of the spectral features observed in the dark-blue regions (GSDR spectra) within the 250–450 nm range to probably higher-spin Co species in different coordination and/or oxidation states, rather than to a different pigment component (e.g., manganese-based species). This conclusion was made possible by the ability of XPS to distinguish between high- and low-spin states of transition metals. The surface sensitivity of XPS could be mitigated through the use of synchrotron-based XPS facilities, where the photoelectron escape depth can be significantly increased by employing higher-energy incident X-radiation. This approach could reduce the need to scratch the glaze layer, thereby decreasing the risk of removing part of the pigment together with the glaze.

The analyses, whose results are now presented, suggest that, during the late sixteenth and seventeenth centuries, the Portuguese obtained their supplies chiefly from Jingdezhen. However, over the following two centuries, owing not only to Portuguese demand but also to that of the English and the Dutch, through their powerful trading companies established in the East, the consumption of porcelain appears to have risen exponentially, and production centers such as Quanzhou, in Fujian Province, either emerged or underwent significant development.

Author Contributions: Conceptualization, L.F.V.F., A.M.B.d.R., R.V.G., M.V.G., S.L. and M.F.C.P.; Methodology, L.F.V.F., A.M.B.d.R. and M.F.C.P.; Validation, L.F.V.F., A.M.B.d.R. and M.F.C.P.; Formal analysis, L.F.V.F. and A.M.B.d.R.; Investigation, L.F.V.F. and A.M.B.d.R.; Resources, L.F.V.F.; Data curation, L.F.V.F. and A.M.B.d.R.; Writing—original draft, L.F.V.F., A.M.B.d.R., R.V.G., M.V.G., Shanshan Li and M.F.C.P.; Writing—review & editing, L.F.V.F., A.M.B.d.R. and M.F.C.P.; Visualization, M.F.C.P.; Supervision, L.F.V.F.; Project administration, L.F.V.F.; Funding acquisition, L.F.V.F. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financed by national funds from FCT—Fundação para a Ciência e a Tecnologia, I.P., in the scope of the project UIDB/04565/2020 and UIDP/04565/2020 of the Research Unit Institute for Bioengineering and Biosciences—iBB and UIDP/04028/2025 (DOI: 10.54499/UIDP/04028/2025)—CERENA—Research Centre for Natural Resources and Environment.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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