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Colouration characteristics and mechanisms of Kangxi-period underglaze copper-red porcelain

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The underglaze copper-red porcelain of the Kangxi period (AD 1662–1722) of the Qing dynasty (AD1616–1912) occupies a significant position in the history of Chinese ceramics, and its vivid colouration and refined craftsmanship have attracted considerable attention. As copper oxide serves as its colourant, the ware is highly sensitive to the firing atmosphere and temperature, developing different hues under different firing conditions. To reveal the compositional characteristics and colouration mechanism of Kangxi-period underglaze copper-red porcelain, this study employed energy-dispersive X-ray fluorescence spectrometry (EDXRF), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS), polarised light microscopy, and X-ray photoelectron spectroscopy (XPS) to analyse the coloured regions of 20 Kangxi-period underglaze copper-red specimens. The results revealed notable differences in elemental composition between the red-pigment and green-spot regions. Green spots show enrichment in CuO, CaO, and Fe₂O₃, along with spherical, phase-separated droplets approximately 10–20 nm in size. Green colouration primarily originates from Cu²⁺. The red hue mainly comes from Cu₂O microcrystals (Cu⁺), which may partially coexist with minor amounts of metallic copper colloids (Cu⁰). These specimens were fired under a weakly reducing atmosphere. The relative valence-state ratio of Cu⁰, Cu⁺, and Cu²⁺ is the core factor controlling hue variation in underglaze copper-red. Sulfur (S) and arsenic (As) in the pigment raw material alter Cu₂O crystal morphology and, in turn, modulate colour appearance. This study characterises the elemental and structural features of Kangxi-period underglaze copper-red porcelain and identifies multiple mechanisms responsible for its colouration.

Underglaze copper-red porcelain is a key category of traditional Chinese underglaze decorated porcelain. Production involves applying copper-containing pigments to bisque bodies, covering them with a transparent glaze layer, and firing at high temperatures in a reducing atmosphere to produce ruby-red decorative patterns beneath the glaze. It represents a landmark achievement of ancient Chinese ceramic technology. According to historical records and archaeological evidence, underglaze copper-red porcelain first appeared in the Yuan dynasty (AD 1271–1368), and during the Yongle period (AD 1403–1424) of the Ming dynasty (AD 1368–1644), it yielded fairly vivid red hues, though colour appearance remained unstable. By the Kangxi period, production had achieved markedly improved control over colour development, yielding wares with stable colouration, vivid, intense hues, and diverse tonal gradations^[1]. Because underglaze copper-red uses copper as its colourant, copper readily volatilises at high temperatures and diffuses easily within the glaze, making production hard to control. Copper ions are also highly sensitive to kiln atmosphere, and the acceptable firing temperature range is relatively narrow. Small shifts in atmosphere or large temperature deviations can therefore prevent underglaze copper-red from developing its target colour, producing greyish or blackish tones or, in some cases, colour loss ("fei-hong")^[2]. These technical limitations explain the rarity and research significance of underglaze copper-red porcelain.

Current research on underglaze copper-red falls into two major categories: art historical studies and technical analyses. Within art historical research, studies predominantly focus on archaeological finds, chronological investigation, decorative features, and reconstruction of historical contexts^[3–12].

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In terms of technical analysis, Guan et al. have investigated glaze and pigment composition for underglaze copper-red specimens dating to the Hongwu period (AD 1368–1398) and Yongle period of the Ming dynasty^[13-14]. Zhang et al. conducted a comparative study of underglaze copper-red and “filled red”, identifying differences and characteristics in appearance, chemical composition, and microstructure. These studies clearly defined the conceptual boundary between “filled red” and underglaze copper-red and laid the foundations for later classification-related research^[15-16]. Cui et al. studied raw material sources for Hongwu-period underglaze copper-red pigment via compositional analysis. Combining these findings with the historical-document term “bright red clay”, they proposed that the pigment originated from natural cuprite-type copper ore containing minor chalcopyrite impurities, and that depletion of this raw material was likely a key factor behind interrupted copper-red glaze production in the mid-Ming period^[17]. Zhang et al. performed precise elemental quantitative analysis on multi-period specimens to trace evolutionary features of underglaze copper-red formulas. By detecting Cu-S and Cu-As phase compositions inside micron-scale particles within red glaze zones, their study confirmed cuprous oxide and realgar as the main raw materials used for pigment preparation^[18]. Zhang et al. further focused on copper-bearing colourants. They performed systematic tests to explore intrinsic correlations between copper distribution state, copper occurrence forms, and the colour-generating appearance of underglaze copper-red. Their results verified that red colouration in high-temperature copper-red glazes arises from metallic copper colloidal particles, Cu₂O microcrystallites, or their co-existing phases^[19-25].

Most ancient underglaze copper-red pieces were specially produced for the imperial court, making extant specimens exceedingly rare and precious. Alongside the limitations of traditional testing approaches, the microstructure and elemental valence characteristics of Kangxi-period underglaze copper-red porcelain haven’t been systematically investigated. In particular, no unified understanding has been achieved regarding the microscopic formation mechanisms behind its variable colour appearances, such as bright red, dark red, colour loss, and some red pigments with green spots.

Based on the above issues, this study examines 20 Kangxi-period underglaze copper-red ware specimens. Representative photographs of the selected samples are displayed in [Fig. 1]. Through comprehensive scientific testing, the study systematically analyses specimen characteristics to clarify the colouration mechanism of Kangxi-period underglaze copper-red porcelain and identify the key factors driving its colour differences. The results provide new evidence for understanding the technological control of copper-red colouration in Kangxi-period porcelain.

Methods

All 20 Kangxi-period underglaze copper-red specimens used in this study were provided by the Research Center of Ancient Ceramics, Jingdezhen Ceramic University, and sequentially numbered QYLH-1 to QYLH-20. All specimens are porcelain fragments with linear underglaze copper-red decorations and exhibit obvious colour differences. QYLH-1 presents a pure and bright red hue, QYLH-8 shows a dull, blackish red hue, QYLH-9 exhibits a deep red hue, and QYLH-10 displays severe colour loss. Notably, green spots frequently coexist with red pigments on individual specimens, as demonstrated by QYLH-9. Table S1 lists full details of the specimen characteristics.

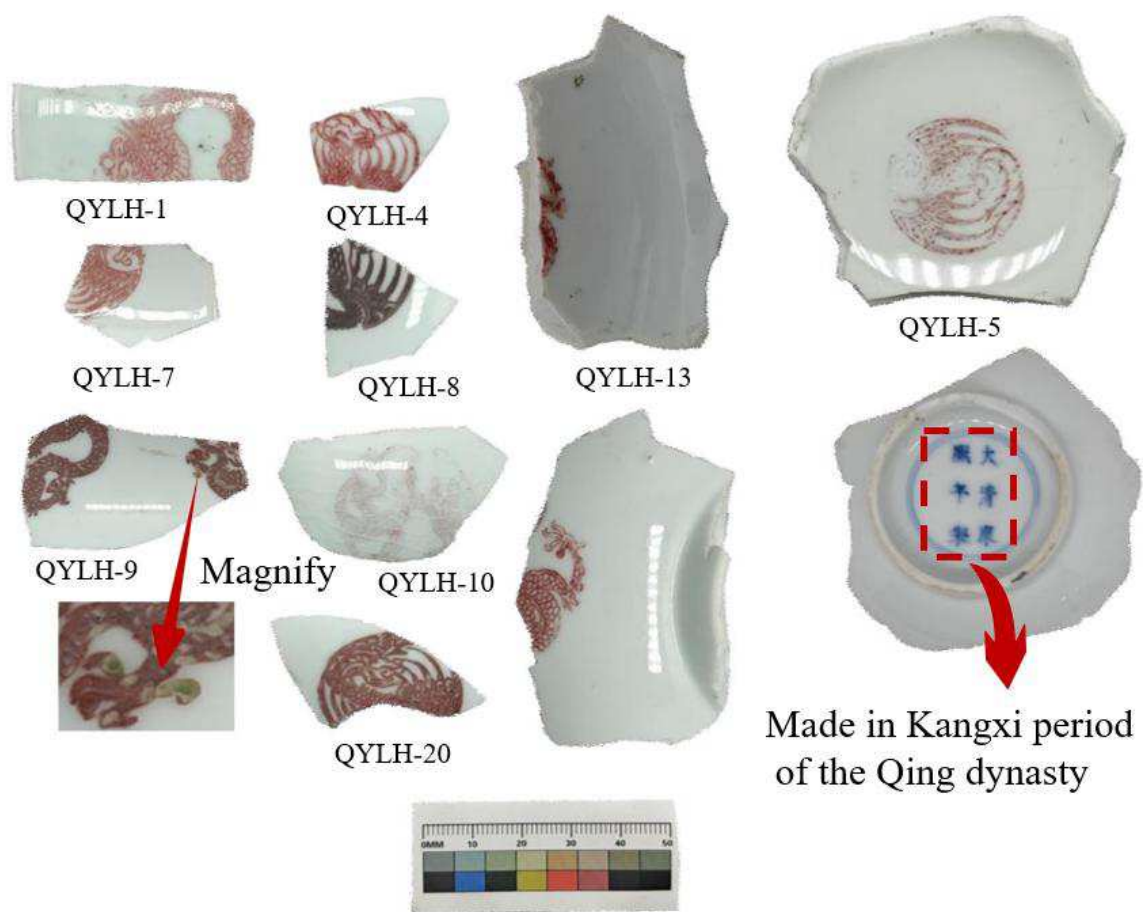


Fig.1 The specimens of Kangxi-period underglaze copper-red porcelain

Energy-dispersive X-ray fluorescence spectrometry(EDXRF)

Each specimen was ultrasonically cleaned in deionised water for 30 min and then dried in a forced-air oven at 100 °C for 2 h before testing. Samples were cut into 5 mm*5 mm*5 mm cubic blocks. An Eagle III XXL micro-focus energy-dispersive X-ray fluorescence spectrometer (EDXRF, EDAX Inc., USA) was used to determine the major and trace elemental compositions of the red-pigment and green-spot regions. Measurements were performed with a beam spot size of 300 μm , a tube voltage of 50 kV, a tube current of 200 μA , and an acquisition time of 300 s. Elemental concentrations were quantified using in-house calibration curves established with reference standards; the results are listed in Table S2.

colourimetric analysis

Specimens showing different underglaze copper-red hues were selected, and their red pigments were subjected to colourimetric testing using an NF-333 spectrophotometer (Nippon Denshoku Industries Co., Ltd.). Measurements were performed with a spot diameter of 8 mm and a wavelength range of 400-700 nm. All tests were carried out under standard 10° viewing conditions with a D65 standard illuminant.

X-ray photoelectron spectroscopy(XPS)

Three specimens exhibiting distinct variations in underglaze copper-red colouration and associated green spots were selected and cut into small blocks of 5 mm*5 mm*2 mm. A Thermo Scientific Nexsa X-ray photoelectron spectrometer (USA) was used to characterise valence-state variations of

Cu and Fe ions in specimens with different colouration. A monochromatic Al K α X-ray source was adopted with an accelerating voltage of 12 kV. The analysis chamber vacuum was maintained below 10⁻⁹ mbar, the pass energy for survey scans was set to 100 eV, and the calibrated work function was 4.20 eV.

Optical microscope (OM)

The cross-sections and glaze-surface microstructures of the specimens were characterised using a KEYENCE VHX-6000 ultra-depth-of-field 3D digital microscope. For further detailed observation, representative cross-section specimens containing red-pigment and green-spot regions were analysed via a ZEISS Axio Scope.A1 polarising microscope under reflected light and cross-polarised light to clarify the microstructural and optical characteristics of the glaze surface and cross-sectional layers.

Scanning electron microscopy and energy-dispersive X-ray spectroscopy(SEM-EDS)

Specimens with obvious red pigment and green spots were selected and etched with 5% hydrofluoric acid (HF) for 30 s. After etching, the specimens were ultrasonically cleaned in distilled water for 30 min and dried, then gold-sputtered for microscopic imaging. Thin sections with well-defined crystalline microstructures were finally screened for subsequent testing. A Hitachi SU-8010 scanning electron microscope (SEM, Hitachi Ltd., Japan) was employed to observe the micro-morphology of glaze colourant layers, while the coupled energy-dispersive X-ray spectroscopy (EDS) system was used to determine localised elemental compositions.

Results

Major and trace elements in the pigment of the analysed specimens

Green spots are commonly found adjacent to the red pigments regions on specimens. The elemental compositions of the red pigments and green spots regions are presented in Table S2. The average SiO₂ contents are approximately 72.71 wt% (red pigments) and 72.28 wt% (green spots); the average Al₂O₃ contents are 13.95 wt% and 13.93 wt%; the average Na₂O contents are 3.42 wt% and 3.20 wt%, and the average K₂O contents are 3.47 wt% and 3.26 wt%, respectively. Further comparison of CuO, CaO, and Fe₂O₃ concentrations between the two regions reveals average CuO values of 0.14 wt% (red pigments) and 0.23 wt% (green spots), average CaO values of 4.88 wt% and 5.75 wt%, and average Fe₂O₃ values of 0.49 wt% and 0.58 wt%.

Chromaticity and reflectance spectral characteristics

Specimens with a light-to-dark underglaze copper-red colour gradient were selected for chromaticity measurement, as shown in Table S3. Their corresponding reflectance spectra are plotted in [Fig. 2]. The red-band reflectance of specimens QYLH-1 and QYLH-4 reached approximately 30% and 35%, respectively, and was markedly higher than that of other wavelength bands, corresponding to a bright, vivid red appearance. In contrast, the reflectance spectrum of QYLH-8 was relatively flat across the visible-light range, with reflectance stabilized between 17% and 21%; its red-band reflectance was only slightly higher, resulting in a blackish-red hue. The main reflectance peaks of QYLH-9 and QYLH-20 were in the orange-red region (600–650 nm), with strong absorption at shorter wavelengths, producing dark-red to brownish-red hues. QYLH-10 showed high full-spectrum reflectance of 35%–42%, with most incident visible light directly reflected; thus, its colour appeared extremely pale red.

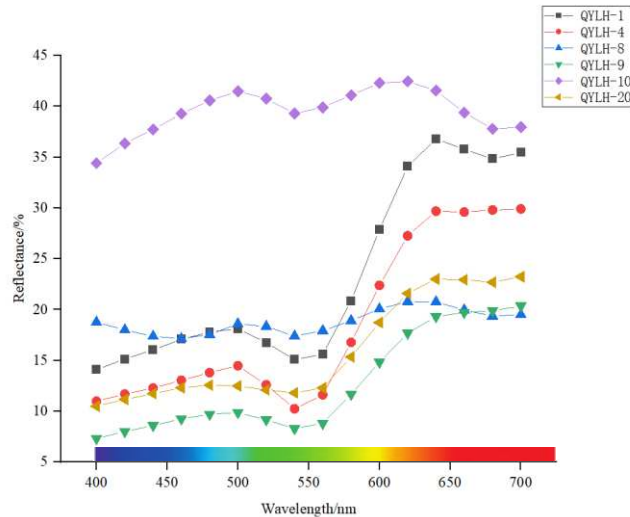


Fig.2 Visible reflectance spectra of selected underglaze copper-red specimens.

Optical image of glaze surface and cross section

Specimens QYLH-1, QYLH-9, and QYLH-10 were selected for optical microscopic observation [Fig.3]. Observations revealed that the glaze layers of QYLH-1 and QYLH-10 displayed clear colour stratification: a red pigment layer was situated directly above the ceramic body, overlaid by a relatively pale diffusion layer and a thin transparent glaze layer. For specimen QYLH-9, the surface transparent glaze layer was nearly absent as the pigment colour deepened. Bubbles within the glaze layers of all tested specimens were small and densely distributed, with an average diameter of around 40 μm , and the total glaze thickness ranged from 250 μm to 350 μm . Green spots approximately 400 μm in diameter were scattered within the red pigments of QYLH-1; these green spots were largely bubble-free and exhibited a smooth glaze surface.

Polarized light microscopy (PLM) observations were conducted on specimens QYLH-1, QYLH-4, QYLH-8, QYLH-9, and QYLH-20 [Fig. 4]. Crossed-polarized-light imaging [Fig. 4a] revealed an anorthite crystallisation reaction layer at the body-glaze interface; however, no clear boundary is discernible between the pigment regions and the overlying glaze. This observation indicates mutual diffusion and dissolution between the pigment and glaze components during firing, demonstrating that the glaze plays a critical role in pigment colour development. Bubbles of varying sizes were identified within the glaze layer, accompanied by red particles of diverse morphologies inside and adjacent to some of the bubbles. Supplementary reflected-polarized-light microscopy [Fig. 4b] revealed numerous dispersed particles with a bright metallic lustre distributed around the red pigment regions. Given that metallic particles exhibit bright-white or iridescent lustre under reflected-light microscopy^[26], these highly reflective particles were tentatively attributed to copper-bearing phases and were subsequently examined by SEM-EDS. Distinct variations in the density, morphology, and size of copper particles were identified among different specimens. Compared with bright red QYLH-1 and blackish-red QYLH-8, dark-red specimens QYLH-9 and QYLH-20 exhibited a much higher abundance of copper particles within and around glaze gas bubbles. In QYLH-9, green spots formed adjacent to red-pigment regions and were surrounded by zones of marked copper enrichment. The green-spot regions also contained markedly fewer gas bubbles than the adjacent red-pigment regions. Together, the peripheral copper enrichment and the difference in bubble density indicate that the red pigments and green spots regions have distinct glaze microstructures.

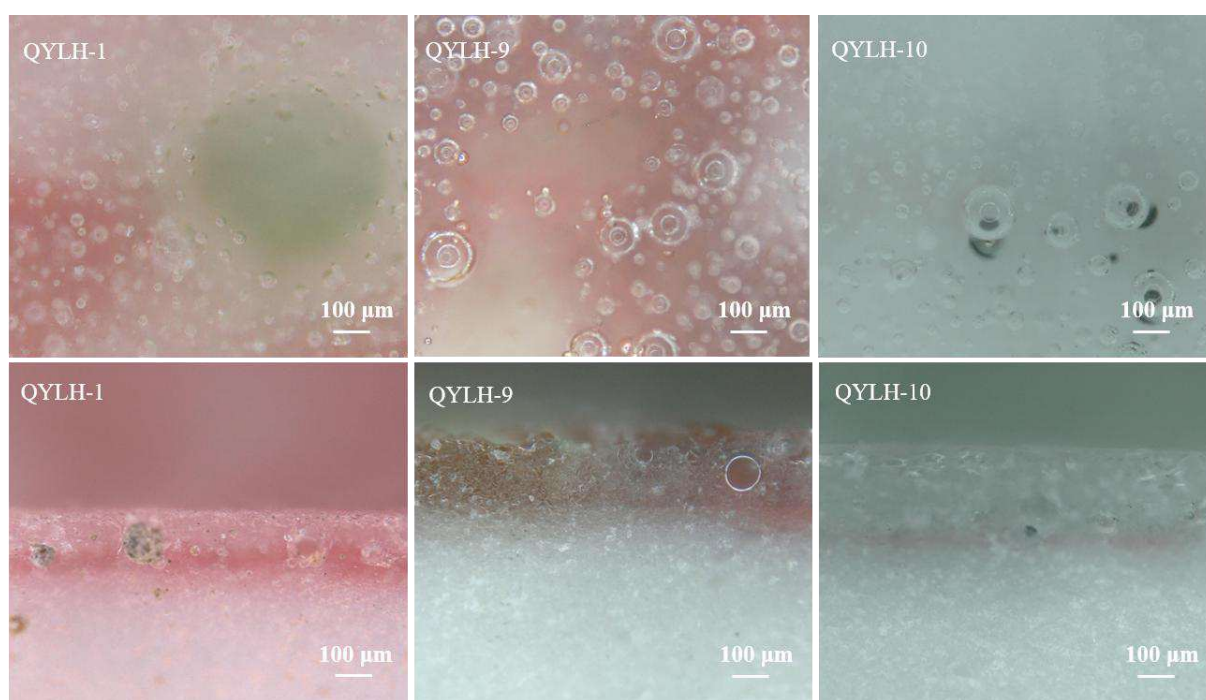
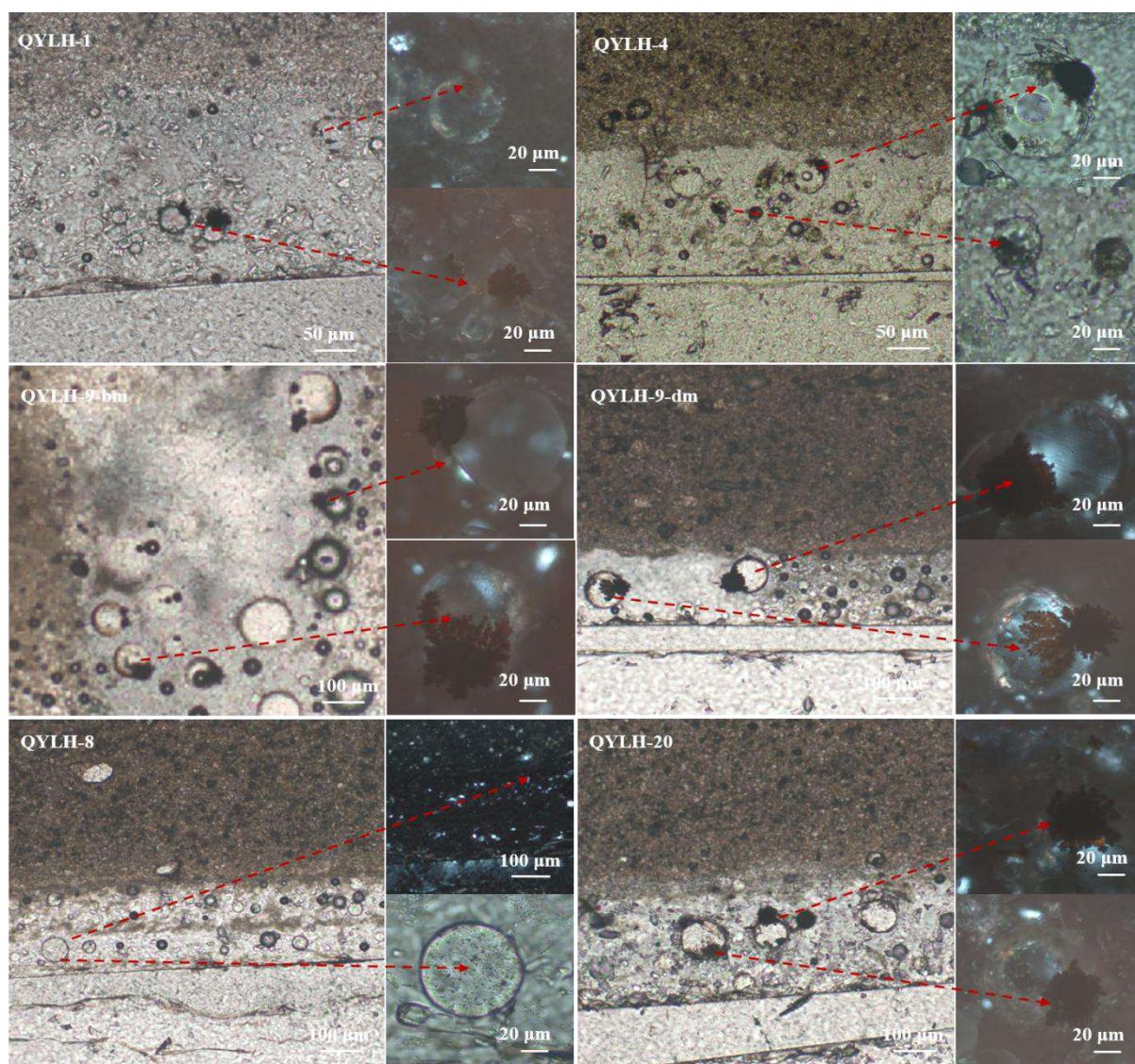


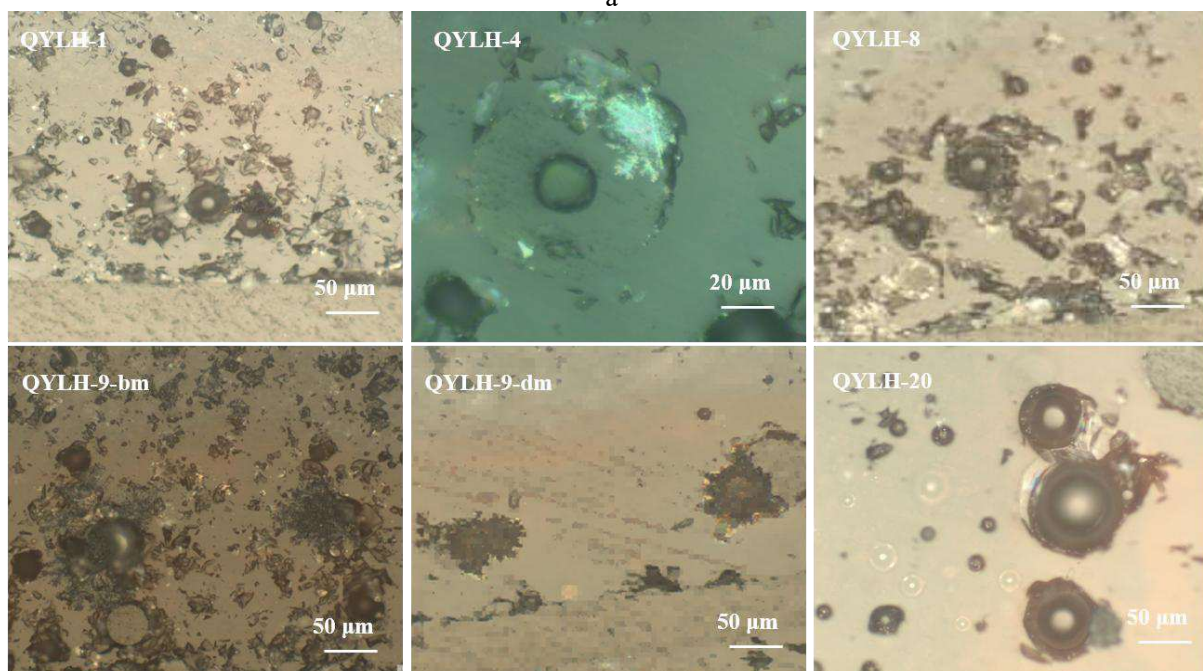
Fig.3 Extended-depth-of-field optical micrographs of the glaze and cross-sections of selected specimens.

Microstructural characteristics and micro-area composition of copper particles

Further SEM observations of crystals adjacent to glaze bubbles are presented in [Fig. 5]; EDS compositional analysis was carried out on crystals of different morphologies (Table 1), and the results showed significant differences in the elemental composition between the various crystals. At most test points, the core elements were Cu and O, while some points also contained higher levels of S and As. These copper-bearing phases displayed a strongly heterogeneous distribution linked to the incorporation of As and S. As shown in [Fig. 5a], the microcrystals adopted diverse morphologies, including dendrites, spherical, acicular, and spherical aggregates. Elemental mapping of sample QYLH-1 is shown in [Fig. 5b], revealed variable Cu and S concentrations even within an individual gas bubble. Backscattered-electron images [Fig. 5c] demonstrated clear heterogeneity in copper-particle-size distribution across specimens. Copper particles were relatively large in the dark-red samples, whereas the bright-red specimen (QYLH-4) contained a high fraction of fine-grained copper particles. SEM imaging of the red-pigment and green-spot regions in several specimens [Fig. 6a] revealed isolated, spherical, droplet-like phase-separation structures (10–20 nm in diameter) exclusively within the green-spot regions. Elemental mapping of the same regions in specimen QYLH-7 [Fig. 6b] confirmed the enrichment of Cu, Ca, and Fe in these regions, consistent with our earlier compositional findings.



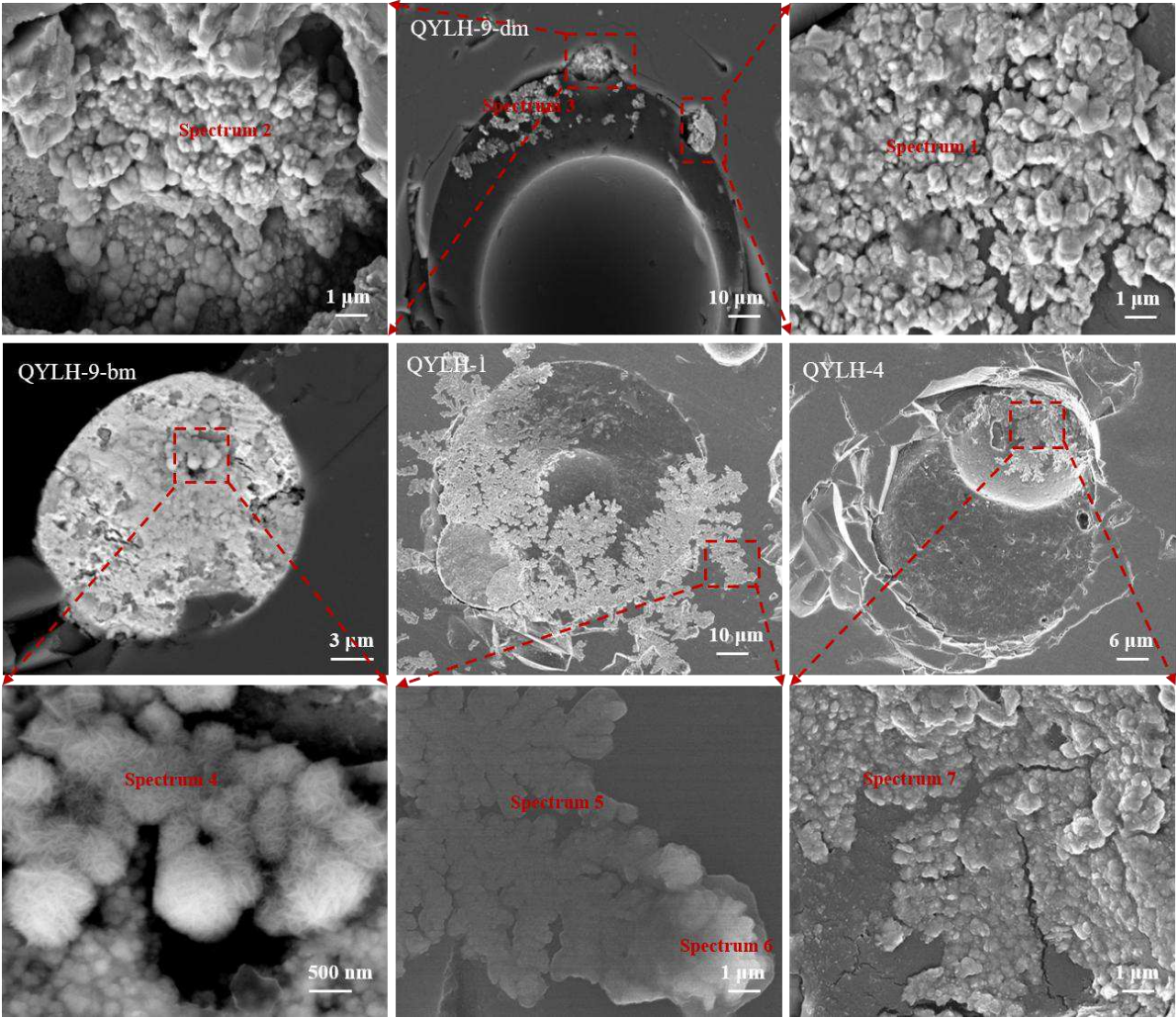
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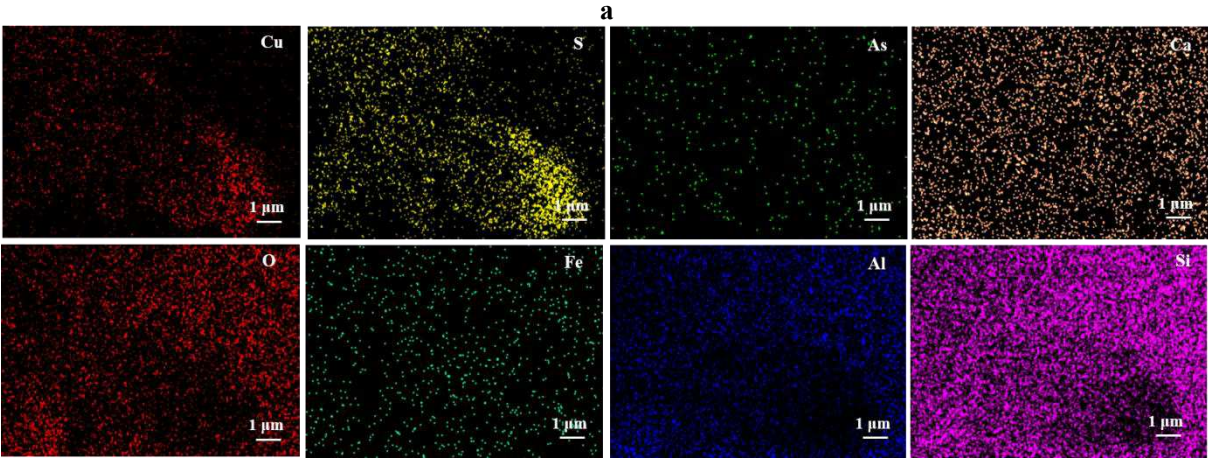
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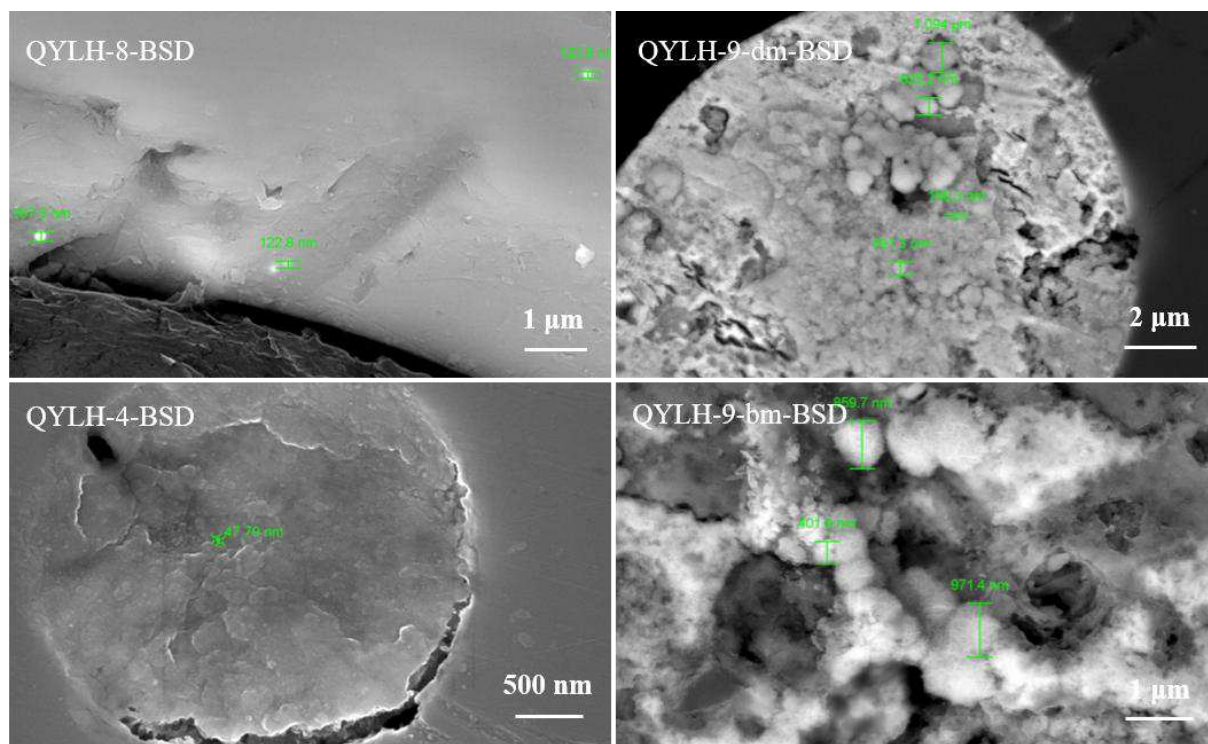
Fig.4 Polarized-light micrographs of glaze surfaces and cross-sections of selected specimens
(a) Cross-polarized light (b) Reflected light



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203



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205



c

Fig. 5 SEM images of copper-bearing particles associated with glaze bubbles

(a) SEM images of selected specimens; (b) Elemental distribution map of QYLH-1 specimen; (c) Backscatter images of selected specimens

Table. 1 The EDS analysis results of the corresponding points in Fig.5a

No.	Atomic(%)			
	Cu	O	S	As
Spectrum1	66.20	20.68	13.12	0.00
Spectrum2	86.76	13.24	0.00	0.00
Spectrum3	38.95	36.73	24.32	0.00
Spectrum4	54.40	22.91	21.43	1.26
Spectrum5	42.96	22.35	28.40	6.29
Spectrum6	35.99	31.24	27.48	5.29
Spectrum7	43.36	38.47	15.94	2.23

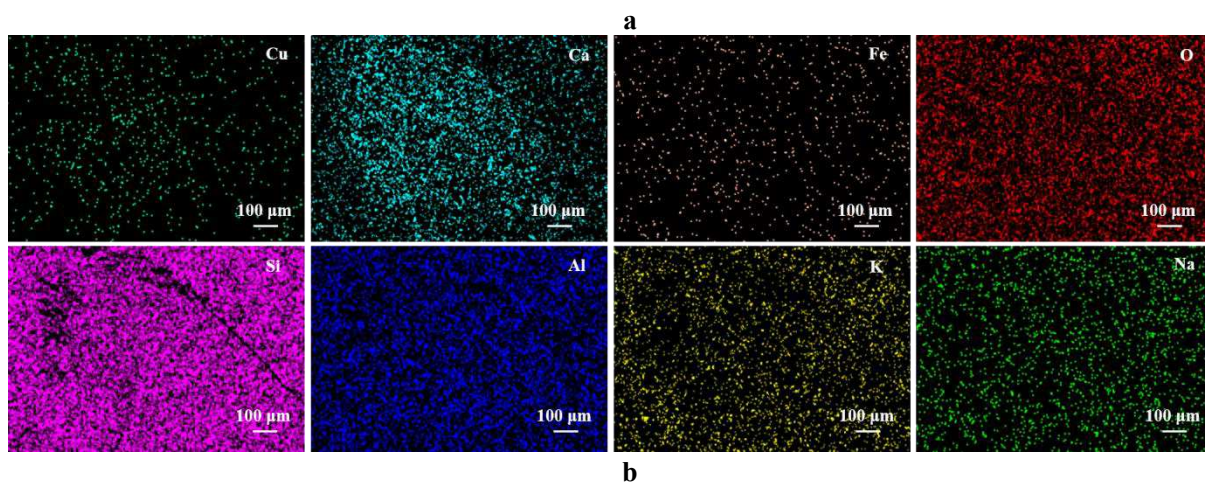
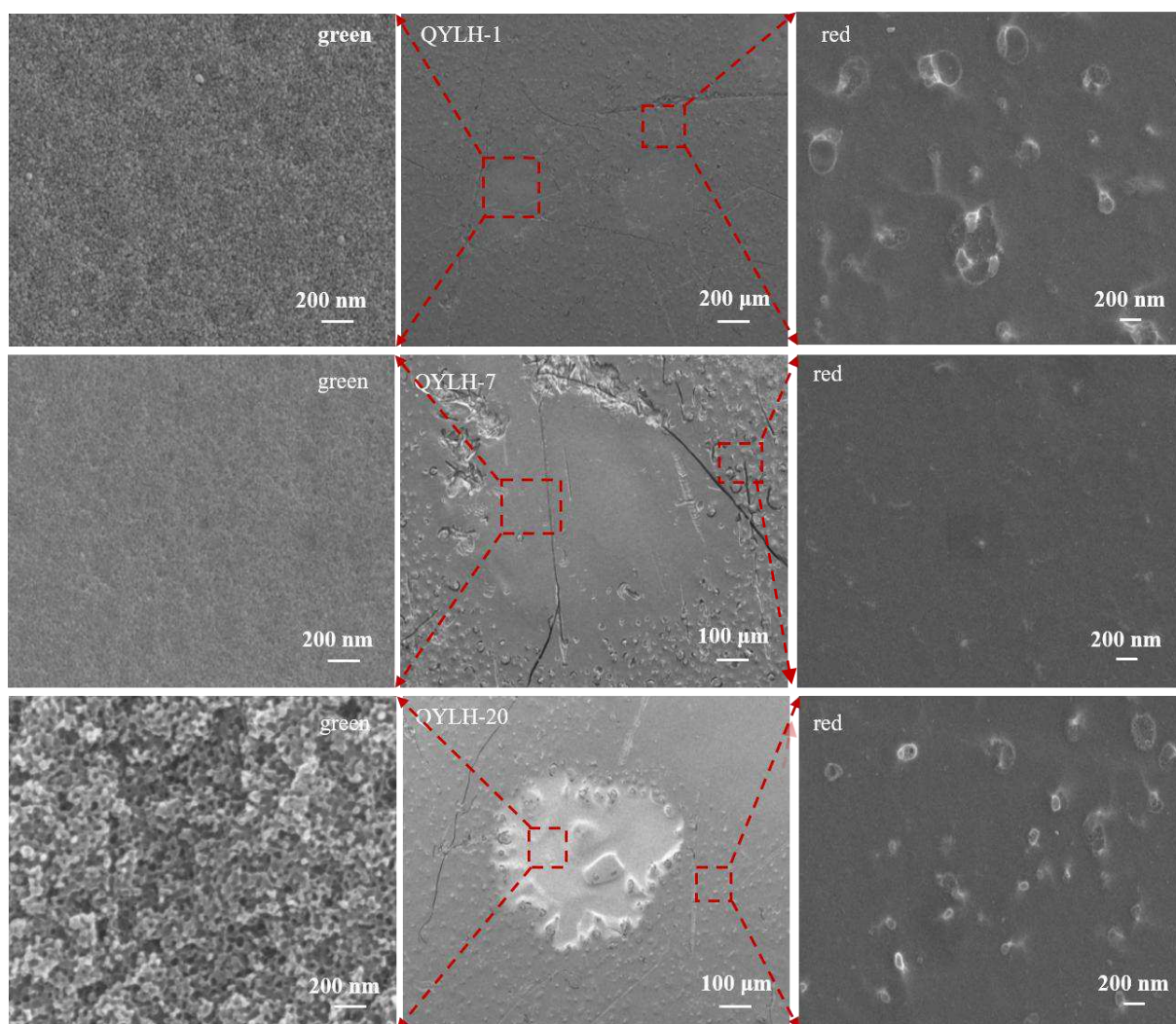
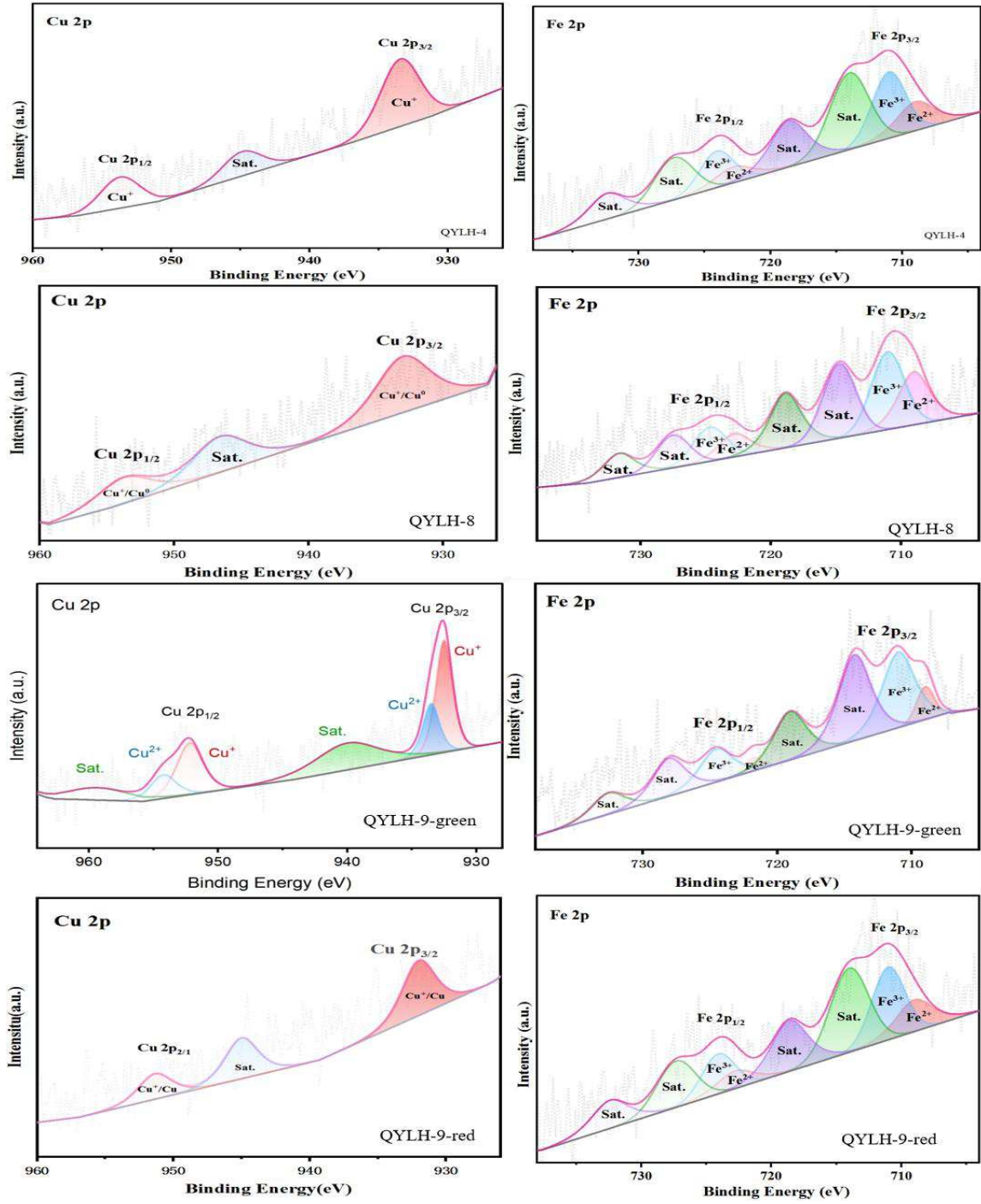


Fig. 6 (a) SEM images of the red and green colouration areas in specimens
(b) Elemental distribution map of red and green colour regions in QYLH-7 specimen

Valence-state distribution ratios of copper and iron

Specimens QYLH-4, QYLH-8, and QYLH-9, which displayed marked differences in underglaze copper-red colouration, were selected for valence-state analysis of Cu and Fe in their pigment-bearing glaze regions. [Fig. 7a] shows the fitted high-resolution XPS spectra of the Cu 2p and Fe 2p orbitals for these specimens, while [Fig. 7b] shows the fitted Fe 2p XPS spectrum acquired

223 from the glaze of specimen QYLH-9. According to the published literature^[27], the Cu 2p_{3/2}
 224 binding-energy peaks for Cu⁰, Cu⁺, and Cu²⁺ are located at 932.6 eV, 932.8 eV, and 933.6 eV,
 225 respectively. Given the minimal binding energy gap between Cu⁰ and Cu⁺, these two copper species
 226 cannot be differentiated from the Cu 2p peak positions alone. In contrast, their corresponding Cu
 227 Auger-peak energies are 568.1 eV (Cu⁰), 570.2 eV (Cu⁺), and 568.9 eV (Cu²⁺). Peak deconvolution
 228 and curve fitting were performed using the combined Auger peak and Cu 2p spectral data. The
 229 calculated valence-state ratios of Cu and Fe ions are summarized in Table 2.



a

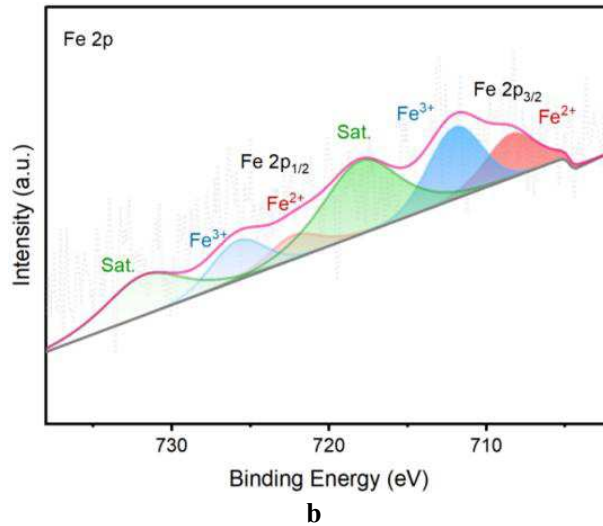


Fig.7 (a) XPS fitting plots of colour regions in selected specimens
(b) XPS fitting plot of the surface glaze on specimen QYLH-9

Table. 2 Valence-state ratios of the colouring elements in QYLH-4, QYLH-8, and QYLH-9

Sample ID	colour Appearance	Valence-state ratio(Cu,Fe)	
QYLH-4	Bright red	Cu ⁺ : 100%	Fe ³⁺ : 65.78%, Fe ²⁺ : 34.22%
QYLH-8	Red-black	Cu ⁺ : 81.31%, Cu ⁰ : 18.69%	Fe ³⁺ : 59.01%, Fe ²⁺ : 40.99%
QYLH-9	Green	Cu ⁺ : 64.52%, Cu ²⁺ : 35.48%	Fe ³⁺ : 82.19%, Fe ²⁺ : 17.80%
QYLH-9	Deep red	Cu ⁺ : 94.67%, Cu ⁰ : 5.33%	Fe ³⁺ : 75.83%, Fe ²⁺ : 24.17%
QYLH-9	Slight bluish tint	/	Fe ³⁺ : 61.67%, Fe ²⁺ : 38.33%

Discussion

Colour in vitreous glaze layers arises from structural colouration, chemical colouration, or a coupling of the two mechanisms. As a transition-metal ion, copper produces selective absorption in the visible region through electron transitions within its 3d orbitals. Copper ions in different valence states exhibit distinct colours and spectral properties. Meanwhile, the coordination field formed by oxygen ions around chromophoric ions inside the vitreous glaze structure modulates the spectral characteristics of these ions and thereby influences the final colouration^[28].

Formation mechanisms of green spots

The mechanism underlying the colour difference between the red pigment and green-spot regions was further explored by integrating elemental composition data and SEM micromorphological observations. According to the results compiled in Table S2, the bar chart of characteristic element contents for the two regions [Fig. 8a] shows that Si, Al, Na, and K concentrations were broadly comparable and displayed no obvious correlation with colour variation. This indicates that these elements were not the primary factors responsible for the colour discrepancy between the red pigment and green-spot zones. Results from [Fig. 8b] further reveal significant CuO enrichment in green-spot regions, and the concentrations of CaO and Fe₂O₃ were positively correlated with CuO content. Because these 10–20 nm domains are markedly smaller than visible wavelengths, their contribution to optical scattering is expected to be weak, and visible light passes directly through the glaze matrix^[29]. Meanwhile, green-spot regions contained markedly fewer bubbles than adjacent red-pigment regions. Combined with the XPS valence-state results, the relative fraction of Cu²⁺

259 increased markedly in green-spot regions. Within the vitreous glaze matrix, Cu^{2+} preferentially forms
 260 $[\text{CuO}_6]$ octahedral coordination. Alkali-metal and alkaline-earth-metal oxides in the glaze reduce the
 261 ligand-field-splitting energy Δ , shifting the optical-absorption band toward longer-wavelength,
 262 lower-energy regions and ultimately producing a green hue in the glaze layer^[30]. Thus, the green
 263 coloration is more plausibly dominated by selective absorption associated with Cu^{2+} than structural
 264 colouration governed by microstructural features.

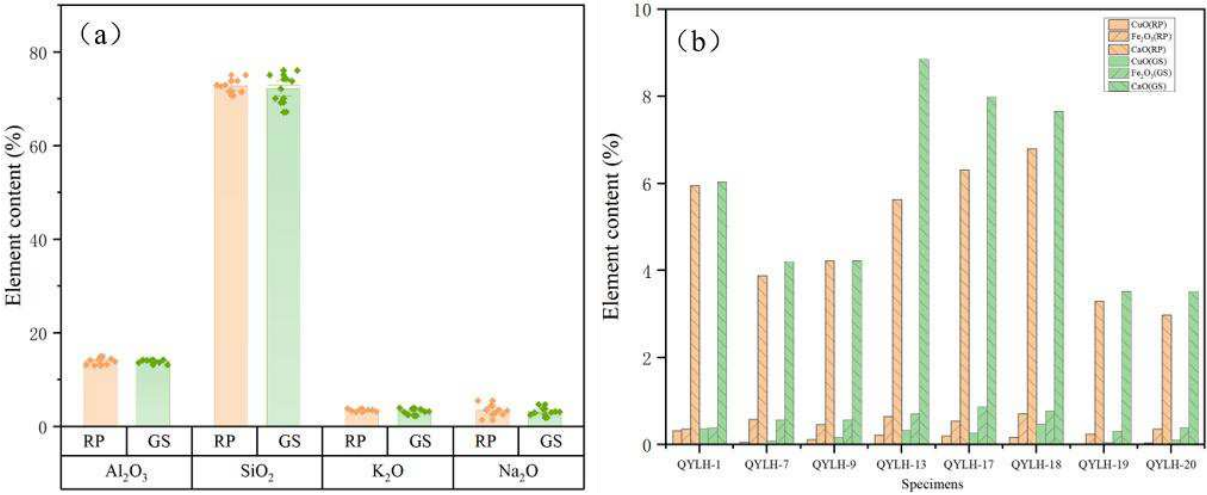


Fig.8 Comparison of selected oxide contents in the red-pigment and green-spot regions

265 Given the homogeneous nature of the glaze matrix, these green spots most likely originated
 266 from manual pigment preparation and application. Either insufficient grinding of the colourants or
 267 localised pigment aggregation caused microscale CuO enrichment, within which copper remained
 268 incompletely reduced and persisted partly as Cu^{2+} . The coexistence of red pigments and green spots
 269 on the same specimen (e.g., QYLH-9) shows that this accumulation was localised rather than
 270 uniform throughout the ware. Consistent with the elemental compositional analysis, CaO and Fe_2O_3
 271 contents in these microdomains were markedly positively correlated with copper concentrations.
 272 CaO acts as a major flux, lowering the initial melting temperature and bulk viscosity of the glaze
 273 melt; within the SiO_2 - Al_2O_3 - Na_2O ternary system, however, Ca^{2+} blocks the diffusion pathways of
 274 copper ions, so that the copper-ion diffusion rate declines with increasing CaO content^[31]. Local
 275 CaO accumulation thus restricts copper-ion migration and facilitates copper enrichment in the
 276 corresponding microregions. Fe_2O_3 is commonly present in the pigment as an inherent impurity or a
 277 raw-material constituent, and part of the Fe^{3+} persists during the firing of underglaze copper-red ware,
 278 mainly in tetrahedral $[\text{FeO}_4]$ coordination, which promotes the melting of crystalline phases and the
 279 formation of amorphous frameworks, enhancing glaze immiscibility and inducing liquid-phase
 280 separation^[32]. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of the red-pigment matrix and green-spot regions,
 281 calculated from the elemental data in Table S2, averaged 8.87 and 8.83, respectively. Although both
 282 lie below 10, distinct phase-separated microstructures were clearly observed in the green-spot
 283 regions^[33], indicating that the ratio contributes to, but does not solely govern, phase separation,
 284 which is also modulated by CuO , Fe_2O_3 and CaO . Together, these factors govern the phase-separated
 285 microstructure, whereas the green colouration reflects the local Cu^{2+} enrichment and is not produced
 286 by the phase separation itself.

289 Synergistic Control of Copper Phase, Particle Size, and (S, As) on the Colouration of

290 Underglaze Copper-Red Porcelain

291 As summarized in Table 1, combined with the XPS results, the EDS data suggest that Cu^+ bearing

Cu₂O constitutes an important copper-bearing phase in the red regions. Cu and O are the core components of these crystals, whereas partial crystals contain co-occurring S and As. From the perspective of copper-ion electronic structure, Cu⁺ has a filled, stable 3d orbital configuration, which prohibits d-d electron transitions and renders isolated Cu⁺ optically colourless. Nevertheless, Cu₂O exhibits semiconducting properties and exists widely as microcrystals within the glassy glaze phase, dominating the red colouration of Kangxi-period underglaze copper-red porcelains. Mixed phases of elemental Cu and Cu₂O were detected at specific microscopic sites (e.g., Spectrum 2), whereas crystalline copper-bearing compounds coupled with S and As were observed in other, more localised regions. Under reducing conditions, Cu⁺ possesses strong polarization ability and tends to bond covalently with the large-radius, highly polarizable S²⁻, thereby forming sulfide minerals. Meanwhile, As is incorporated into the Cu-S-bearing phase^[28], which may modify the crystal habit by altering the relative surface energies of different facets. Accordingly, the occurrence of sulfur and arsenic bearing copper-rich particles suggests that these trace components may markedly influence copper nucleation and crystallization during roasting. Notably, even on the same bubble, variations in the Cu and S contents can induce the formation of crystals with different morphologies (Specimen QYLH-1, Fig. 5b).

colouring glass with colloidal copper can produce a series of hues ranging from pale red, bright red, medium red, dark red to brownish-red. For copper-ruby glass, the minimum threshold size for colour-generating colloidal-copper particles is 3–5 nm; no colouration occurs when the particles are smaller than this value. The upper-size threshold of colloidal particles in copper-ruby glass is generally 70–80 nm. If a large fraction of particles sized 70–80 nm remains in the glass matrix after heat treatment, the resulting glass will exhibit opalescence or an extremely deep dark-red hue. Therefore, the preparation process must be carefully controlled to promote the formation of a marked number of particles within the 5–60 nm size range, allowing the final product to display a bright-red colouration^[31]. In most archaeological specimens, copper particles show relatively large grain sizes, corresponding to a duller-red hue overall.

In comparison, specimen QYLH-4 contains uniformly fine copper particles, yielding the most vivid red colouration among all tested samples. Moreover, the coexisting secondary Cu-S phase further darkens the red tone. The type of copper-bearing phase, microcrystalline morphology, and particle size constitute the intrinsic foundation of underglaze copper-red colouration. Meanwhile, the kiln-firing atmosphere, as a critical external technological parameter, further modulates the valence equilibrium of copper and ultimately governs the final colour appearance of underglaze copper-red.

The effect of firing atmosphere on copper valence state and colouration

As listed in Table 2, Fe³⁺ predominates over Fe²⁺ in the iron valence distribution, while the coexistence of Cu⁺ and metallic Cu⁰ likewise attests to reducing conditions from the perspective of copper. Considered jointly, these observations indicate that the firing atmosphere was weakly reducing. Specimen QYLH-4 displays a vivid red tone, with its Cu⁺ content directly governing the colouration of underglaze copper-red. By contrast, specimen QYLH-8 possesses a relatively high proportion of Cu⁰, which induces a duller, blackish-red hue through colour superposition. For specimen QYLH-9, the green spot contains abundant Cu²⁺, whereas no Cu²⁺ is detected in its red pigment. The present data demonstrate that the colouration of underglaze copper-red specimens is primarily governed by the relative proportions of Cu⁰, Cu⁺, and Cu²⁺. At the same time, the kiln-firing atmosphere acts as the dominant external factor regulating copper valence distribution. Under moderately weak reducing conditions, Cu⁺ remains the dominant copper valence state,

generating vivid and pure red colouration due to the precipitation of abundant Cu_2O microcrystals, as observed in specimen QYLH-4. In contrast, excessively strong reducing atmospheres drive the extensive reduction of Cu^+ to Cu^0 , promoting the continuous aggregation of metallic copper colloids and the coarsening of copper particles. These microstructural changes reduce red chroma and produce a darkened, blackish-red glaze tone characteristic of specimen QYLH-8. In local regions where excessive CuO accumulation locally exceeds the reducing capacity of the atmosphere, copper ions remain partly unreduced, leading to significant Cu^{2+} enrichment and the subsequent formation of green spot defects, as exemplified by specimen QYLH-9.

Furthermore, the prominent Cu^{2+} enrichment within green spots and the complete absence of Cu^{2+} in the adjacent red decorative regions of specimen QYLH-9 further verify that localised fluctuations in CaO , CuO , and Fe_2O_3 contents alter copper valence ratios and coordination environments, thereby modulating the colour evolution of underglaze copper-red. The dynamic proportions of multivalent copper species constitute the fundamental mechanism underlying the diverse colour characteristics of Kangxi-period underglaze copper-red porcelains, covering bright red, dark red, and sporadic green spot defects. Accordingly, precise regulation of the firing atmosphere is identified as the core technical prerequisite for achieving stable, controllable colouration in underglaze copper-red glazes.

In summary, this study clarifies the inherent technical principles of traditional craftsmanship responsible for colour variations and green-spot defect formation in Kangxi-period underglaze copper-red porcelains of the Qing dynasty. The diverse colour appearances of these artifacts stem from the synergistic effects of multiple factors, including multivalent copper valence ratios, localised compositional enrichment, glaze matrix liquid-liquid phase separation, and regulatory effects of trace sulfur and arsenic impurities. Such formation mechanisms were gradually refined and finalized through long-term empirical exploration in ancient ceramic production. Several limitations of this study warrant careful consideration. First, the analytical scope was restricted to a limited set of representative Kangxi-period specimens; consequently, the observed patterns may not fully reflect the breadth of compositional and microstructural variability inherent in contemporary copper-red porcelain production. Second, although EDS mapping reveals a consistent spatial correlation between minor impurities, specifically sulfur (S) and arsenic (As), and distinct particle morphologies, the underlying crystallographic mechanism by which these elements influence crystal habit remains incompletely resolved. Finally, because the specimens are heterogeneous, hand-made artefacts, local microchemical gradients may obscure direct, bulk-level correlations between overall composition and macroscopic colour appearance. Overall, this study systematically elucidates the intrinsic mechanisms driving the differential colouration of Kangxi-period underglaze copper-red porcelain, providing a scientific basis for the technical discrimination of Qing dynasty underglaze copper-red wares and establishing a feasible framework for future research on traditional Chinese ceramic manufacturing technologies.

Data availability

The data generated and analysed during this study are presented in the supplementary tables. The XPS pattern was generated using the Avantage and Origin software. The dataset underlying the findings of this study is available from the author, W.J., upon reasonable request.

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Author Contributions

J.W.: methodology, conceptualization, investigation, experimentation, data collection, and writing—original draft. Q.L.: conceptualization, methodology, writing—review and editing, funding acquisition, software. C.W.: validation, investigation. Z.Q.: investigation, conceptualization. All authors have read and agreed to the published version of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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