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Technological integration and innovation in architectural ceramics in the Yuan Dynasty: chemical investigation for the glazed tiles of the Prince Anxi' s mansion, China

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Glazed tiles, a symbol of high-grade architecture in ancient China, first appeared in the Northern Wei Dynasty (AD. 386–534). They reached their peak in the Ming and Qing Dynasties (AD. 1368–1912), and the Yuan Dynasty (AD. 1271–1368) was a key stage in the development and maturity of the glazed tile technology. As one of the representatives of royal architecture in the early Yuan Dynasty, scientific research on the unearthed glazed tiles from the site of Prince Anxi's mansion can assist to understand how glazed tile technology matured during the Yuan Dynasty. Using compositional analysis and microscopic observation, 24 glazed tiles from the Prince Anxi's mansion were systematically examined in this study. The findings revealed that the glazed tiles were made using four different production formulas and came from three different technological traditions, which originated from the integration of various regions' glazed tile production technologies and enhanced innovation within the currently used technologies. The resulting glazed tile production technologies exhibit a high degree of similarity with the Yuandadu 's glazed tile production technologies, suggesting that integration and innovation are crucial for the Yuan Dynasty's glazed tile technologies to mature.

The development of ceramic tile roofs has significantly increased building roofs' long-term durability, defense, and wind resistance, reduced house maintenance costs, and had a major impact on the structure and form of the materials used in house construction. Tiles are an essential part of modern human construction roofs. Terracotta tile use in ancient China dates to the early Longshan Culture (BC 2400–2200), according to fragments of the tiles discovered at the Qiaocun site in Lingtai County, Gansu Province, China[1]. The use of glazed tiles to decorate architectural roofs traces back to the Northern Wei Dynasty (AD 386–534) in China[2], where clay tiles with green glaze were embellishing the religious temples established at the top of the Yungang Grottoes[3]. After this initial phase, clay tiles covered with various lustrous colors such as green, yellow and turquoise were ornamenting the imperial palaces and pagodas in the capital cities of the Tang Dynasty (AD 618–907)[4] and the Northern Song Dynasty (AD 960–1127)[5]. Later, in the Yuan Dynasty (AD 1271–1368), the use of glazed tiles climbed a new peak in Chinese architecture whose colors and the sculpts of tiles were more abundant than ever before, influencing the technology and production of the glazed tiles during the Ming Dynasty (AD 1368–1644)[6] and the Qing Dynasty (AD 1636–1912)[7].

Prince Anxi, whose name is Mangora, as the third son of Kublai Khan and one of the most trusted nobles of the royal family from Mongol tribes in the Yuan Dynasty, was appointed as the 'Prince Anxi' in 1272, in charge of guarding the northwest part of China, controlling the authority of both politics and military. The construction of his mansion was completed of extremely high standard in 1273 which preserved the similar appearance with the imperial palaces in the capital cities of the Yuan Dynasty. Based on historical documents and archaeological discoveries, the Yuan Dynasty had three capital cities: Yuan Shangdu in Inner Mongolia Autonomous Region, Yuan Dadu in Beijing, and Yuan Zhongdu in Hebei Province and these cities were built in chronological order. During Kublai Khan's reign, the Yuan

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Shangdu and Yuan Dadu were built in 1256 and 1267 AD, respectively. The former was built to withstand the hot weather in the summer palace's steppe region, while the latter was built to handle daily political affairs in the capital's central region. As a result, "two capitals to visit the system" were created[8]. Building the Yuan Zhongdu between the central plains and the steppe zone was ordered by Yuan Wuzong Haishan, Kublai's great-grandson, and it was completed a bit later than the first two[9]. Numerous shards of glazed tiles have been discovered during the archaeological excavations of these three cities, which is crucial comparison data for our research on the glazed tiles of the Prince Anxi's mansion. Following the traditional custom of mongol nomads like Kublai Khan, Mangora also selected two places as his habitation for dealing daily issues and relaxation individually. One is located in Kaicheng Town, Guyuan City, Ningxia Hui Autonomous Region and the other one is found in Xi'an City, Shaanxi Province (Fig. 1.)[10]. In large-scale archaeological excavations by the Ningxia Hui Automous Region Institute of Cultural Relics and Archeology, a large number of cultural relics such as glazed tiles, ceramics, metals and stoneware were found in the ruins[11]. It is worth noting that these glazed tiles are characterized with a high gloss and vibrant colors employed emerald green, bright yellow, turquoise blue and pure white.

Some previous analytical studies have been focused on the body and glaze examination of glazed tiles in the Yuan Dynasty, especially on the clay tiles adorned with green and yellow glaze[12]. Comparative research on the composition of the blue and white with glazed tiles are still little to known. Considering its obscure in the literature and a limited number of shards, their information of production are not always well established. The purpose of this research is to compare characteristics related to the glaze production of tiles in capital and regional architecture in the Yuan Dynasty.

In order to develop an further understanding of glazing techniques and the features of raw materials, glazed tiles excavated from the site of the Prince Anxi's mansion were investigated in the present study using a combination of major elemental and petrology analysis. The data will be compared to the previous studies of the glazed tiles excavated from other archaeological sites at the same period as the construction of Prince Anxi's mansion which can provide us with a panoramic view of whole developing process in the production technology of the glazed tiles in the Yuan Dynasty.

Materials and methods

All the samples were from the archaeological discovery of the site of the prince Anxi's mansion and provided by the Ningxia Autonomous Region Institute of Cultural Relics and Archeology. Among them, 24 samples with complete and smooth glaze are selected (Fig. 2), named AXWF-001 ~ 006 as green glaze, AXWF-007 ~ 012 as yellow glaze, AXWF-013 ~ 018 as white glaze and AXWF-019 ~ 024 as blue glaze. Besides, the body of the samples AXWF-001 ~ 012 is brick red clay, the body of samples AXWF-013 ~ 018 is brownish yellow clay with sand and the samples AXWF-019 ~ 024 are in gray body. The samples were first documented and representative sections of each were then cut through the body and glaze. All samples were ground and polished using standard procedures.

EDXRF

The chemical compositions of the glaze and body of the glazed tiles were analyzed using a BRUKER ARTAX 400 XRF instrument. The voltage used was 30 kV and the current was 900 mA. High purity helium gas (99.95%) was used to reduce the absorption of secondary X-rays. The diameter of the beam was 1 mm and the counting time was 300 s. For most elements, the detection limit was 0.02%. All the surfaces of the testing area were cleaned with ethyl alcohol. Corning Glass Standards (Corning glass A, B, C, and D) were used for calibration and the concentration results were calculated using ARTAX software[13]. The glaze and body of each sample were tested at least 3 times and the mean value was used to represent the chemical composition of the tested area.

Petrology

Representative sections of these glazed tile samples were cut through the body and glaze, and mounted in resin blocks. These pieces of samples were examined microscopically using a polarizing microscope in order to observe the micro structure of the glazed tiles' body[14].

XRD

Every representative glazed tiles' body in 4 colors was analyzed using micro-XRD (Smartlab, Rigaku Corp., Tokyo, Japan) with CuKα radiation at 45 kV and a tube current of 200 mA. The diameter of the analyzed area was limited to about 50 mm by the collimator. The diffracted X-rays were collected from 5 to 90 by using a D/tex detector at 298 K, and the measurement time was 10 min. The experimental backgrounds were corrected using the Jade 6.5 software package, with which phase identification was performed[15].

Results

Micro structure of glazed tiles' body

The microscopic composition and morphology of the base material were determined by observing thin sections of the four types of glazed ceramic tiles using a polarizing microscope (Fig. 3). Figure 3a, b illustrate the micro-morphology of the body of green-glazed and yellow glazed tiles. The microscopic morphology of the base material in green glazed tiles is highly similar to that of yellow glazed tiles. The mineral particles have a particle size

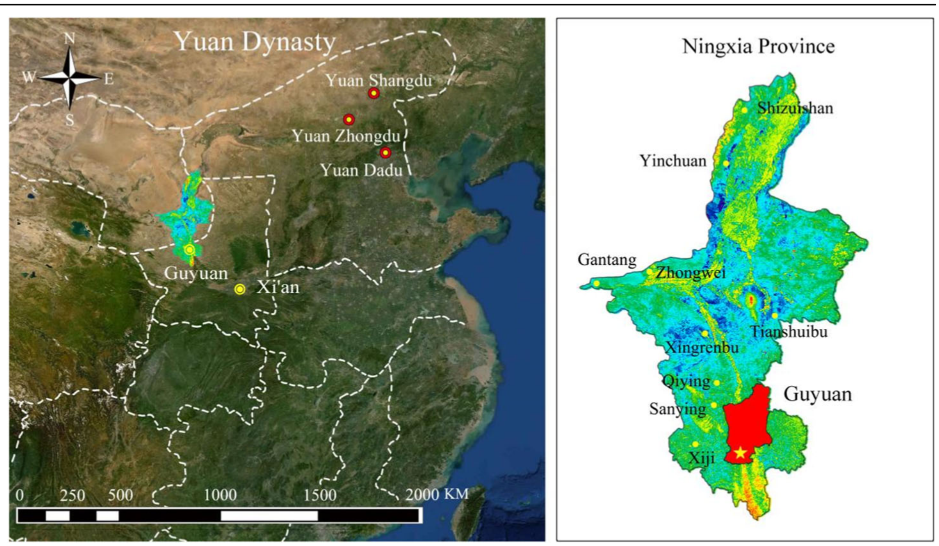
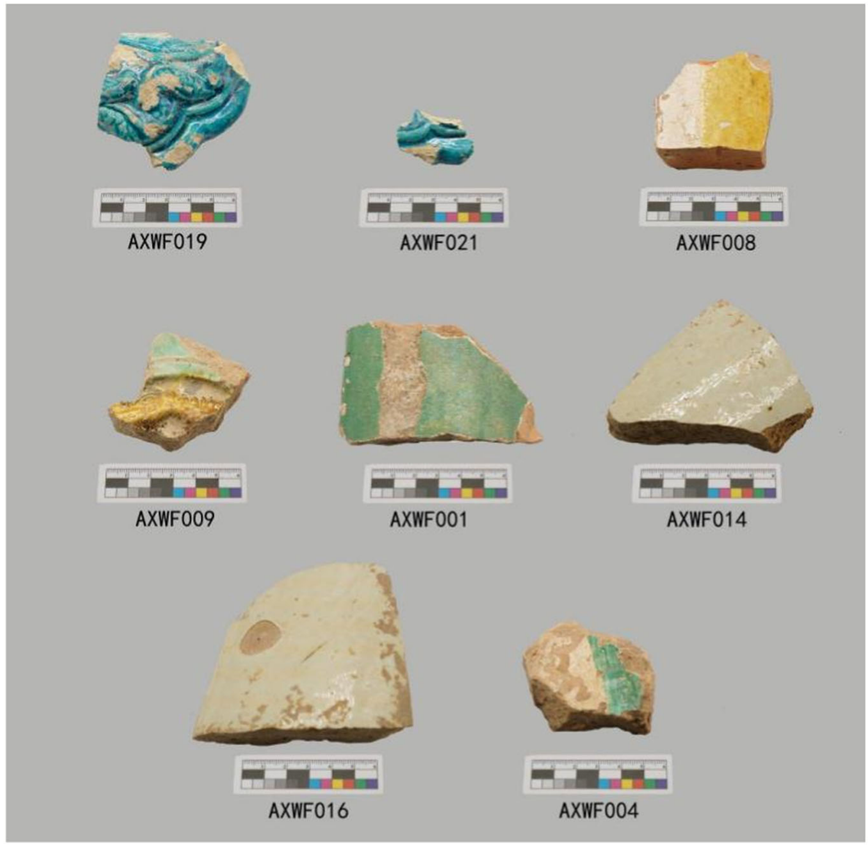


Fig. 1 | Location of the prince Anxi' s mansion.

Fig. 2 | The samples of the Prince Anxi' s mansion.



ranging from 10 to 20 μm, with well-defined angular rock fragments and relatively low roundness. The composition is relatively simple, mainly consisting of quartz, feldspar and chlorite. Figure 3c present the microstructural morphology of the white glazed ceramic tile bodies. In white glazed tiles, the mineral particles of the base material vary in size. They can be classified into two types: particles below 20 μm and particles around 200 μm. The mineral composition is also simple, including cristobalite (SiO_2) and mullite, with a higher degree of roundness. Figure 3d illustrates the microstructural morphology of the blue glazed ceramic tile body. The base body material of blue glazed tiles has the most complex mineral particle types, with particle sizes ranging from 50 to 250 μm. The roundness of the particles varies, and the mineral composition is diverse, including quartz, muscovite, caminite, and chlorite.

Mineralogical composition of glazed tiles' body

Potential raw materials were subjected to XRD to determine the crystalline content (Fig. 4). In all samples, the base materials of different colored glazed ceramic tiles vary. For green glazed tiles as AXWF-002, the main component of the base body material is quartz and chlorite. Yellow glazed tiles like AXWF-011, on the other hand, are composed primarily of quartz and chlorite as well. The base body material of white glazed tiles such as AXWF-015 is predominantly cristobalite and mullite. Lastly, blue glazed tiles are mainly composed of quartz, caminite, muscovite and chlorite for the example of AXWF-020.

These minerals are confirmed in the microscopic observations in Fig. 3. Each base material includes quartz, which is essential for the preparation of ceramic tile bases. Like feldspar, muscovite, chlorite, these are very common in the mud or clay used to make ceramics. What is different, however, is that cristobalite and mullite, which are found in the body of white glazed tiles, are new minerals that are created at higher temperatures. Cristobalite is formed at about 500–600 °C[16] and secondary mullite forms from reaction of feldspar and clay (2 varieties) and feldspar, clay and quartz (3 varieties) during 1100–1300 °C[17]. Obviously, these are newly formed mineral. Based on the above discussion of petrology and XRD results, most of the minerals in the glazed tiles' body of these four glazed colors are pre-existing, such as quartz and chlorite in the green and yellow glazed tile body, caminite and muscovite in the blue glazed tile body, while cristobalite and mullite in the white glazed tile body are newly generated.

Major chemical composition of glazed tiles' body

According to Table 1, the base materials can be divided into three groups based on their colors. The first group consists of red base materials found in green and yellow glazed tiles. The second group includes brownish-yellow base materials found in white glazed tiles and the third group consists of gray base materials observed in blue glazed tiles.

In the chemical composition of the red base materials, the fluctuation in the content of SiO_2, Al_2O_3, and Fe_2O_3 is relatively small, ranging from 64.31% to 68%, 15.08% to 16.03%, and 4.53% to 6.28%, respectively. The content of CaO varies significantly, ranging from 6.36% to 11.34%. The sum of these four compounds exceeds 95%, reflecting the fundamental characteristics of the base material's chemical composition. In the chemical composition of the brownish-yellow base materials, the content of SiO_2, Al_2O_3, and Fe_2O_3 is 53.96% to 55.65%, 33.11% to 35.32%, and 4.73% to 7.47%, respectively. The sum of these three compounds exceeds 95%, providing information about the chemical composition of the base material. Regarding the gray base materials, the fluctuation in the content of SiO_2, Al_2O_3, and Fe_2O_3 is relatively small, ranging from 57.25% to 60.28%, 14.97% to 15.37%, and 5.87% to 6.3%, respectively. The CaO content is relatively high, ranging from 15.1% to 17.16%. The sum of these four compounds also exceeds 95%, reflecting the fundamental information about the base material.

Micro structure of glazed tiles' glaze

Through the use of a high-depth-of-field microscope, the observations and records of the glaze layers of the four types of glazed ceramic tiles have

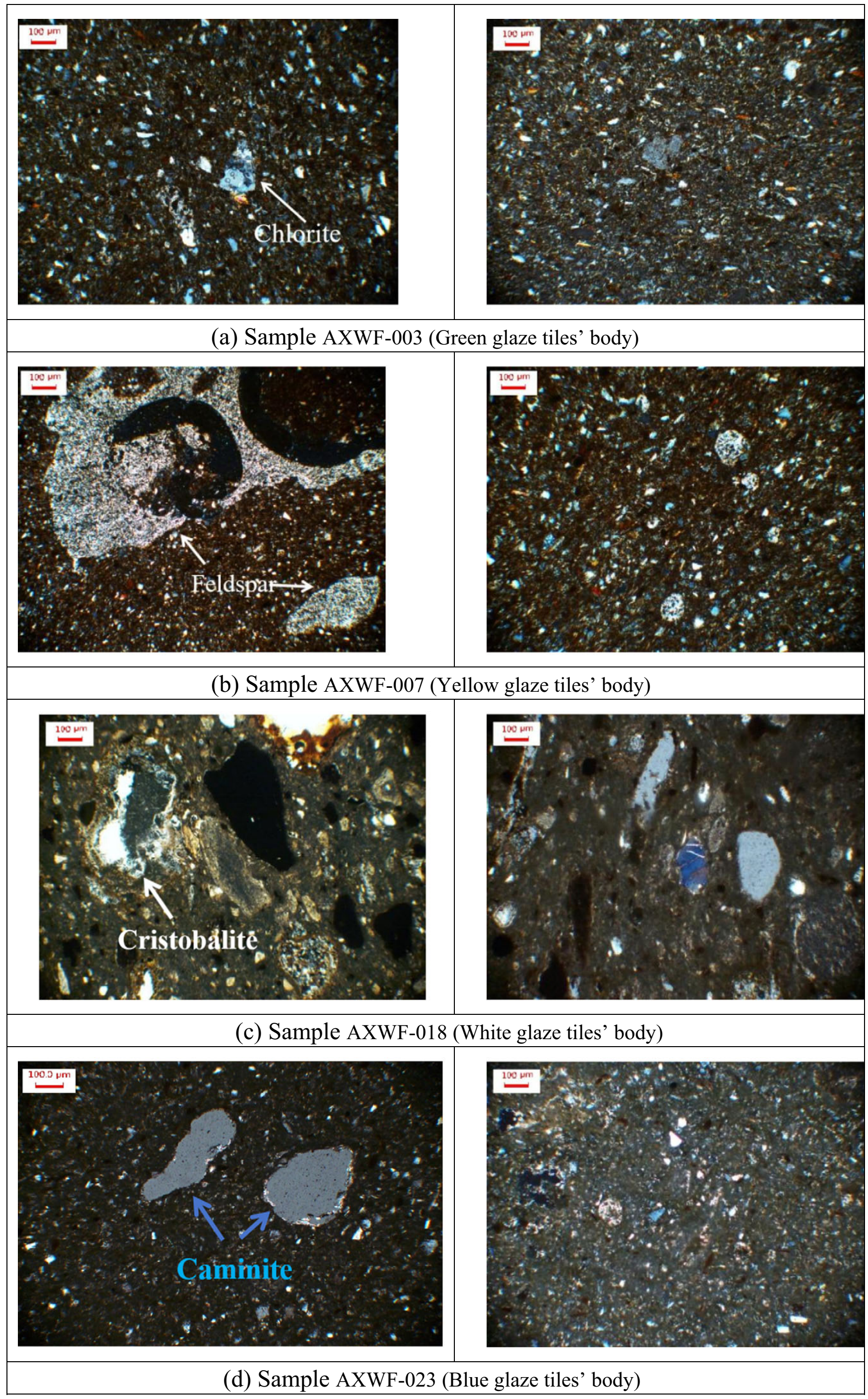


Fig. 3 | Petrological pictures of tiles' body materials with four different colored glazes which are used to study the mineral composition in glazed tiles a Chlorite is found in the typical green glazed tiles' body (scale bar is 100 µm). **b** Bright yellow glazed tile body contains a significant amount of feldspar (scale bar is 100 µm). **c** Cristobalite appears in pure white glazed tiles' body (scale bar is 100 µm). **d** Blue glazed tiles' body consists of caminite (scale bar is 100 µm).

revealed distinct differences and characteristics (Fig. 5.). However, a common trait among all of them is that they are dense and free from air bubbles.

In the case of green glazed tiles, the glaze layer thickness is about 130 µm. The glaze layer appears as a deep green color, displaying a glossy and dense surface. There is no a slip between the glaze and body. Yellow glazed tiles have a glaze layer thickness of roughly 160 µm. The glaze layer exhibits a yellow-brown color, with a glossy and dense surface. There is a layer of milky-white slip with a thickness of ~200 µm between the glaze and body. White glazed tiles possess a glaze layer thickness ranging from 250 to 300 µm. The glaze layer is smooth and even, with a milky-white color and a hint of gray. It is extremely dense and does not contain any slip. Blue glazed tiles have a glaze layer thickness rounds about 110 µm. The glaze layer appears as a deep blue color, with some signs of weathering. There is no slip present. All of the glaze layers exhibit a dense and glossy surface, indicating a high-quality finish.

Major chemical composition of glazed tiles' glaze

As mentioned before, the thickness of glazed tile's glaze layer is around 100–200 µm, according to Beer Lambert's law in the XRF test of ceramic artifacts[18], elements like those with higher mass fraction, such as Pb, Fe, etc., are tested to exceed the thickness of the glaze layer, and thus it is very likely to be tested to the data of the body. In order to verify the authenticity of the data, we added the EDS test on the glaze layer profile, taking the yellow glazed tile as an example, and the specific data are shown in Fig. S-1 and Table S-1 (attached in the Supplementary Data File), and the results show that the ratios of the major elements, such as Pb/Si, etc., are still within the

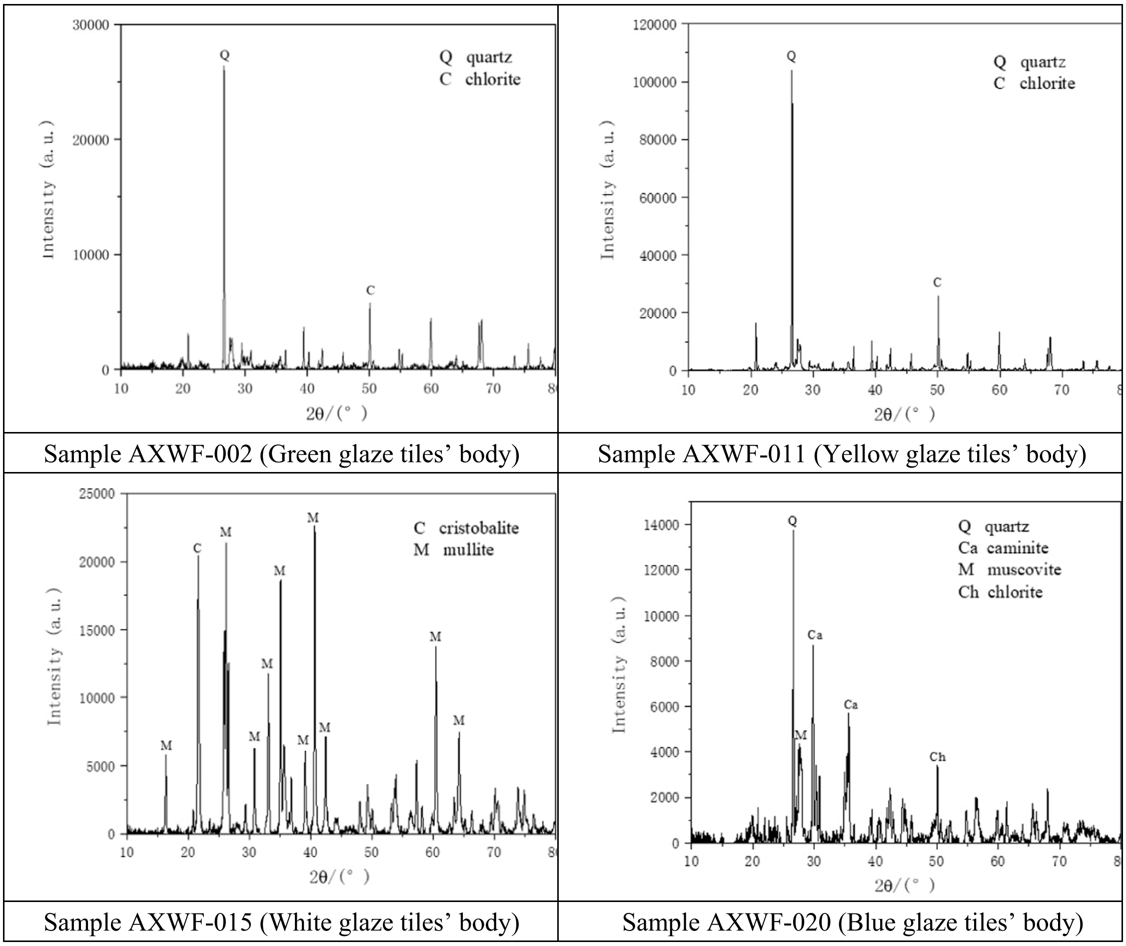


Fig. 4 | The XRD results of the glazed tiles' body.

range of the XRF test data, which have little effect on the following discussion. According to the composition of glaze layer in Table 2, SiO_2 and Al_2O_3 are the basic materials of glaze, K_2O, CaO and PbO may be used as fluxes, Fe_2O_3 and CuO as colorants.

In the chemical composition of green glaze, the content of SiO_2 is between 37% and 40%, the content of PbO is between 40% and 50%. In the chemical composition of yellow glaze, the content of SiO_2 is between 21% and 27%. The content of PbO is between 66% and 72%. The colorant is Fe_2O_3 with content between 2% and 4%, which is also in line with the Chinese traditional characteristics of low temperature lead glaze[19]. In the chemical composition of white glaze, there is no colorant, the content of SiO_2 is 66%–69%, Al_2O_3 is 11%–20%, CaO is 14%–16%. In the chemical composition of blue glaze, the content of SiO_2 is between 62%–68%, the content of PbO and Al_2O_3 is lower, between 6%–8% and 1.2%–3.7% respectively. In addition, the content of Na_2O is 1.5%–1.6% and K_2O is 9.5%–12.7%, the colorant should be CuO, the content is between 4% and 7%.

Discussion

Composition and technological characteristics of the tile bodies

The production of ceramic bodies forms the foundation for creating glazed tiles, and the general steps for making glazed tile bodies involve selecting clay raw materials, crushing and kneading, drying and shaping, and then firing[20]. The results of previous studies on mineralogy and diffraction revealed significant differences in the mineral composition of the tile bodies for the four colored glazed tiles.

Based on the understanding of the chemical composition of the tile bodies, a comparison was made with the composition data of glazed tile bodies unearthed from contemporaneous Yuan Dynasty sites[21], including Yuanshangdu (labeled YSD in Fig. 6), Yuandadu[22] (labeled YDD in Fig. 6), Yuanzhongdu (labeled YZD in Fig. 6), all the data are from green glazed tiles' body. And the prince Anxi's mansion's glazed tiles in four colors (labeled AXWF-B for blue, AXWF-G for green, AXWF-W for white, and AXWF-Y for yellow). Using principal component analysis, the chemical composition of the glazed tile bodies was reduced to three factors for comparison of the similarity in tile body composition from different regions, as shown in Fig. 6. Clearly, the seven different types of glazed tile bodies in the figure can be roughly grouped into five categories. The green and yellow glazed tiles from the prince Anxi's mansion form one group, while the glazed tiles from Yuanshangdu and Yuandadu form another group with similar chemical compositions. However, there are significant differences in the tile body composition between these groups and the white and blue glazed tiles from the prince Anxi's mansion.

The research results demonstrate that the production of glazed tile bodies at the prince Anxi's mansion utilized three different formulations, involving distinct criteria for raw material selection and grinding methods, which directly resulted in the observed color variations in the tile bodies.

Composition and technological characteristics of the glaze layer

Following the production of the ceramic body for glazed tiles, the next step involves preparing the glaze material and applying it to the surface of the ceramic body before firing. Under high-depth-of-field microscopy, it was observed that in samples like AXWF-002, a green glazed tile, and including samples like AXWF-011, a yellow glazed tile, there exists a layer of slip between the glaze and the body. The slip in the former is relatively thin, with a thickness much smaller than that of the glaze layer, while in the latter, the slip is thicker and similar in thickness to the yellow glaze layer. No slip is found in white and blue glazed tiles. Slip, also known as protective glaze, is applied between the body and glaze layers. It is a slurry made from specially

Table 1 | Chemical compositions of the bodies determined through XRF analyses (wt%)

Sample	Body Color	Glaze Color	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
AXWF-001	Red	Green	0.01	0.02	15.61	66.14	0.05	2.8	8.44	0.85	0.12	6.01
AXWF-002	Red	Green	0.04	0.01	15.08	64.31	0	2.5	11.14	0.76	0.12	6.05
AXWF-003	Red	Green	0.02	0.01	16.03	66.71	0.21	2.6	7.5	0.86	0.12	5.95
AXWF-004	Red	Green	0.01	0.01	15.34	65.76	0.13	2.9	9.25	0.79	0.1	5.76
AXWF-005	Red	Green	0.02	0.01	15.98	65.25	0.09	2.6	8.67	0.81	0.11	6.45
AXWF-006	Red	Green	0.2	0.07	15.64	65.46	0	2.7	10.76	0.78	0.12	4.53
AXWF-007	Red	Yellow	0.02	0.01	15.5	67.32	0.22	2.7	7.04	0.85	0.12	6.24
AXWF-008	Red	Yellow	0.01	0.02	15.28	68	0.05	2.9	6.69	0.74	0.11	6.28
AXWF-009	Red	Yellow	0.01	0.01	15.79	66.7	0.22	2.9	7.01	0.84	0.1	6.4
AXWF-010	Red	Yellow	0.01	0.01	15.43	66.75	0.15	2.8	7.67	0.77	0.13	6.28
AXWF-011	Red	Yellow	0.02	0.01	15.55	67.61	0.12	3	6.66	0.76	0.11	6.23
AXWF-012	Red	Yellow	0.01	0.01	15.5	68.36	0.1	2.8	6.36	0.8	0.11	6.01
AXWF-013	Brownish	White	0.01	0.01	35.32	54.62	0	1.3	1.49	1.75	0	5.53
AXWF-014	Brownish	White	0.01	0.01	34.04	53.96	0	1.2	1.54	1.74	0	7.7
AXWF-015	Brownish	White	0	0	34.99	55.67	0.11	1.3	1.52	1.72	0	4.73
AXWF-016	Brownish	White	0.01	0.01	33.38	54.23	0.08	1.2	2.13	1.68	0	7.27
AXWF-017	Brownish	White	0	0.02	34.32	55.65	0	1.3	1.65	1.69	0	5.41
AXWF-018	Brownish	White	0.01	0	33.11	54.81	0.07	1.4	2.2	1.66	0.02	6.71
AXWF-019	Gray	Blue	0.01	0.07	15.34	57.25	0	2.8	17.16	0.97	0.08	6.3
AXWF-020	Gray	Blue	0.02	0.01	15.37	58.54	0	2.8	16.48	0.78	0.08	6.01
AXWF-021	Gray	Blue	0.01	0.04	15.15	58.25	0	2.8	16.64	0.84	0.08	6.23
AXWF-022	Gray	Blue	0.01	0	14.97	60.28	0	2.9	15.1	0.81	0.08	5.88
AXWF-023	Gray	Blue	0.02	0.01	15.18	59	0	2.8	16.09	0.77	0.09	6.1
AXWF-024	Gray	Blue	0.01	0.01	15.16	59.28	0.04	2.6	16.14	0.86	0.09	5.87

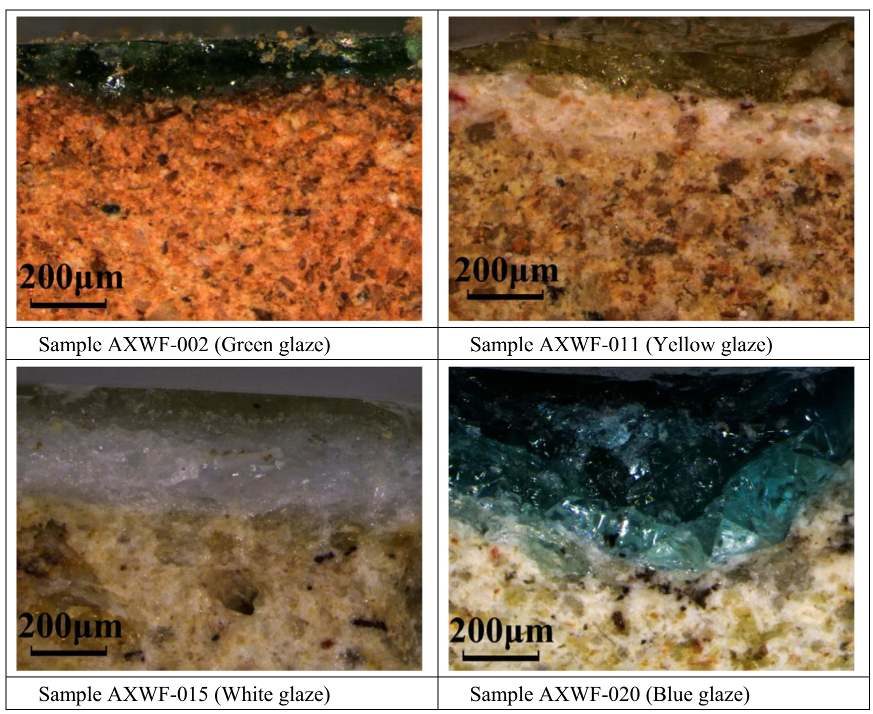


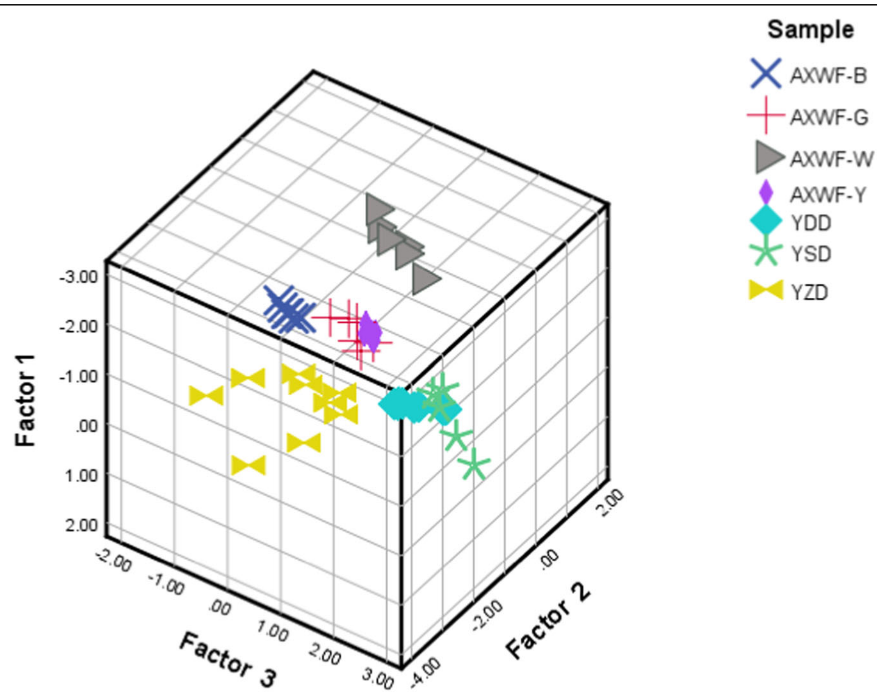
Fig. 5 | Microscopic observation the section of glazed tiles' glaze.

processed fine porcelain clay or selected raw materials to improve the quality of ceramic ware and enhance glaze coloration, the quality of the glaze was significantly improved by the use of make-up clay in glazed tiles[23]. Previous research has shown that green, yellow, and blue glazed tiles from Yuandadu[24], Yuanshangdu, and Yuanzhongdu all have slip[25]. This practice significantly improves the quality of glazed tiles, resulting in a smooth and glossy surface of the ceramic body for glaze painting. Undoubtedly, this represents an improvement and innovation. However, among the four

Table 2 | Chemical compositions of the glazes determined through XRF analyses (wt%)

Sample	Glaze Color	Body Color	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	CuO	SnO_2	PbO
AXWF-001	Green	Red	0.01	0.01	5.85	35.59	0	1.12	3.19	0.35	0.03	1.08	0.01	0.79	0.08	51.81
AXWF-002	Green	Red	0.01	0	5.52	36.71	0	1.06	3.96	0.28	0.03	1.31	0.02	0.65	0	50.35
AXWF-003	Green	Red	0	0.32	4.84	38.68	0	0.92	4.15	0.3	0.01	1.24	0.01	0.61	0.01	48.81
AXWF-004	Green	Red	0	0.4	6.38	36.65	0	0.88	4.63	0.38	0.02	1.45	0.01	0.71	0	48.49
AXWF-005	Green	Red	0.01	0.02	4.35	36.39	0	0.47	3.15	0.19	0.01	1.06	0.01	0.73	0	53.64
AXWF-006	Green	Red	0	0.01	6.35	40.47	0	1.04	3.72	0.24	0.02	1.47	0.01	0.66	0	45.88
AXWF-007	Yellow	Red	0	0.02	2.34	21.67	0	0.34	0.29	0.04	0.01	2.46	0.01	0.12	0.02	72.69
AXWF-008	Yellow	Red	0.02	0.2	2.05	21.71	0	0.26	0.29	0.11	0.02	2.39	0.01	0.12	0.28	72.78
AXWF-009	Yellow	Red	0	0.02	1.89	21.05	0	0.27	0.42	0.12	0.01	2.47	0.01	0.12	0	73.64
AXWF-010	Yellow	Red	0.03	0	1.71	23.82	0	0.41	0.93	0.1	0.01	3.37	0.01	0.11	0.25	69.26
AXWF-011	Yellow	Red	0.01	0	2.32	25.62	0	0.51	0.81	0.08	0.02	3.06	0.02	0.11	0	67.46
AXWF-012	Yellow	Red	0.02	0.01	1.85	26.88	0	0.42	1.05	0.08	0.01	2.92	0.01	0.11	0.01	66.65
AXWF-013	White	Brownish	0	0.02	12.33	67.35	0.65	2	15.6	0.12	0.1	1.5	0.01	0.01	0.29	0.03
AXWF-014	White	Brownish	0.01	0.01	12.01	67.42	0.54	2.11	15.77	0.13	0.1	1.55	0.01	0.02	0.3	0.05
AXWF-015	White	Brownish	0.02	0.01	12.34	67.78	0.67	2	15.44	0.12	0.1	1.5	0.01	0.01	0	0.04
AXWF-016	White	Brownish	0	0.01	19.16	64.66	0.42	1.97	9.85	0.64	0.06	2.94	0.01	0.01	0.24	0.04
AXWF-017	White	Brownish	0	0.01	11.81	68.02	0.64	2.05	15.38	0.1	0.11	1.56	0	0.01	0.27	0.04
AXWF-018	White	Brownish	0	0.01	12	67.99	0.67	1.88	15.42	0.13	0.1	1.44	0.01	0.02	0.3	0.04
AXWF-019	Blue	Gray	1.56	0	3.82	63.46	0	9.47	5.28	0.21	0.02	2.23	0.02	4.69	3.07	6.19
AXWF-020	Blue	Gray	1.65	0.01	0.97	66.42	0	11.08	2.59	0.06	0.01	0.64	0.01	5.34	3.51	7.71
AXWF-021	Blue	Gray	1.67	0.01	1.14	67.38	0	11.12	2.47	0.06	0.02	0.95	0.01	4.66	3.57	6.95
AXWF-022	Blue	Gray	1.54	0.02	2.58	62.2	0.05	12.74	2.49	0.06	0.02	0.88	0.01	6.15	4.09	8.73
AXWF-023	Blue	Gray	1.57	0	2.3	63.88	0.02	10.36	4.56	0.13	0.02	1.37	0.01	5.15	3.17	7.45
AXWF-024	Blue	Gray	1.49	0.01	2.07	66.5	0.09	11.19	2.88	0.1	0.02	1.09	0	4.88	3.75	7.44

Fig. 6 | Principal component analysis comparison chart of glazed tile body.



glazed tile colors discovered at the prince Anxi's mansion, there are significant differences in the glaze production of green and yellow glazed tiles compared to that of white and blue glazed tiles, indicating a more mature production process for green and yellow glazed tiles.

Preparing the glaze material is a crucial step in creating the glaze layer, and its process is further analyzed through chemical composition. First, regarding the green and yellow glazed tiles from the prince Anxi's mansion, the test results indicate that both belong to the lead glaze formulation

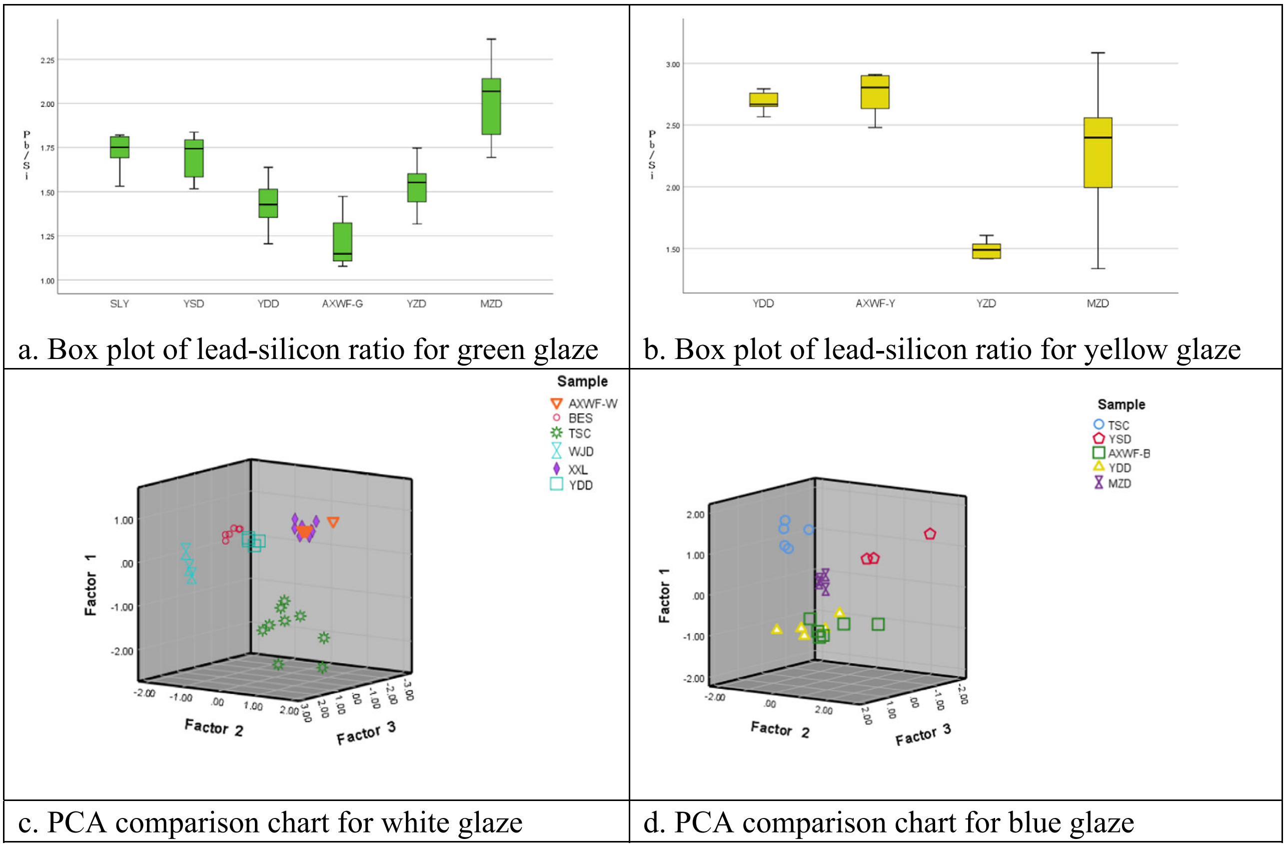


Fig. 7 | The lead-silicon ratio and Principal Component Analysis (PCA) comparison charts for tiles with different colored glazes. a A box plot of the lead-silicon ratio for green glaze, showing the distribution of the lead-silicon ratio across different samples. **b** A box plot of the lead-silicon ratio for yellow glaze, displaying the variation in the lead-silicon ratio for yellow glazed samples. **c** A PCA comparison chart for white glaze, used to analyze the compositional differences among white glazed samples. **d** A PCA comparison chart for blue glaze, illustrating the compositional distribution of blue glazed samples.

system. The sum of the basic substances SiO_2 and flux PbO in the glaze is above 75% and 85%, respectively, directly determining the main formulation of the glaze. Therefore, the lead-silicon ratio is an important value for comparing the glaze formulations of glazed tiles. Building upon the existing data, box plots were generated to compare the datasets, resulting in the four diagrams presented in Fig. 7. Figure 7a illustrates the trend in the lead-silica ratio of green glazed tiles from the same period, while Fig. 7b demonstrates the variation in the lead-silica ratio of yellow glazed tiles. Comparing the lead-silicon ratio values of the green and yellow glazes from the prince Anxi's mansion with that from contemporaneous Yuan Dynasty capital cities, the Northern Song Dynasty's Luoyang City[26] (labeled SLY in Fig. 7a) and the Ming Dynasty capital city[27] (labeled MZD in Fig. 7a, b), result provides insight into the proportion of their main materials. These two capitals were built in 960 AD and 1369, the construction of the prince Anxi's mansion in the time frame of the two, can be analyzed by comparing the production of glazed tiles in the Yuan Dynasty glazed glaze production whether to carry on the past and the glaze ratio of the changes. As seen in Fig. 7a, the lead-silicon ratio of the prince Anxi's mansion's green glaze samples ranges between 1 and 1.25, similar to the Yuandadu samples, both falling within the 1 to 1.5 range and lower than the data from the other four city sites. For yellow glazed tiles, the data from the prince Anxi's mansion is shown in Fig. 7b, with the lead-silicon ratio ranging between 2.5 and 3, similar to the Yuandadu samples and higher than the data from the other two city sites. Yuandadu was founded in 1267 AD, and the prince Anxi's mansion was established in 1272 AD, suggesting that the two constructures were built around the same time. Based on this, it can be inferred that the technology for firing glazed tiles was relatively stable.

Figure 7c presents a Principal Component Analysis (PCA) comparison of the glaze layer compositions of white glazed tiles with similar components. The composition system of white glaze on architectural ceramics is not yet clear because it is rare in Chinese ceramic history, currently only found in the Wenjiangduo site from the Tubo period[28], the Xixia mausoleum site[29], and the Yuandadu site[30]. To clarify the formulation system of the white glaze from the prince Anxi's mansion, principal component analysis was used to compare it with the white glazed tiles from the Wenjiangduo site[31] (labeled WJD in Fig. 7c), white-glazed Tang Dynasty three-color wares[32](labeled TSC in Fig. 7c), white-glazed tiles from the Xixia mausoleum site[33] (labeled XXL in Fig. 7c), white-glazed porcelain from Yuandadu[34] (labeled YDD in Fig. 7c), and white glazed tiles from the Baoensi Temple site in Ming Dynasty from Nanjing[35] (labeled BES in Fig. 7c). The results, as shown in Fig. 7c, reveal a high similarity between the composition of the white glaze from the prince Anxi's mansion and the white porcelain from the Xixia mausoleum site, both belonging to the high-temperature calcium glaze system and differing significantly from other white-glazed items. The Xixia mausoleum site is located in Yinchuan City, Ningxia Hui Autonomous Region, less than 350 km from Guyuan City where the prince Anxi's mansion is situated. The Xixia mausoleum was built for the burial of the emperors in XiXia period (1038–1227 AD), a large number of glazed tiles were found during the excavation of the site, including green-glazed and white-glazed glazed tiles, which provided important information for the study of the glazed tile production technology in the Song and Yuan dynasties and the interaction of technology in different regions. During the Yuan Dynasty, both sites fell under the governance of prince Anxi, suggesting that the political organization managed by prince Anxi in the adjacent region likely gathered craftsmen and adopted the technology of white glazed tiles from the Xixia period.

Lastly, for the blue glaze, principal component analysis was similarly used to compare the technological systems of blue glazed tiles from the

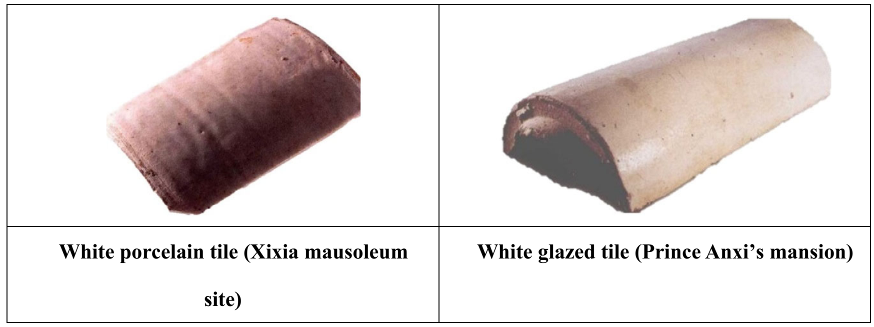


Fig. 8 | White glazed tiles in Xixia and Yuan periods.

Fig. 9 | Blue glazed pottery and tile in Jin and Yuan periods.

prince Anxi's mansion with Tang Dynasty three-color blue-glazed wares, and glazed tiles with turquoise blue glaze from Yuandadu, Yuanshangdu, and Mingzhongdu. While Fig. 7d illustrates a Principal Component Analysis (PCA) comparison of the glaze layer compositions of blue glazed tiles with similar components. Compared to the blue-glazed Tang Dynasty three-color wares with higher lead content, the blue glaze samples from the prince Anxi's mansion, Yuanshangdu, Yuandadu, and Ming zhongdu all belong to the $PbO\text{-}K_2O\text{-}SiO_2$ system (Fig. 7d). However, the turquoise blue glaze technique originated in the Islamic regions of West Asia, and after its introduction to China during the Tang Dynasty[36], it was improved during the Jin and Yuan periods[37]. Nonetheless, regional variations in formulations exist, with the Yuanshangdu turquoise blue glaze having a higher CaO content, resembling the intentional introduction of raw materials such as calcium feldspar or high-calcium fusible clay. The high similarity between the data from the prince Anxi's mansion and Yuandadu suggests that the two sites employed similar production formulations, likely due to their proximity in construction times.

Reasons for technological integration and innovation

Through a comparative analysis of the composition of the ceramic body and glaze of glazed tiles from the prince Anxi's mansion, it is evident that both the production techniques and technological systems for the ceramic body and glaze can classify the four colors of glazed tiles into three categories. The first category belongs to the lead glaze system, represented by the green and yellow glazed tiles, with production techniques similar to those of Yuandadu. The second category is the white glaze, and its chemical composition classifies it as a calcium glaze, highly similar to the white glazed tiles from Xixia mausoleum site. The third category is the blue glaze, more precisely referred to as turquoise blue glaze, with production techniques closely associated with Yuandadu.

It can be stated that the richness of colored glazed tiles in the prince Anxi's mansion is attributed to the thorough blending of ceramic production techniques from different regions. This also showcases technological innovation, particularly in the white and blue glazes. The white glaze, which is a member of the calcium glaze chemical composition, is quite similar to the white glazed tiles that were discovered during the excavation of the Xixia Mausoleum. An example of government architecture from the Xixia period is the Xixia Mausoleum site. It is situated in the western suburb of Yinchuan City, Ningxia Hui Autonomous Region, at the eastern base of Helan Mountain. Numerous architectural elements, mostly white porcelain tiles and different green glazed tiles, that represent the traits of official architecture have been discovered as a result of archaeological research and excavations. Among them, the white porcelain tiles are the most unique, being the only ones with white glaze, most likely used for architectural walls, as shown in the Fig. 8 below. According to scientific archaeological research, the production technology of the white porcelain tiles of the Western Xia royal tombs came from Lingwu kiln in Ningxia. After the conquest of Xixia by the Mongol and Yuan regimes, Kublai appointed Prince Anxi to rule over the conquered areas of Xixia (1227 AD) and applied the technique of white-glazed porcelain production to tiles and other types of tiles. This was a technological innovation.

The turquoise blue glaze, more precisely termed, originated in the Islamic regions of West Asia and was introduced to China during the Tang Dynasty. It underwent significant improvements during the Jin and Yuan periods, with its production technique closely associated with Dadu, the capital of the Yuan Dynasty. Despite its widespread popularity during the Jin Dynasty, the blue glaze was only used on a large scale for the production of colored glazed tiles (as shown in the following Fig. 9) in the Yuan Dynasty. Additionally, utilizing ceramic technology to produce glazed tiles represented an innovative approach. Therefore, whether it is the white or blue glaze, both adopted the production techniques of pottery and porcelain, which constituted a technological innovation in the production of glazed tiles by the Anxi Wangfu during the Yuan Dynasty. Different craftsmen created various types of glazed bricks with different colors. This marked a significant reform in the production system of glazed tiles, enabling craftsmen from different regions to engage in their production. Furthermore, the manufacturing process of these four types of glazes also integrated techniques from various regions.

The dissemination of technology relies on people, with craftsmen dedicated to the production of glazed bricks and tiles being the carriers. Glazed bricks and tiles have always been in high demand, traditionally produced using locally sourced clay. Considering the discovery of glazed tiles in three different colors, although all used for palace construction, it is evident that there were three different selection criteria and processing methods. Based on this, it is inferred that at least three groups of craftsmen, each with expertise in different ceramic technologies, were involved in the production of glazed tiles. Technology disseminates across regions through the migration of craftsmen, which is influenced by the management system in place. The reform of the craftsman management system during the Yuan Dynasty facilitated the mobilization of craftsmen from various regions, allowing them to master diverse technologies and engage in simultaneous production. This ultimately culminated in the creation of the intricate architectural design characterized by colorful glazed tile roofs. The complexity in the source of craftsmen and the reform of the craftsman management system contributed to the diversity in technology, which are the two major reasons for the innovation in glazed tile technology during the Yuan Dynasty.

Situated in the northwest, not having a geographical advantage, how did the prince Anxi gather craftsmen from diverse sources? According to historical records, starting from "Genghis Khan's later years, when he campaigned against the Xixia, he established a summer camp in the mountains to escape the heat." After undergoing the campaigns and garrisoning by Mongke Khan and Kublai Khan, the Guyuan region had become the political and military center at that time, with a vast jurisdiction extending to the northwest border of the Yuan Dynasty. After the establishment of the Yuan Dynasty by Kublai Khan, Mangora, as the son of Kublai Khan, was in charge of this region. The population composition was very complex, mainly consisting of various Central Asian ethnic groups, collectively referred to as "Semu" people. According to the records of Tao Zongyi's "Nancun Chuogeng Lu", there were more than 30 ethnic groups called Semu people, such as the Hui, Uighurs, and Khitans. These conquered ethnic groups had diverse religious beliefs, including followers of Buddhism, Islam, and Nestorianism (a term used by the Yuan Dynasty for Christians of various denominations). According to the records of Rashid al-Din's "Jami' al-Tawarikh", the residents in the Hexi region under the jurisdiction of prince Anxi were mostly "Musuman" - a term used by the Yuan Dynasty for Muslims[38]. In areas conquered, it was a common practice for nomadic tribes to raid craftsmen and engage in technical production, thus inadvertently promoting the exchange and integration of technology.

Furthermore, after Mangora was conferred the title of prince Anxi, a palace was also established in the Jingzhao Mansion in Xi'an, with the purpose of "both capitals coexisting, residing in Jingzhao during winter, and relocating to Liupan during summer." The establishment of the two prince Anxi's mansions is actually a microcosm of the dual capital system of Yuandadu and Yuanshangdu. This explains why the use of glazed tiles with four colors is exclusive to the prince Anxi's mansion and Yuandadu. In reality, behind the fusion and innovation of glazed tile technology, it is an imitation of the construction system of the Yuan Dynasty capital cities by the prince Anxi's mansion.

Conclusion

The research through microscopic observation and chemical composition analysis reveals the following findings: the composition of the ceramic body of green and yellow glazed tiles is similar, primarily consisting of quartz and mica, with finely crushed impurities, and the glaze system belongs to the lead glaze category, showing a high similarity to the green and yellow glazed tiles from Yuandadu. The mineral composition of the ceramic body of white glazed tiles is mainly quartz and corundum, and the glaze formula belongs to the calcium glaze system, likely originating from the technology of Xixia. The ceramic body of blue glazed tiles is composed of high-calcium minerals, and the glaze formula is similar to the turquoise blue glaze popular during the Jin and Yuan periods, representing a Chinese craftsmen's improvement on Islamic ceramic technology, with a high similarity to the turquoise blue glaze from Yuandadu. Therefore, the production technology of glazed tiles in the prince Anxi's mansion include three systems, with craftsmen employing different production techniques, contributing to a diverse source. Beside inheriting the technological expertise from the capital regions, craftsmen in the prince Anxi's mansion could also incorporate local production techniques, promoting technological integration and innovation in the use of glazed tiles.

Combining the historical literature, the complexity in the source of craftsmen is attributed to the extensive jurisdiction of prince Anxi and significant differences in population composition. The management system of the Yuan Dynasty for tile craftsmen played an irreplaceable role in facilitating collaboration among artisans from various regions. This system encouraged craftsmen to converge at the prince Anxi's mansion, where they worked together to produce colorful glazed tiles. Based on these factors, prince Anxi learned from the construction system of the Yuan Dynasty capital cities, indirectly facilitating the innovation of glazed tile technology. This paper analyzes the reasons for the different colors and textures of glazed tiles in the prince Anxi's mansion during the Yuan Dynasty from the perspective of archaeometry and discusses the contributing factors through historical literature. This provides a new perspective and method for the study of the political system and construction technology of the Yuan Dynasty.

Data availability

No datasets were generated or analysed during the current study.

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References

1. Xu, Y. et al. Reconstructing the earliest known composite-tiled roofs from the Chinese Loess Plateau. *Sci. Rep.* **13**, 8163 (2023).
2. Pang, T. Some Chinese glazed tiles of the 6th Century. Oriental Art, 61–68 (1999).
3. Meng, T. H., Du, R. Q., Hou, Z., Yang, J. & Zhao, G. Z. THz spectra-based SVM prediction model for Yungang Grottoes samples. *J. Archaeol. Sci.* **55**, 280–285 (2015).
4. Guo, M. & Shen, Y. Interpretation of appropriate places: state ceremonies and the imperial main halls of the Tang and Song dynasties. *Fronti. Archit. Res.* **11**, 1007–1029 (2022).
5. Hou, W. D., Wang, W. & Yan, X. The protection project of Hanyuan Hall and Linde Hall of the Daming Palace. *Front. Archit. Res.* **1**, 69–76 (2012).
6. Hou, J. Y. et al. The origins of imperial yellow glazed porcelain in the Ming Dynasty (1,368 to 1,644) China: technical comparison to low-fired tile with yellow glaze. *Archaeometry* **64**, 59–70 (2022).
7. Shen, J. et al. Architectural glazed tiles used in ancient chinese screen walls (15th–18th century AD): ceramic technology, decay process and conservation[J]. *Materials* **14**, 7146 (2021).
8. Ding, C. Agricultural and pastoral conflicts in the Yuan dynasty metropolitan area and the system of two capitals patrol. *J. Tsinghua Univ.* **26**, 94–106 (2011).
9. Chen, G. H. The rise and fall of Yuan Zhongdu[J]. *Cult. Relics Spring Autumn* **03**, 20–23 (1998).
10. Ma, D. Z. Record of the survey of the Anxi royal residence of the Yuan dynasty in Xi'an. *Archaeol.* **05**, 20–26 (1960).
11. Ma, D. H. & Cheng, Y. X. Investigation brief on the architectural site of the Yuan Dynasty Anxi Wangfu in Kaicheng, Guyuan, Ningxia. *J. Chin. History Museum* **01**, 110–127 (2000).
12. Shi, R. Y. Research on the characteristics and origin of architectural glazing process in the Yuan Dynasty capital city. *Northwest Univ*. **3**, 56–60 (2022).
13. Wen, R. et al. The compositional characterization and painting technique of Chinese red and white porcelain by EDXRF and SR-μXRF mapping analysis. *Analyt. Methods* **9**, 4380–4386 (2017).
14. Montana, G. Ceramic raw materials: how to recognize them and locate the supply basins—mineralogy, petrography. *Archaeol. Anthropol. Sci.* **12**, 175 (2020).
15. Pei, D., Li, Y. & Cang, D. In situ XRD study on sintering mechanism of SiO2-Al2O3-CaO-MgO ceramics from red mud. *Mater. Lett.* **240**, 229–232 (2019).
16. Aras, A. & Kristaly, F. α-Cristobalite formation in ceramic tile and sewage pipe bodies derived from Westerwald ball clay and its effect on elastic-properties[J]. *Appl. Clay Sci.* **178**, 105126 (2019).

17. Lee, W. E. & Iqbal, Y. Influence of mixing on mullite formation in porcelain[J]. *J. Eur. Cer. Soc.* **21**, 2583–2586 (2001).
18. Colomban, P., Simsek Franci, G., Gerken, M., Gironda, M. & Mesqui, V. Non-Invasive On-Site XRF and Raman classification and dating of ancient ceramics: application to 18th and 19th Century Meissen Porcelain (Saxony) and Comparison with Chinese Porcelain. *Ceramics* **6**, 2178–2212 (2023).
19. Yin, X. S., Huang, T. J. & Gong, H. Chemical evolution of lead in ancient artifacts -A case study of early Chinese lead-silicate glaze. *J. Eur. Cer. Soc.* **40**, 2222–2228 (2020).
20. Guo, Q. Tile and Brick Making in China: a Study of the" Yingzao Fashi". *Construction History* **16**, 3–11 (2000).
21. Wen, R. et al. Detection and analysis of glazed tile body excavated from Yuan Shangdu and Yuan Zhongdu site. *J. Palace Museum.* **4**, 95–103 (2021).
22. Miao, J. M. & Wang, S. W. Research on Yuan, Ming and Qing Architectural Glazed Tiles. In *Proc. 2005 International Symposium on Ancient Ceramic Science and Technology,* (Science Press, 2005).
23. Wu, Y. C. et al. Influence of make-up clay on glaze quality of glazed components from Huaiwangfu. *Poyang. J. Cer.* **38**, 415–420 (2017).
24. Li, Y. & Miao, J. M. Preliminary study of the Yuan dynasty architectural glaze slip process. China Heritage Protection Technology Association. In *Proc. seventh annual conference of the Chinese heritage conservation technology association* (Science Press, 2012).
25. Shi, R. Y. et al. X-Ray fluorescence spectroscopy combined with SEM-EDS analysis to glaze composition of glazed tiles in Yuan Dynasty. *Spectrosc. Spectral Anal.* **41**, 3808–3814 (2021).
26. Li, J. Z. Research on Chinese ancient ceramics Vol. 2, 35–36 (Science Press, 1987).
27. Yang, G. M. et al. Process analysis of glazed tile glaze excavated from the Ming Zhongdu site in Fengyang. *Chin. Cer.* **54**, 66–73 (2018).
28. Zhang, B., Xi, L. & Zhang, N. Brief report on the excavation of the Wenjiangduo site in Qushui, Tibet from 2021 to 2022. *Archaeol. Cult. Relics*. **04**, 14–30 (2024).
29. Y, J. Excavation Brief on the Site of No.3 Mausoleum of Xixia in Yinchuan City, Ningxia. *Archaeology.* **08***,* 25–40 (2002).
30. Li, Z. Y. A preliminary study of the ceramics excavated from the underground of the Yuan Dynasty Palace of the Forbidden City. *Chin. Museum of History.* **01**, 73–78 (1986).
31. Shi, R. Y. et al. Research on the composition and process of glazed tiles from the Wenjiangduo site in Qushui. *Tibet. Archaeol. Antiquities.* **4**, 111–120 (2024).
32. Chang, D. et al. Characterizing the chemical composition of Tang Sancai wares from five Tang dynasty kiln sites. *Ceram. Int.* **46**, 4778–4785 (2020).
33. Shi, R. Y. et al. Study on the technology of architectural porcelain and glaze tiles unearthed from Xixia mausoleum site. *Conserv. Archaeol. Scie.* **6**, 37–46 (2021).
34. Zhao, G. L. Several ancient glazed kiln sites discovered in Beijing in recent years. *Archaeol.* **07**, 628–631 (1986).
35. Tang, X. M. et al. Classification and compositional analysis of glazed building materials excavated from the Dajianen Temple in Nanjing. *J. Palace Museum.* **08**, 101–110 (2022).
36. Lane, A. Early Islamic Pottery. Mesopotamia, Egypt and Persia. *Faber Faber* **1**, 18–23 (1947).
37. Feng, M. The technical origin of peacock-blue glaze. *Zhongyuan Cult. Relics*. **01**, 124–130 (2020).
38. Xu C. Observation on the Development and Spread of Islam and Muslim in China under Tang, Song, and Yuan Dynasties (618-1368): a Chinese View. George Washington University. Vol. 5, 116–118 (2021).

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Author contributions

R.W. designed research; R.S. performed research; Q.M. contributed the samples and the excavation information; R.S., and W.W. analyzed data; R.S. wrote the paper. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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