

<https://doi.org/10.1038/s40494-025-02262-0>

Non-destructive analysis reveals provenance and techniques of glassware excavated from the Jiu Jian site in China

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This study investigates the provenance and manufacturing process of glassware excavated from the Jiu Jian Site in Heilongjiang Province, China, dating to the Liao and Jin Dynasties (A.D. 907–1234), using multiple non-destructive analytical techniques including XRD, LRS, PIXE and SEM-EDS. The results categorize the glassware into three distinct systems: K_2O - CaO - SiO_2 , K_2O - CaO - PbO - SiO_2 , and K_2O - PbO - SiO_2 . The composition was consistent with indigenous Chinese glass systems, distinguishing them from contemporary Islamic glassware. The blue glassware was mainly coloured by Cu^{2+} , with some samples incorporating fluorite (CaF_2) as an opacifier. During the firing and cooling processes, CaF_2 crystals precipitate and accumulate within the glass matrix, causing light scattering and thereby producing an opacifying effect. This study has expanded the understanding of ancient glassware research by overcoming single-method limitations, confirmed the early application of fluorite opacification technology, and perfected the technological lineage of indigenous glassware production in China during the Liao and Jin Dynasties.

As a complex carrier of the integration of technology and art in early civilizations, the technological characteristics of ancient glassware profoundly reflect the technological choices and interactions of different civilizations. From the low-temperature sintering technology of faience in Mesopotamia to the unique lead-barium glass formula system (PbO - BaO - SiO_2) created during the Warring States Period in China^{1,2}, the regional differences in the composition of glass reveal the diversity of raw material acquisition and technological traditions. Meanwhile, the widespread distribution of glassware artifacts along the Silk Road also serves as crucial physical evidence for cross-regional technological exchange and the reconstruction of historical trade networks³. Particularly in ancient China, glassware has long embodied the dual characteristics of “jade imitation” aesthetics and the localized adaptation of foreign technologies^{4,5}, making its study irreplaceable in understanding the integration of Eastern and Western material civilizations. Therefore, glassware recovered through archaeological excavations has consistently been regarded as a valuable resource by researchers. However, in comparison with large-scale archaeological remains such as bronze wares and ceramics, the excavation of ancient glassware reveals a notable imbalance in both temporal distribution and spatial coverage. In terms of geographical distribution, the glassware remains within China is predominantly concentrated in key regions along

the Land and Sea Silk Road, such as Xinjiang, Guangdong and Guangxi^{6–8}. In inland areas, apart from rare examples occasionally found in noble tombs, complete glass vessels are seldom unearthed at ordinary archaeological sites. Regarding the chronological distribution, although a technological peak in local glassware production occurred from the Warring States Period to the Han Dynasty, the total number of surviving artifacts remains significantly lower compared to other material types from the same period. This state of “scarcity” endows each ancient glassware specimen with exceptionally high informational value. Consequently, destructive analytical methods (e.g., ICP-AES) are typically avoided in their analysis. However, this constraint simultaneously limits the advancement of in-depth research on ancient glass to some extent.

Against this background, the 2019–2022 excavation at Jiu Jian site in Heilongjiang Province, China, holds particular significance. It revealed a large settlement dating to the Liao and Jin dynasties (A.D. 907–1234). The site unearthed diverse artifacts, including abundant pottery and iron objects (primarily utilitarian items) alongside smaller quantities of glassware artifacts (predominantly ornamental pieces)^{9,10}. Critically, the recovered glassware artifacts provide valuable material evidence for investigating the composition and manufacturing techniques of ancient glassware during the Liao and Jin period in China.

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Fig. 1 | Map of the Jiujian Site. The geographical location of the Jiujian Site during the Liao and Jin Dynasties, marked with a red spot.

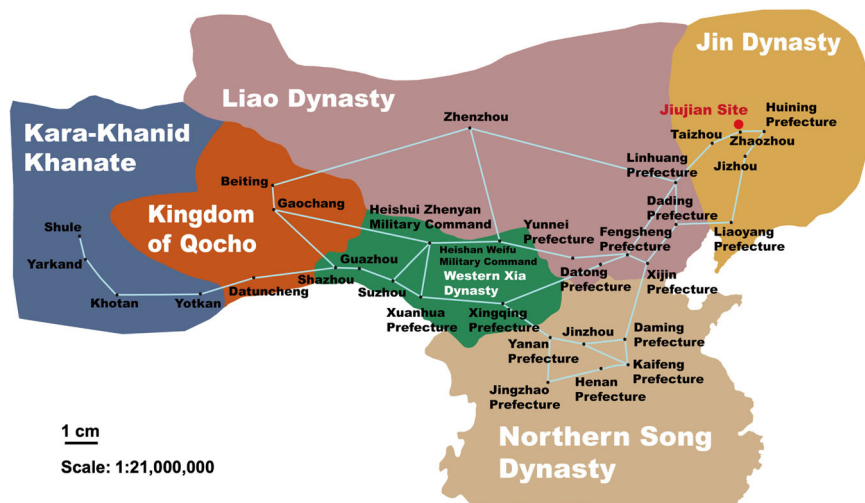


Table 1 | Introduction of Selected Ancient Chinese Glasses from Jiujian Site

No.	Shape and type	Colour	Date and Unearthed Site
JJ-01	Irregular ellipse-shaped, clothing decorations	Transparent blue with white coagulation	
JJ-02	Columnar and slightly curving, fragments of earrings	Opaque light blue with matte texture	
JJ-03	Globular fragments of earrings	Opaque light blue with certain glossiness	The period of Liao and Jin Dynasties
JJ-04	Flattened with one side pointed-shaped, clothing decorations	Opaque white with surface abrasions	Unearthed from ash pit for life uses at Jiujian Site, Heilongjiang Province
JJ-05	Flower-shaped, clothing decorations	Opaque creamy white	
JJ-06	Flower-shaped, clothing decorations	Opaque white and slightly yellowish	
JJ-07	Prolate stripe-shaped, a broken segment of a hair clasp	Transparent blue within numerous of tiny bubbles	

At present, the research on ancient Chinese glassware is confronted with dual challenges. On the one hand, the majority of studies focus on ancient glassware dating from the Western Zhou Dynasty to the Han Dynasty, while studies from the Song Dynasty (A.D. 960–1279) and later periods remain relatively limited. On the other hand, although non-destructive testing techniques such as Proton induced X-ray emission (PIXE) and X-ray diffraction (XRD) have been widely applied in the study of ancient glassware^{11,12}, due to the destructive nature of traditional testing methods, the investigation of critical technical features such as glassware microstructure still faces certain limitations. Therefore, this study focuses on the glassware excavated from the Jiujian Site, which dates to the Liao and Jin Dynasties, serving as a crucial point for in-depth analysis. A multi-method non-destructive analytical approach was employed, incorporating techniques such as laser Raman spectroscopy (LRS), XRD, PIXE, and low-vacuum scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDS), to investigate the structural characteristics and compositional systems of the excavated artifacts. Especially the measurement of chemical composition plays a significant role in determining the origin of the glassware from the Jiujian Site.

The history of glassmaking in ancient Western Asia and Egypt (16–17th century B.C.) predates that of China by a significant margin. These early glasses had relatively simple composition, primarily belonging to the sodium calcium silicate (Na₂O-CaO-SiO₂) glass system^{13–15}. This compositional classification extends to later glassware types such as Roman, Sasanian, and Islamic glassware, all of which fall within the Na₂O-CaO-SiO₂ system, typically containing more than 10% Na₂O, with some samples reaching up to 20%^{16–19}. During the Spring and Autumn Period, the Warring States Period, and the Han Dynasty in China (770 B.C.–A.D. 220), in addition to Na₂O-CaO-SiO₂ glassware, other glassware systems such as

K₂O-CaO-SiO₂, PbO-BaO-SiO₂, or K₂O-SiO₂ were also present, reflecting a significant diversity of chemical composition²⁰. After the Qin and Han Dynasties (221 B.C.–A.D. 220), the Silk Road across the northern grasslands of China came under the control of ethnic groups such as the Xiongnu, Xianbei, Turks and Khitans, and was not unobstructed during the early period. However, following the Northern Song Dynasty, the Liao and Jin Dynasties facilitated the opening of an east-west passage. Consequently, trade and cultural exchanges between Central Asia, West Asia, and north-eastern China could be carried out through the Northern Grassland Silk Road. Therefore, a considerable number of Islamic glassware artifacts from the Liao and Jin periods have been unearthed in Northeast China^{21,22}. For instance, the well-known glassware excavated from the tomb of princess of the State of Chen (A.D. 1000–1018) also belongs to the Na₂O-CaO-SiO₂ system²². Hence, it is essential to analyze the chemical composition to investigate the origin of the glassware artifacts unearthed at the Jiujian Site. Meanwhile, the Jiujian Site is located at a crucial node in the network of technological, material and cultural exchanges across the Eurasia continent⁹ as shown in Fig. 1. Therefore, this research not only contributes to the integrity of the technological lineage of ancient glassware, but also utilizes the Jiujian Site as a point to offer a scientific and technological perspective on the multi-integrated development process of frontier civilization of China.

Methods Samples

The glassware unearthed from the Jiujian Site is presented in Table 1 and Fig. 2. The sample was provided by the Heilongjiang Provincial Archaeology and Cultural Relics Institute. We have engaged in detailed discussions with specialists in ancient glassware studies and proposed preliminary classifications for the potential types of the samples, as summarized in Table 1.

Experimental methods

Before the test, the samples were wiped with anhydrous ethanol and ultrasonically cleaned in deionized water to remove surface contaminants. Phase identification was conducted using XRD (Bruker D8 Advance, Germany) equipped with a Cu source and an EIGER2 R 250 K detector. Measurements were performed at 40 kV and 40 mA over a 2θ range of 10–80°, with a sampling time of 420 s. Qualitative analysis of phase structures at specific points was performed using LRS (Renishaw inVia, UK). The system, equipped with a pinhole confocal microscope and a 50–200 X objective lens, was operated with a 532 nm laser (50 mW power, spectral resolution $\leq 1 \text{ cm}^{-1}$) and an acquisition time of 300 s. Under the low-vacuum mode, the microstructure of the samples was observed and analyzed using SEM-EDS (Thermo Fisher Quattro S, USA) in the backscattered electron (BSE) mode. The charges on the sample surface were directly neutralized under low-vacuum conditions without the need for platinum spraying, thereby avoiding any damage to the sample. For SEM, a Schottky thermal field emission source, with an acceleration voltage of 30 kV and an electron beam resolution of 2.5 nm (BSE), was utilized. EDS was employed in combination for micro-area composition analysis, and the energy resolution was better than 127 eV. The elemental composition of the different samples was analyzed non-invasively using PIXE in the atmospheric environment

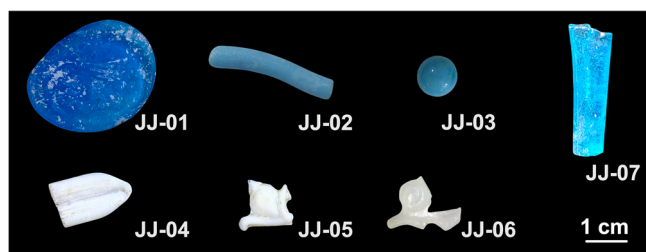


Fig. 2 | Figures of selected samples. The morphology and appearance of the glassware unearthed at the Jiujiang Site.

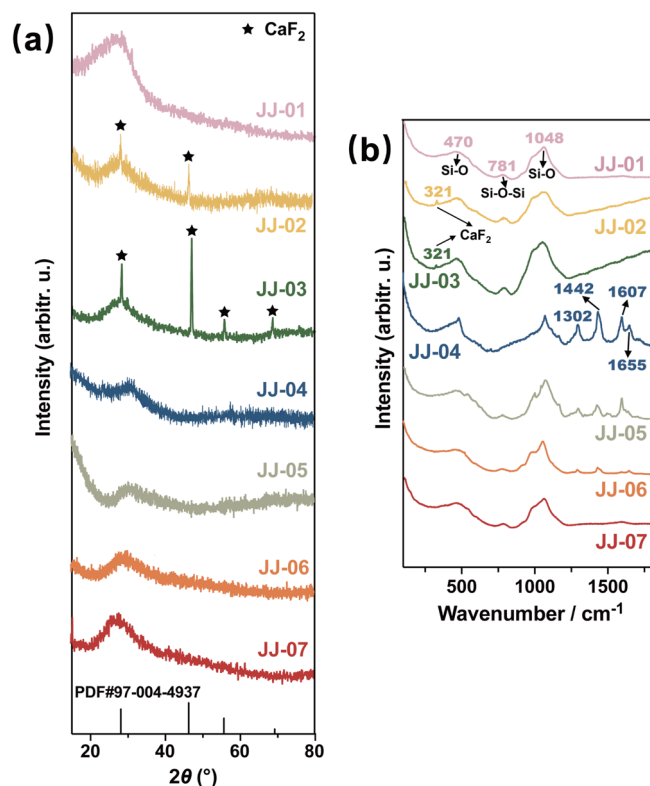


Fig. 3 | Phase structure of the samples. The XRD (a) and LRS (b) results of the glassware unearthed at the Jiujiang Site.

with an extracted beam at the tandem accelerator NEC 9SDH-2 (3 MV) at the Institute of Modern Physics, Fudan University. During the test, a 3.0 MeV collimated proton beam from the tandem accelerator passed through a 7.5 μm thick Kapton film (polyimide film), which served as the vacuum-atmosphere interface. The samples, positioned in air approximately 10 mm from the Kapton film, were irradiated by the proton beam with an actual energy of 2.8 MeV, a beam spot diameter of 1 mm, and a beam current of 0.1 nA, resulting in the generation of characteristic X-rays. For quantitative chemical analysis, the energy spectrum data of characteristic X-rays were collected using a high-resolution Si(Li) detector and interpreted with the GUPIX software. A helium flush was applied between the detector's beryllium window and the sample to minimize atmospheric absorption and enhance accuracy for light elements (Na and Mg). Under the above conditions, the theoretical penetration depth of the PIXE analysis for the sample is $\sim 90 \mu\text{m}$. Calibration was performed using the GSD-6 stream sediment standard, and the uncertainty of the content of each element does not exceed 3% of the result.

Results and discussion

Structural characteristics

To scientifically investigate and advance the understanding of the technical lineage of ancient glassware, it is essential to first conduct scientific analysis of the artifacts in order to determine whether the samples are artificial glassware, natural jade, or gemstones²³. At this stage, the structural state of the sample can be analyzed using XRD and LRS, with results cross-validated through complementary techniques.

The atomic number arrangement within the glassy structure exhibits short-range order, in contrast to the arranged periodicity of atoms in three-dimensional space that characterizes crystalline materials. As a result, the diffraction patterns of glass are markedly distinct from those observed in crystals. Glass does not exhibit characteristic diffraction peaks; instead, it displays a broad amorphous hump or dispersion curve, as illustrated in Fig. 3(a). All samples exhibit distinct amorphous characteristic peaks within the angular range of $2\theta = 20\text{--}35^\circ$, indicating that they are all glassy materials. Meanwhile, the Raman spectroscopy results presented in Fig. 3(b) reveal that the sample exhibits characteristic peaks associated with Si–O vibrational modes. Specifically, the broad peaks observed near 500 cm^{-1} and 1000 cm^{-1} correspond to the bending vibration and symmetric stretching vibration of the $[\text{SiO}_4]^{4-}$ tetrahedral Si–O bonds, respectively, and the spectral region between 600 and 800 cm^{-1} is attributed to the symmetric stretching vibration of Si–O–Si linkages^{21,24–26}, further confirming that these samples are indeed ancient glassware artifacts. In addition, three samples (JJ-04 to JJ-06) exhibited characteristic Raman peaks associated with organic compounds. Specifically, these include the N–H bending vibration and C–N stretching vibration corresponding to amide III (1302 cm^{-1}), the CH_2/CH_3 deformation vibration in aliphatic chains (1442 cm^{-1}), the C=C stretching vibration in aromatic rings (1607 cm^{-1}), and the C=O stretching vibration characteristic of amide I (1657 cm^{-1})^{27–31}. This phenomenon may be explained by prolonged burial weathering, during which surrounding organic materials (e.g., animal or plant remains and microbial biomass) underwent decomposition, resulting in surface deposition and subsequent internal penetration within the artifacts. Observation of the samples revealed that the surface of JJ-04 showed a few parallel weathering streaks. The detection of organic signals in the Raman spectrum is likely attributable to weathering processes. In contrast, the surfaces of JJ-05 and JJ-06 appeared relatively smooth, with no obvious signs of weathering, suggesting that any potential weathering is minimal. This preliminary assessment can be further verified through chemical composition analysis. During the weathering of glass, certain cations such as Na^+ and Mg^{2+} are typically leached out, leading to an increase in the content of their corresponding oxides. Chemical composition results (Table 2) indicated relatively elevated levels of Na_2O and MgO in sample JJ-04. Combined with the observed surface streaks, these findings support the interpretation that JJ-04 has undergone weathering, which resulted in the deposition and penetration of organic materials into the sample. In comparison, JJ-05 and JJ-06 exhibited lower Na_2O and

Table 2 | Chemical composition of the glass excavated from the Jiujiang site (wt%)

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	CuO	PbO
JJ-01	0.78	1.47	0.58	67.67	1.25	17.59	8.72	/	0.24	0.89	0.07
JJ-02	1.95	0.58	9.50	59.73	1.08	5.85	12.15	/	0.13	0.53	8.19
JJ-03	1.16	0.52	6.06	54.64	1.36	6.50	17.04	/	0.35	0.78	10.62
JJ-04	2.77	1.69	0.82	51.01	1.13	6.14	6.61	0.10	0.17	/	28.40
JJ-05	1.70	0.47	1.63	58.07	1.30	11.32	11.16	/	0.09	/	13.56
JJ-06	0.40	0.50	0.56	41.89	1.36	11.36	0.71	0.25	0.32	/	41.32
JJ-07	0.74	0.73	0.44	58.63	1.68	5.42	0.77	0.04	0.15	0.82	30.02

MgO contents along with well-preserved surfaces, implying that any weathering that may have occurred is likely limited in extent.

It is noteworthy that both XRD and LRS analyses of samples JJ-02 and JJ-03 exhibited the characteristic peak corresponding to CaF₂, which is the primary constituent of fluorite²⁵. During the Tang Dynasty of China (7–10 th century), fluorite was employed as an opacifying agent in milky glassware production²¹. Furthermore, during the Jiaping period of the Ming Dynasty and the Kangxi period of the Qing Dynasty (16–17th century), fluorite (named as “Zi stone, 紫石” at that time) was similarly utilized in Yanshen Town (Boshan glassware) to produce opaque white glassware and enhance its opacifying effect^{32,33}. In contrast, fluorite was not used for this purpose in Western glassmaking until the 19th century²¹. Based on this evidence, it can be preliminarily inferred that the glassware artifacts unearthed at the Jiujiang Site originated in China. To ensure the accuracy of the analytical results, we further examined the microstructure of the samples using low-vacuum SEM (Fig. 4). It was observed that samples JJ-02 and JJ-03 exhibiting columnar or needle-like crystals within the glassy matrix. EDS analysis confirmed the presence of high fluorine and calcium content, corresponding to a CaF₂ composition, which is consistent with the findings from XRD and LRS. Fluorite decomposes or reacts with SiO₂ at elevated temperatures, generating calcium silicate (CaSiO₃) and fluoride ions (F⁻). During cooling of the molten glass, free Ca²⁺ ions within the melt can combine with F⁻ and recrystallize as micrometer or nanometer-sized CaF₂ crystals³⁴. The crystallization and subsequent enrichment of CaF₂ create a differential refractive index relative to the surrounding glass matrix. This disparity causes light scattering through reflection and diffraction, thereby imparting an opacifying effect to the glass. The presence of other elements such as Si, Al, and Pb in the EDS results originates from the glass matrix itself, which is related to the compositional system of the glassware, and needs further investigation.

Chemical composition system

The PIXE results of the glassware unearthed at the Jiujiang Site are shown in Table 2. Based on chemical composition, the seven specimens can be divided into three types of glass systems: (I) JJ-01, K₂O-CaO-SiO₂ (K₂O/Na₂O ≈ 1). (II) JJ-02 to JJ-05, K₂O-CaO-PbO-SiO₂. (III) JJ-06 and JJ-07, K₂O-PbO-SiO₂. Except for JJ-01, which contains no Pb, the remaining samples all exhibit relatively high PbO content. Most of the glassware produced in China after the Eastern Han Dynasty contained PbO but either lacked BaO or contained only trace amounts, which was collectively referred to as high-lead glassware. The tradition of high-lead glass in China began during the Eastern Han Dynasty, became widespread in the Tang and Song Dynasties, and persisted into modern times. Meanwhile, although JJ-01 lacks PbO, it only contains a small amount of Na₂O, so it does not belong to the Na₂O-CaO-SiO₂ system. Therefore, based on the chemical composition, the glassware unearthed from the Jiujiang Site should be domestically produced in China rather than imported. In addition, the variation in chemical composition also accounts for the differing applications of domestic high-lead glassware and Islamic glassware. Due to the differences in chemical composition, domestic high-lead glassware exhibits inferior thermal resistance and a more fragile structure compared to Islamic glassware, making it less suitable for use as tableware³⁵. However, Islamic glassware, primarily produced using plant ash as raw material, exhibits high transparency,

excellent thermal stability, and superior chemical corrosion resistance. Characterized by refined craftsmanship and aesthetic sophistication, it served not only for elaborate decorative items but also as utilitarian vessels, including bottles, flasks, and dishes³⁶.

It should be noted that there are no definite glassware production kilns or associated archaeological remains that have been identified in the Heilongjiang region to date. Consequently, the glassware artifacts unearthed at the Jiujiang site were most likely introduced from regions with well-developed craft industries, such as the Central Plains, through commercial trade and other forms of material circulation.

In addition to the chemical composition system, the colouring mechanism of ancient glassware represents another significant area of research. The glassware specimens JJ-01 and JJ-07 exhibit a transparent blue hue, whereas specimens JJ-02 and JJ-03 are opaque, milky in appearance, and display a light blue colouration. Blue glassware represents a significant category within ancient coloured glassware artifacts, which frequently contain multiple coloring agents, such as Fe, Co and Cu. The PIXE results revealed that no Co element was detected in these four blue specimens, and the oxide content of Fe element was also relatively low, lower than that of CuO. Therefore, it is reasonable to conclude that the blue colouration in these four glassware specimens is mainly attributable to CuO. The electron structure of Cu is [Ar]3d¹⁰4s¹, with electrons in both the 3d and 4s orbitals capable of acting as valence electrons. Hence, Cu can exist in three valence states: Cu²⁺, Cu⁺ and Cu⁰. However, Cu⁰ exists in an atomic state, and Cu atoms at the nanoscale typically cause the glass to exhibit a red coloration; Cu⁺ is colourless due to the fully filled 3d orbitals³⁷. Therefore, the blue glassware unearthed at the Jiujiang Site was most likely primarily coloured by Cu²⁺ ions. On this basis, the two samples, JJ-02 and JJ-03, have formed CaF₂ crystals, resulting in an opaque appearance.

Regarding the source of fluorine in CaF₂, three naturally occurring minerals containing fluorine would have been accessible in ancient times, i.e. cryolite (Na₃AlF₆), fluorapatite (Ca₅F(PO₄)₃), and fluorite³⁴. However, given that the Na and P contents listed in Table 2 are significantly lower than their respective theoretical proportions in cryolite (32.8%) and fluorapatite (18.4%), fluorite must be the sole plausible source of fluorine. According to modern glass technology, fluorine-containing opacifiers such as sodium fluosilicate (Na₂SiF₆) and fluorite must be introduced together with raw materials containing Al₂O₃ to achieve an effective opacification effect³⁸. PIXE analysis revealed that the Al₂O₃ content in samples JJ-02 and JJ-03 was significantly higher compared to other specimens. The Al₂O₃ in ancient glassware was derived from minerals such as feldspar and clay. It is highly probable that ancient artisans intentionally selected raw materials with high Al content to synergize with “Zi Stone” in the production of glassware exhibiting an opalescent effect. Coincidentally, the Al₂O₃ content in the Boshan glassware containing added CaF₂, as mentioned above, is also notably high, further supporting our hypothesis. Boshan glassware utilized “Maya Stone (马牙石)” as the primary raw material, with additional materials including “Zi stone”, massicot, white lead, and verdigris³². Currently, there are several hypotheses regarding the identity of “Maya Stone”, including suggestions that it might be feldspar, calcite, or quartzite minerals. Based on historical records indicating that feldspar minerals were not included in ancient glassware formulations³², as well as the findings of this

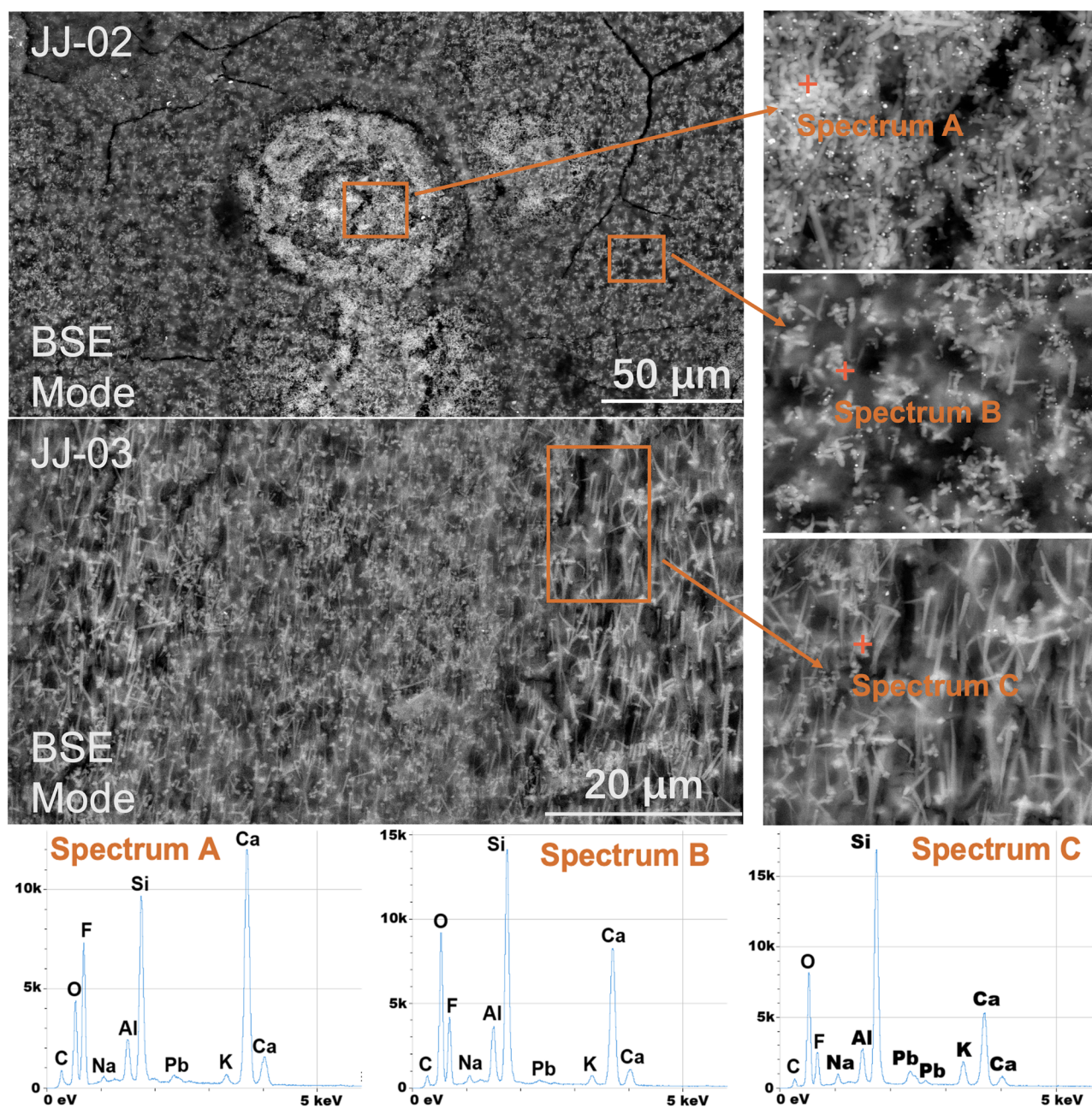


Fig. 4 | Microstructure of some samples. The SEM-EDS results of samples JJ-02 and JJ-03 conducted under low-vacuum conditions and backscattered electron mode.

study, we propose that “Maya Stone” is most likely a type of quartz mineral with a higher Al content compared to other quartz varieties. The elevated levels of Si and Al contribute to the formation of a stable glass network structure, which synergizes with CaF_2 to produce an opacifying effect in the glassware. Certainly, further investigation involving additional samples is required to substantiate this mechanism; however, this finding offers a new perspective for our subsequent research on ancient glassware.

This study systematically investigates the glassware from the Liao and Jin Dynasties excavated at the Jiujian Site through the application of non-destructive analytical techniques, effectively overcoming the limitations associated with reliance on a single methodological approach and providing a valuable reference for the analysis of fragile cultural relics. The research reveals that the glassware artifacts exhibit distinct local technological features and can be categorized into three compositional systems: $\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$, $\text{K}_2\text{O}-\text{CaO}-\text{PbO}-\text{SiO}_2$, and $\text{K}_2\text{O}-\text{PbO}-\text{SiO}_2$, all of which were domestically produced in China. These artifacts may have been introduced to Northeast China through cross-regional trade from more economically,

culturally and technologically advanced regions such as the Central Plains. The blue-coloured glassware was mainly chemically coloured by Cu^{2+} ions. The detection of CaF_2 crystals in certain blue glassware samples confirms the early application of fluorite opacification technology. The crystallization and enrichment of CaF_2 imparting an opacifying effect to the glassware. Moreover, the glassware contains CaF_2 crystals also exhibits high alumina content ($\text{Al}_2\text{O}_3 > 6\%$), a characteristic comparable to that observed in glassware artifacts from Boshan, China. This suggests that artisans during the Liao and Jin Dynasties may have already been proficient in producing opaque glassware by combining fluorite opacifiers with high-alumina raw materials—a hypothesis that warrants further investigation.

Data availability

Data is provided within the manuscript.

Received: 3 July 2025; Accepted: 9 December 2025;

Published online: 23 December 2025

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Acknowledgements

This work was supported by the Heilongjiang University Distinguished Young Scientists Fund (Humanities and Social Sciences) (Grant No. JC2021W4).

Author contributions

Shuangguang Bao and He Tian wrote the main manuscript text, and Hongxi Huang and Zhendong Su conducted Raman and XRD experiments. Bin Zhang conducted PIXE experiments. Bo Wu conducted FTIR and SEM experiments. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

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