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Multi-faceted analysis reveals the characteristics of silk fabrics on a Liao Dynasty DieXie belt

Ruochen Ge¹, Lili Cong², Yongping Fu², Bing Wang³, Guiyun Shen⁴, Bing Xu³, Mingzhou Hu³, Han Yu¹, Jie Zhou³ and Lu Yang^{1*}

Abstract

The Liao Dynasty's highly developed textile industry was characterized as "the best in the world" in ancient Chinese literature. This study analyzed two textiles on a 蹀躞 (DieXie) belt excavated from the No.1 Liao Dynasty noble tomb of Zhangjiayao Forest (Shenyang, China), with one wrapping around the leather belt (T1) and the other on the surface of a leather pouch hanging on the belt (X1). They were identified as silk based on structures by morphological observation and chemical components revealed by Fourier Transform Infrared spectroscopy (FTIR). Proteomics and enzyme-linked immunosorbent assay (ELISA) were used to investigate the animal origin of the silk, and the original color and dyestuffs of T1 were examined by liquid chromatography-mass spectrometer (LC-MS/MS). The results have shown that T1 consists of three layers of *Bombyx mori* silk plain fabric, and its original color was yellow-red dyed with madder and plants containing flavonoid dyeing tissue, consistent with the color of DieXie belts recorded in the ancient literature. The silk on the pouch is a layer of plain fabric, while the upper layer is embroidery on the Four-end-complex gauze, which was made of twisted *Bombyx mori* silk. We believe that the silk wrapping around the leather belt was to provide additional comfort and aesthetics after dyeing while protecting the leather, which is prone to warping and moisture. This study suggests that such silk fabrics with high specifications are one of the manifestations of the distinguished status of the tomb owner. The integration of various analytical methods on ancient silk fabrics enables us to learn various information about their textile forms, silk animal origins, colors and dyestuffs, revealing the highly developed silk waving techniques and prosperous costume culture of the Liao Dynasty.

Keywords Liao Dynasty silk fabrics, DieXie belt, Proteomics, ELISA, LC-MS/MS

Introduction

Silk, as a remarkable product of ancient Chinese civilization, is a textile woven varying from *Bombyx mori* silk, *Antheraea Pernyi* silk, *Eri* silk, to *Chestnut* silk. As archaeological investigations advance, a growing number of silk textiles from various periods have been unearthed, providing valuable insights into the sophisticated textile techniques that existed in antiquity. Identifying and examining ancient silks are crucial in both archaeology and academia, thus many analytical methods have currently been employed in this field. The two most widely used techniques are the observation of

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morphological features of silk textiles using microscopy such as Scanning Electron Microscopy [1] and Transmission Electron Microscopy [2], and the identification of chemical bonds in silks using Infrared Spectroscopy [1, 3, 4]. Recent studies have applied additional methods, including amino acid analysis [5, 6], Synchrotron Microdiffraction [7], Nuclear Magnetic Resonance [8], Differential Scanning Calorimetry [2] and Capillary Electrophoresis-Mass spectrometry [9]. Besides, as silk is a protein fiber mainly composed of silk fibroin and sericin protein, of which the former has a highly organized crystalline structure that can be examined and identified even after millennia of burial, proteomics has emerged as a novel method for analyzing historical silks with applications in several recent studies, including the discovery of silk relics [10, 11], the identification of silk species [12–16], and the study of silk's decomposition processes [17]. In addition, methods based on antigen-antibody immunoreactivity also play an important role in ancient silk analysis. These methods include Western Blot [14, 18], Immunosensor [19], Immunochromatographic Strip [20, 21], Immune-Fluorescence [22, 23], and ELISA. Among these, ELISA has been frequently used in the detection of silk relics [22, 24–26] and other protein-based residues [27–29] because of its high specificity, high sensitivity, and relative rapidity. The study of ancient silk dyeing processes has also gained significant attention, with LC-MS/MS being the most widely utilized detection technique. For instance, on historical fabrics, it can identify yellow dyes based on flavonoids [30–32], red dyes based on anthraquinones [1, 33–35], blue dyes from indigo plants [36], and cochineal and violet bugloss dyes [37, 38].

The Liao Dynasty (AD 907–1125) was a feudal dynasty founded by the Khitan tribe, and it played a significant role in the history of Chinese silk by producing a huge variety of silk products [39, 40]. The DieXie belt is a traditional belt with a few small straps hanging from the main belt, and these straps can be used to hang household objects, embroidered pouches, and weapons. Traces of silk fabrics are common on DieXie belts, such as those found on a DieXie belt excavated from the tomb of the Chen princess of Liao [41]. In this study, two textiles from the DieXie belt excavated in No. 1 Liao Tomb at Zhangjiayao Forest have been identified as silk fabrics. Proteomic and ELISA were both used to determine the silk origin, and LC-MS/MS was used to examine the original color of the fabric and dyeing plants used. This is the first application of a multifaceted analysis of Chinese Liao Dynasty silk fabrics incorporating several novel approaches above. The findings provide compelling evidence for the various colors of silk fabrics mentioned in the ancient literature and valuable insights into understanding the highly

developed silk manufacturing and custom culture of the time.

Materials and methods

Materials

The Zhangjiayao Forest No. 1 Liao Dynasty noble tomb is located in Shenyang, Liaoning Province, China, and is dated to the early Liao Dynasty (AD 907–1050) (Fig. 1a). The tomb was discovered in 2015 (Fig. 1b) and excavated in the laboratory in 2021 (Fig. 1c). A group of silver and copper artifacts were found at the waist of the tomb owner (Fig. 2a), which are considered metal artifacts from a DieXie leather belt according to their placement and shape. Some textile fragments closely attached to the leather were discovered around these metals, and a sample of 2 cm × 1 cm was taken and labeled as T1 (Fig. 2a). The leather and these textiles should be used together as a belt to connect the metal items, according to previous archaeological materials (Fig. 2b). In addition, under the peach heart ornament of the belt, a leather pouch (labeled X1) was found, and three different layers of textiles on its surface were sampled and labeled from top to bottom as X1-1, X1-2, and X1-3, respectively (Fig. 2a).

Sample preparation and instruments

Morphological observation of samples

RX-100 digital microscope (Horix, Japan) and Pro-x scanning electron microscope (Phenom, The Netherlands) were used, with a SEM operating voltage of 5 kV. A desiccator was used to dry out samples for 24 h before they were placed in the sample bin.

Infrared spectral analysis of samples

Single fibers were taken and tested after 24 h in a desiccator. A Nexus-6700 FTIR spectrometer (Thermo-Nicolet, USA) equipped with a MCT-A mid-infrared detector was used, and the main chemical bonds of samples were characterized between 650 and 4000 cm^{-1} . Origin 9.0 was used to analyze the spectra.

Proteomics studies of samples

Since samples X1-1 and X1-2 were difficult to separate, they were treated as one sample. The three samples T1, X1-1&2, and X3 were respectively added to 1 mL of CaCl_2 -Ethanol- H_2O (molar ratio of 1:2:8) solution for a water bath at 95 °C until the samples were completely dissolved. The solution was then dialyzed in deionized water for 96 h (molecular weight cutoff = 1000) to remove impurities and salts, followed by freeze-drying for 24 h to obtain the silk fibroin powder in samples. Afterwards, 90 μL of SDT (4% sodium dodecyl sulfate, 100 mM dithiothreitol, 100 mM Tris-HCL, pH7.6) was added and reacted in a boiling water bath for 5 min and

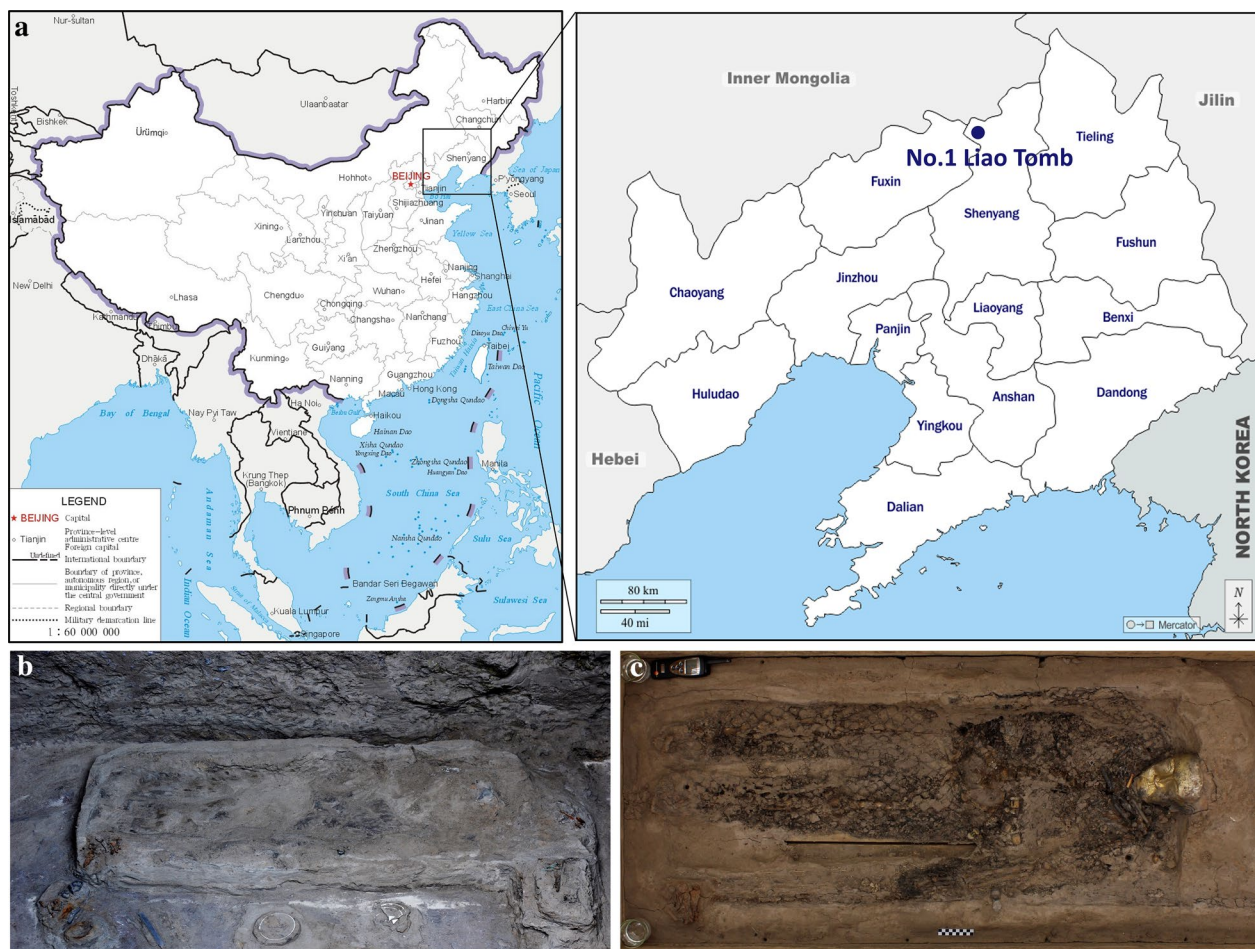


Fig. 1 a Schematic diagram of the location of No. 1 Liao Dynasty noble tomb in Zhangjiayao Forest (Shenyang, China); b Picture of the exterior of the tomb; c Picture of the interior of the tomb

then cooled to room temperature, and the supernatant was removed by centrifugation. After that, 200 μ L of UA buffer (8 M Urea, 150mM Tris-HCl, pH8.0) was added and mixed, and the mixture was transferred to a 10KD ultrafiltration tube, centrifuged at 12,000g for 10 min, and the filtrate was discarded. 200 μ L of 50mM Iodoacetamide was added for alkylation, and then it was oscillated at 600 rpm for 1 min and left at room temperature for 30 min. 100 μ L of NH_4HCO_3 buffer was added, centrifuged at 14,000g for 10 min, and repeated twice. Finally, added 40 μ L of Trypsin buffer (6 μ g Trypsin in 40 μ L NH_4HCO_3 buffer), oscillated at 600 rpm for 1 min, and incubated at 37 $^\circ\text{C}$ for 16 h. The liquid was transferred to a new collection tube and centrifuged at 12,000g for 10 min, and the filtrate was collected. A C18 StageTip was used to desalt it. After being dried in a vacuum, it was re-dissolved with 50 μ L of 0.1% FA (formic acid) for LC-MS/MS analysis. The information on instruments and data processing can be seen in Additional file 1: S1.

ELISA analysis of samples

According to previous studies [22, 23], antibodies to *Bombyx mori* silk fibroin protein were prepared before ELISA testing. The silk fibroin powder described in the proteomics method was dissolved in CB (carbonate buffer, pH9.6) and added to the ELISA plate at 100 μ L per well, with five wells used for each sample. After overnight incubation at 4 $^\circ\text{C}$, the liquid in wells was discarded, and the wells were washed three times with the addition of 200 μ L of PBS (phosphate buffer, pH7.4). Then 200 μ L of BSA (1wt% Bovine serum albumin in PBS) was added and incubated for 2 h at 37 $^\circ\text{C}$, followed by a washing step. Then 100 μ L of the diluted serum protein-specific antibody mentioned above was added to each well and incubated at 37 $^\circ\text{C}$ for 1 h. The washing step was repeated, and 100 μ L of the diluted goat anti-mouse IgG-HRP antibody was added to each well and incubated at 37 $^\circ\text{C}$ for 1 h. After washing, 50 μ L of TMB chromogenic solutions A and B were added to each well, and the reaction was terminated by adding 100 μ L of 2 mol/L

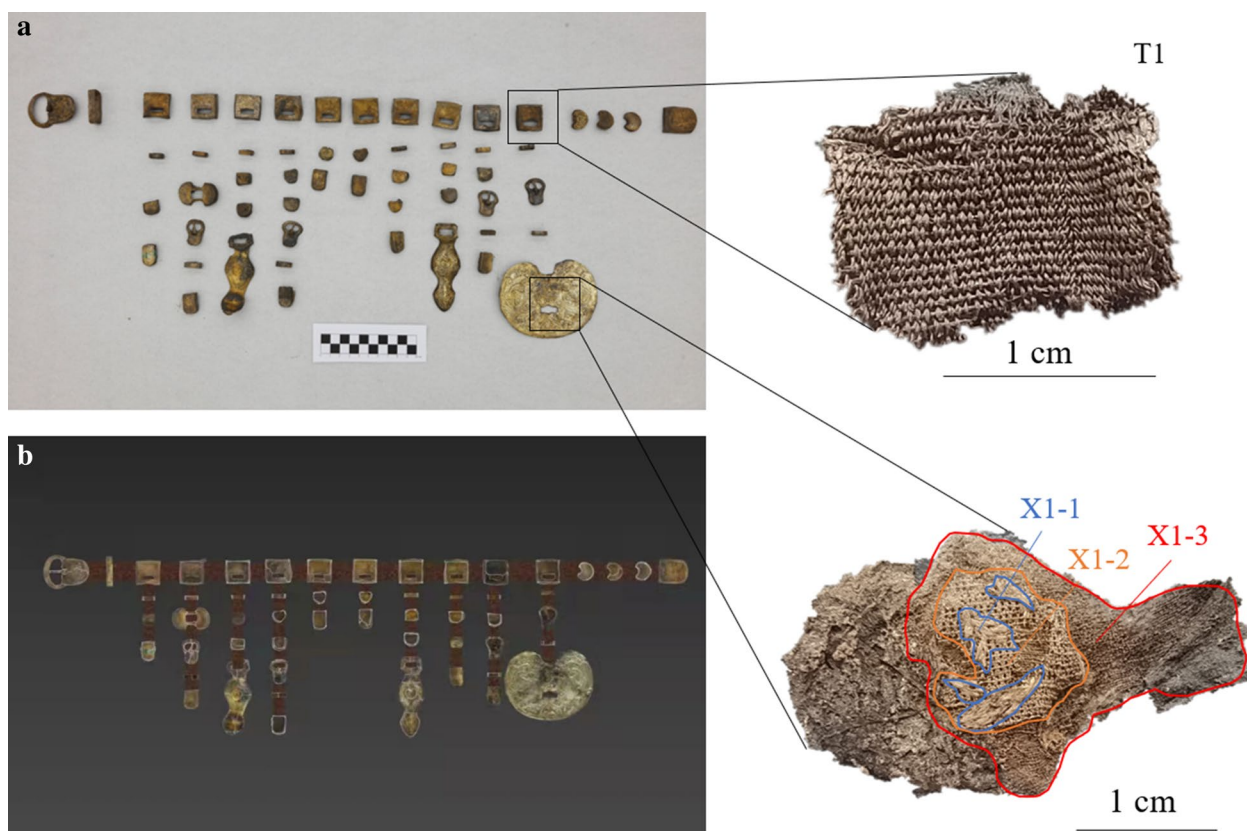


Fig. 2 **a** Picture of the sampling locations and samples. The area within the blue line represents X1-1, the orange line corresponds to X1-2, and the red line defines X1-3; **b** Schematic diagram of the replication of the DieXie belt, the brown belt connected with the metal is leather

H_2SO_4 after 10 min of light avoidance. The absorbance was measured at the wavelength $\lambda=450$ nm using a microplate reader. Negative, blank, and positive controls were set during the analysis. The negative control used CB instead of the sample solution, the blank control used BSA instead of the antibody, and the positive control used *Bombyx mori* silk protein solution (1 $\mu\text{g}/\text{ml}$) instead of the sample solution. The cut-off for a positive result was determined as the mean of the absorbance (OD_{450}) of the negative control plus three times the standard deviation. A result was considered positive when the OD_{450} of a sample was above the cut-off [42].

Dyestuffs analysis of samples

Only the dyes on T1 samples were analyzed because it is challenging to completely separate the three layers of textiles. According to the methods of Li YF and Degano I for the extraction of dyes in ancient textiles [43, 44], 200 μL of dimethyl sulfoxide (for HPLC) was added to a T1 fiber. After being heated in a water bath at 60°C , the supernatant was taken. 100 μL of hydrochloric acid (6 mol/L)-methanol-water (v/v/v=2:1:1) solution was added to the remaining substance, and the solution was

filtered using a 0.45 μm PTFE needle filter and dried under nitrogen after 60 min in a water bath at 60°C . Then the supernatant extracted in the previous step was added, mixed under ultrasonic waves, and centrifuged at 5000g. The final supernatant was used for LC-MS/MS analysis. More details can be found in Additional file 1: S2.

Results

Morphology of the textile

The textile structures revealed by microscopy show that T1 has aged and turned brown-black and it has a warp thread and a weft thread crossing up and down, which is characteristic of plain fabrics. The twisted warp has become loose and splits into two strands (Figs. 3a and 4a). The warp thread density of T1 is 60 threads/cm and the weft thread density is 20 threads/cm. T1 is made up of three such layers overlapping each other (Fig. 3b), resulting in increased thickness and strength of the belt. A single thread was made by twisting multiple fibers (Fig. 3c) as suggested by the mutilated cross-sections of multiple fibers observed (Fig. 3d), which was related to silk ageing. There are three different textiles on the surface of X1 (Fig. 3e). The upper fabric X1-1 are thicker ranging from

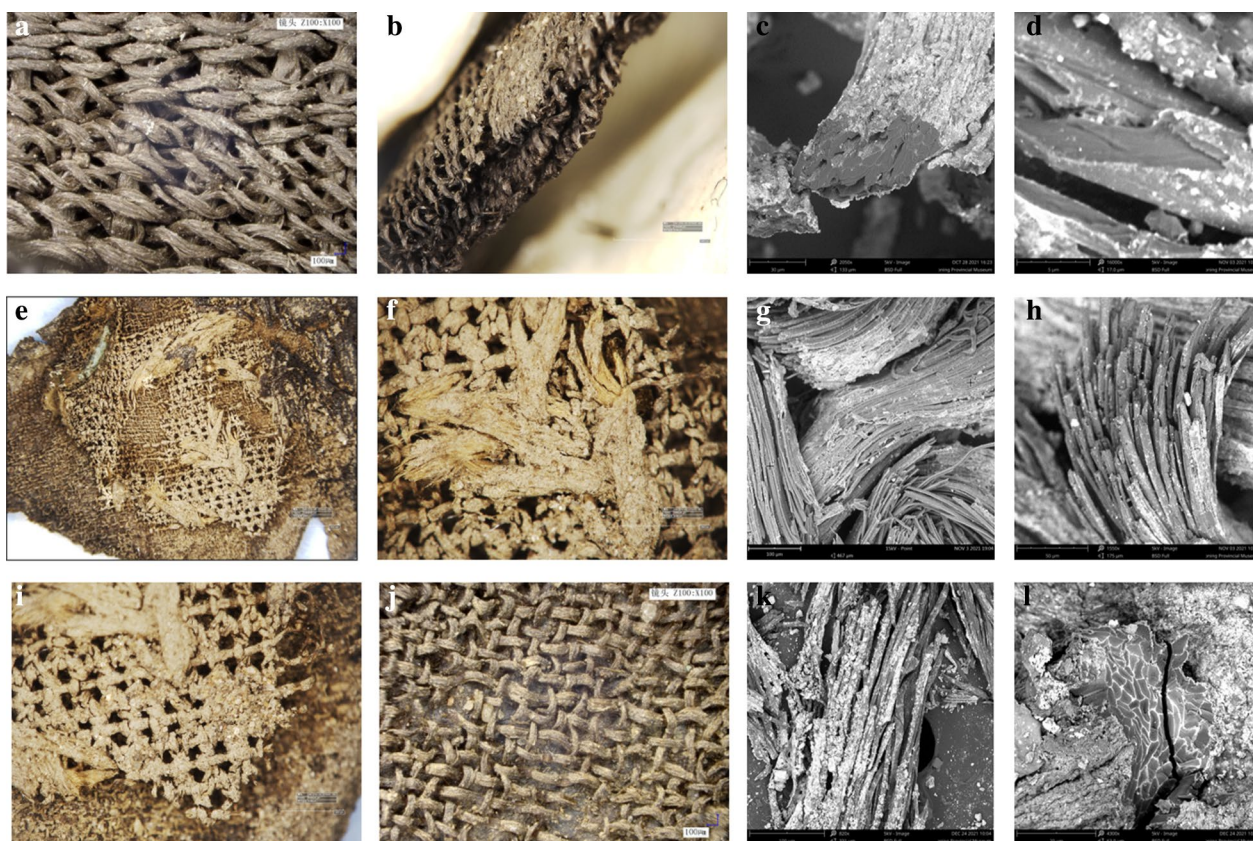


Fig. 3 Photomicrographs of the samples. **a** the surface of T1 $\times 100$; **b** the side of T1 $\times 40$; **c** the cross-section of T1 woven thread $\times 2050$; **d** the single fiber of T1 $\times 16,000$; **e** the surface of embroidery pouch $\times 20$; **f** the uppermost fabric on the surface of embroidery pouch X1-1 $\times 50$; **g** the fiber diameter surface of X1-1 $\times 750$; **h** the fiber diameter surface of X1-2 $\times 1550$; **i** the middle layer of fabric on the surface of embroidery pouch X1-2 $\times 50$; **j** the lower layer of fabric X1-3 on the surface of the embroidery pouch $\times 100$; **k** the fiber surface of X1-3 $\times 820$; **l** the fiber cross-section of X1-3 $\times 4300$

243 to 383 μm and has no regular pattern but only traces of interlocking threads attached to the lower layer, which can be presumed to be surface embroidery (Fig. 3f). It can be seen from Fig. 3i that X1-2 is composed of four warp threads, which are twisted around each other at a predetermined angle and joined by a weft thread, the warp threads overlap where they are twisted, and regular holes appear where they are not twisted. The warp thread density is 40 threads/cm and the weft thread density is 25 threads/cm (Fig. 3i), resulting in a fabric surface pattern of clear and evenly spaced yarn holes. This particular structure corresponds to the traditional Chinese fabric known as “四经绞罗” or the Four-end-complex gauze (Fig. 4b) [45]. The combination of X1-1 and X1-2 constitutes the embroidery on the Four-end-complex gauze, which often has intricate patterns and was a common custom material for ancient nobles. The lowermost fabric X1-3 is a plain fabric with a warp thread density of 60 threads/cm and a weft thread density of 60 threads/cm

(Fig. 3j). It is not connected to the leather and thus probably was a pouch covering to better display the embroidery. The single threads in all three layers of fabric X1 consist of multiple twisted fibers (Fig. 3g, h, k), as manifested by indistinct fiber cross-sections (Fig. 3l).

Chemical bond of the textile

The samples were tested using infrared spectroscopy to identify their materials, and the results are shown in Fig. 5. Infrared spectrograms of T1 and X1 both show a clear peak at wave number 3287 cm^{-1} , which is the amide A band, the stretching vibration of N–H [2, 46]. They also show peaks around 1634 cm^{-1} , 1527 cm^{-1} , and 1261 cm^{-1} , which belong to the amide I band (stretching vibrations from C=O) and amide II band (stretching vibrations from C–H and deformation vibrations from N–H), respectively. These peaks correspond to the α -helix structure in silk. The peak at 1234 cm^{-1} is from the amide III band, corresponding

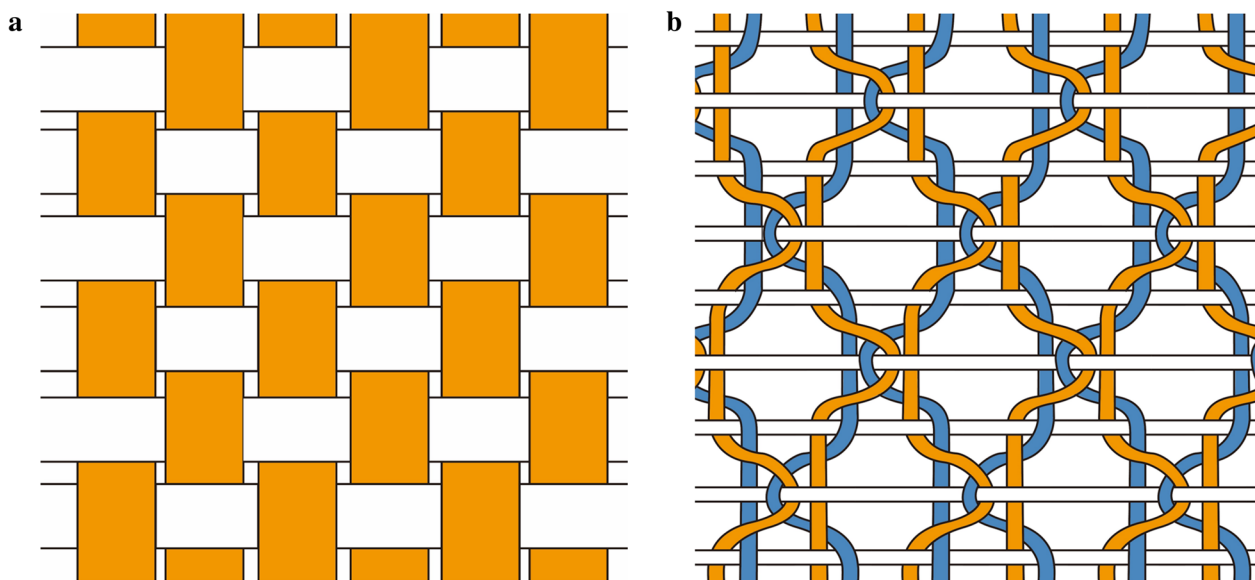


Fig. 4 **a** Schematic diagram of a plain fabric structure; **b** Schematic diagram of the Four-end-complex gauze structure. Note: White indicates the weft thread, and orange and blue indicate the warp thread

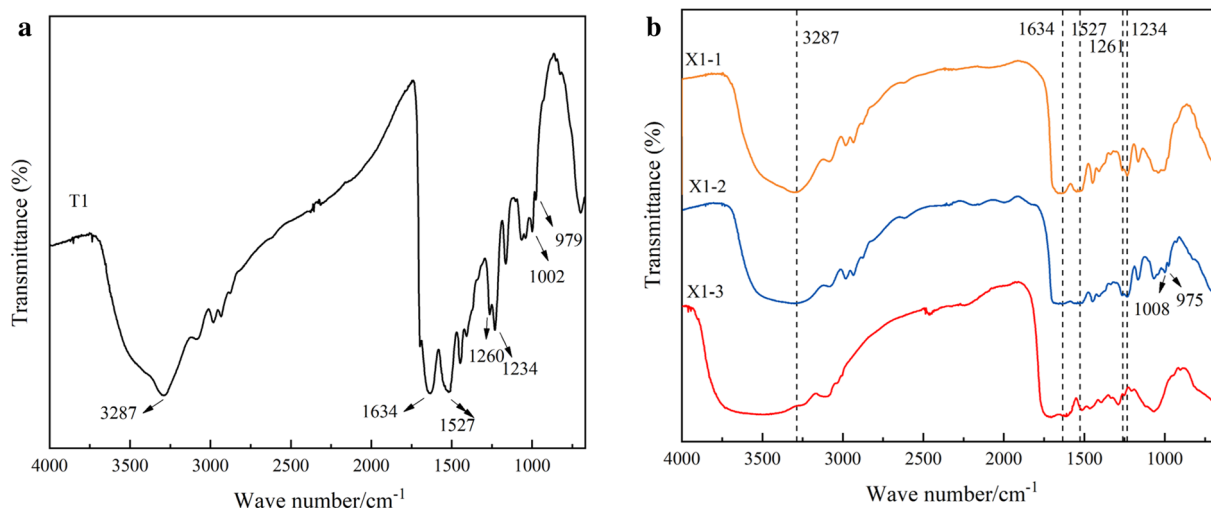


Fig. 5 **a** FTIR spectrum of T1; **b** FTIR spectrum of X1

to the β -sheet structure in silk [2, 26]. Moreover, these samples, especially T1 and X1-2, exhibit clear peaks at 1008 cm^{-1} and 975 cm^{-1} , which were derived from structural vibrations of $-\text{Gly-Ala-Gly}-$ and $-\text{Gly-Gly}-$ peptide sequences, respectively. Hence, these two peaks are often used to distinguish silk from wool as they are characteristic of silk but absent in wool [47]. In summary, the FTIR spectra of T1 and X1 show high similarity to those of silk fibers, suggesting T1 and X1 are silk fibers, though their silkworm origin information is not obtained.

Animal origin of the silk

It is believed that wild silk was used in the ancient textile industry [12], even though domesticated *Bombyx mori* silk has been prevalent since early times. The Liaoning Province has a long history of farming *Antheraea pernyi* and is the primary region in China for producing *Antheraea pernyi* silk. It is thus important to identify the species of Liao Dynasty silk to better understand the development of the silk textile industry. Proteomics analyses of T1, X1-1&2, and X1-3 have demonstrated that most peptides could be detected within 60 min with

molecular weights of 2500 Da or less, indicating that large molecule proteins had been digested into small molecule peptides during the enzymatic digestion process. By comparing with the *Bombyx mori* and *Antheraea pernyi* protein database, a total of 15 peptides were identified in sample T1, which belong to 10 proteins in the *Bombyx mori* group. In sample X1-1&2, a total of 24 peptides were detected and belong to 24 proteins in the *Bombyx mori* group. In sample X1-3, a total of 6 peptides detected belong to 6 proteins in the *Bombyx mori* group, the details of these peptides can be found in Additional file 1: Table S1. These proteins do not match with the *Antheraea pernyi* proteomes, indicating that none of the three silk fabrics originated from *pernyi* silkworms. Silk mainly consists of silk fibroin and sericin protein, with the light chain, heavy chain, and P25 chain in the fibroin [10, 48]. In sample T1, a protein from the heavy chain (protein code: P05790, score:323.31) was detected with the specific peptide **GYGQGAGSAASSVSSASSR**, of which the secondary mass spectrum shown in Fig. 6a

reveals a characteristic protein of the *Bombyx mori* [11, 15]. In addition, another protein, a fragment of the silk fibroin heavy chain (protein code: Q1KS45, score: 323.31), was detected in T1 with the specific peptide **RQLVVK** (Fig. 6b), suggesting an origin from the *Bombyx mori*. Neither of these two characteristic proteins was found in the other two samples. This may be due to the limited sample size or protein loss during pretreatment.

To further investigate the samples' animal origin, the samples were examined by ELISA using antibodies against the *Bombyx mori* silk fibroin protein. As shown in Fig. 7, the OD_{450nm} of both blank control and negative control were below the cut-off, while the positive control was above the cut-off, indicating that this test was valid. The OD_{450nm} of the three samples were all above the cut-off, suggesting that all three samples contain the *Bombyx mori* silk fibroin. Considering the specificity of the immune response and in combination with the proteomic results mentioned above, we believe that all the sample silks originated from *Bombyx mori*.

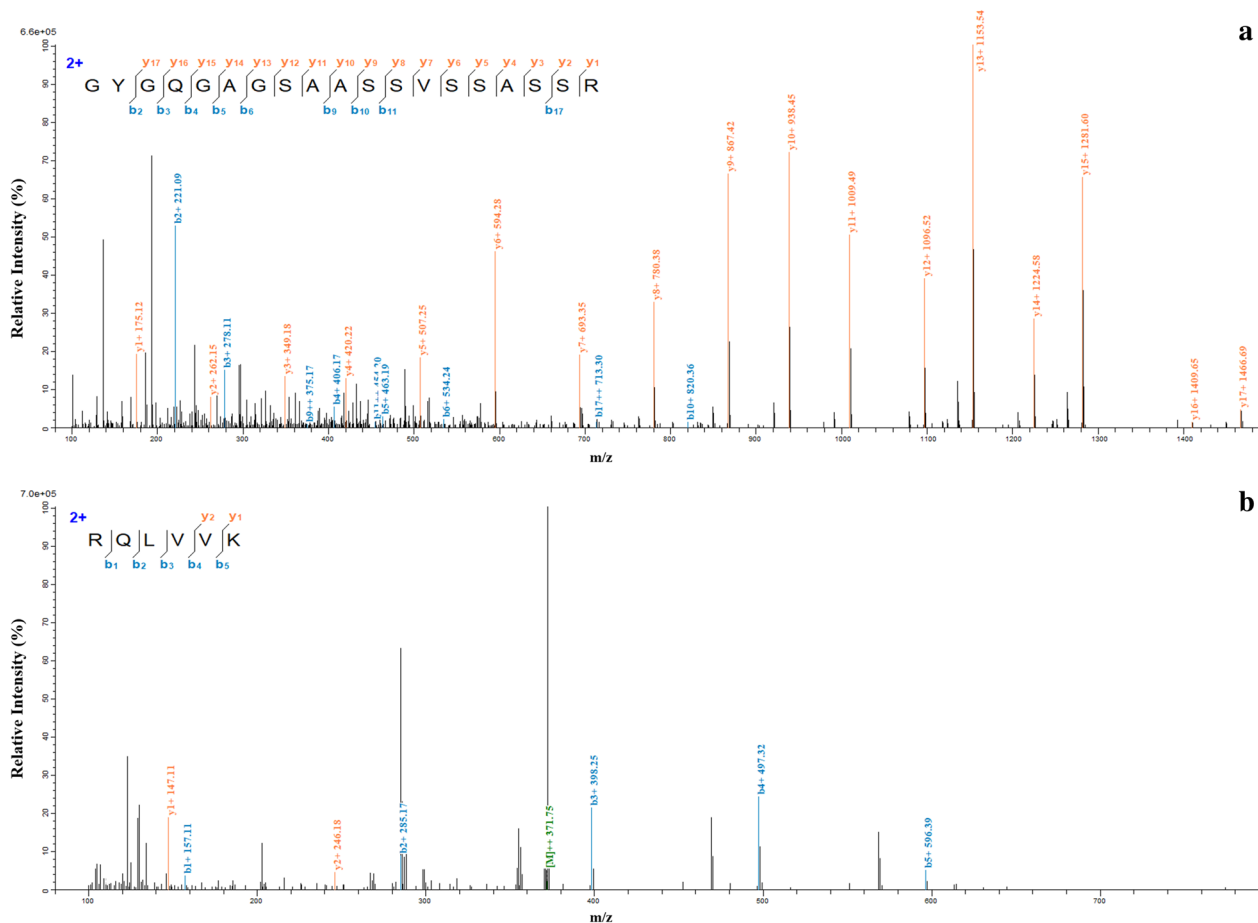


Fig. 6 a Secondary mass spectrum of the specific peptide P05790 in T1; b Secondary mass spectrum of the specific peptide Q1KS45 in T1

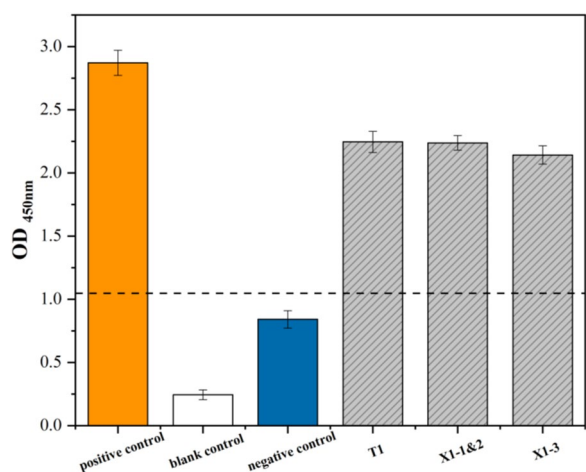


Fig. 7 ELISA test results of the samples

Color of the silk

The LC-MS/MS analyses of dyes have identified anthraquinone (red) and flavonoid (yellow) on T1. Purpurin, a red dye derived from madder, was found on T1 (Fig. 8a) [33]. Madder was a major red dye used in ancient times and has been extensively grown and used in China since the Shang and Zhou dynasties. Its main dyeing constituents

are alizarin and purpurin. Although the peak of purpurin was very significant in T1, alizarin was not detected. In this case, the source of the dye was likely to be *R. cordifolia*, also known as Indian madder [32] which is common in South and Southeast Asia and has been widely cultivated in China for more than 2000 years. Typically, anthraquinone-based dyeing produces bright red fabric. However, T1 fabric appears brown-black (Fig. 1a), which could be attributed to soil contamination or the natural darkening of anthraquinone-dyed silks over time, especially when exposed to sweat [32]. Additionally, the sample exhibits significant peaks of isoflavones (Fig. 8b), flavonoids (Fig. 8c), and chalcones (Fig. 8d), suggesting that T1 probably contains some yellow dyes. However, since no markers of any typical yellow-dyed plants were found, their botanical origin is still unknown. It has been documented that the ancient dyers usually dyed the base color of fabrics yellow with plants such as *Cotinus coggygria*, Turmeric, and Flos sophorae before dyeing the silk red [26]. Such a technique of over-dyeing with yellow can brighten the red color of the textile [49]. Besides, the ancient book of the Liao Dynasty: *History of Khitan State*, also recorded that “the queen of the state and the nobles were all Hu people... wearing DieXie belt made of leather, wrapped with yellow-red silk, decorated with gold, jade, crystal, and jasper...”

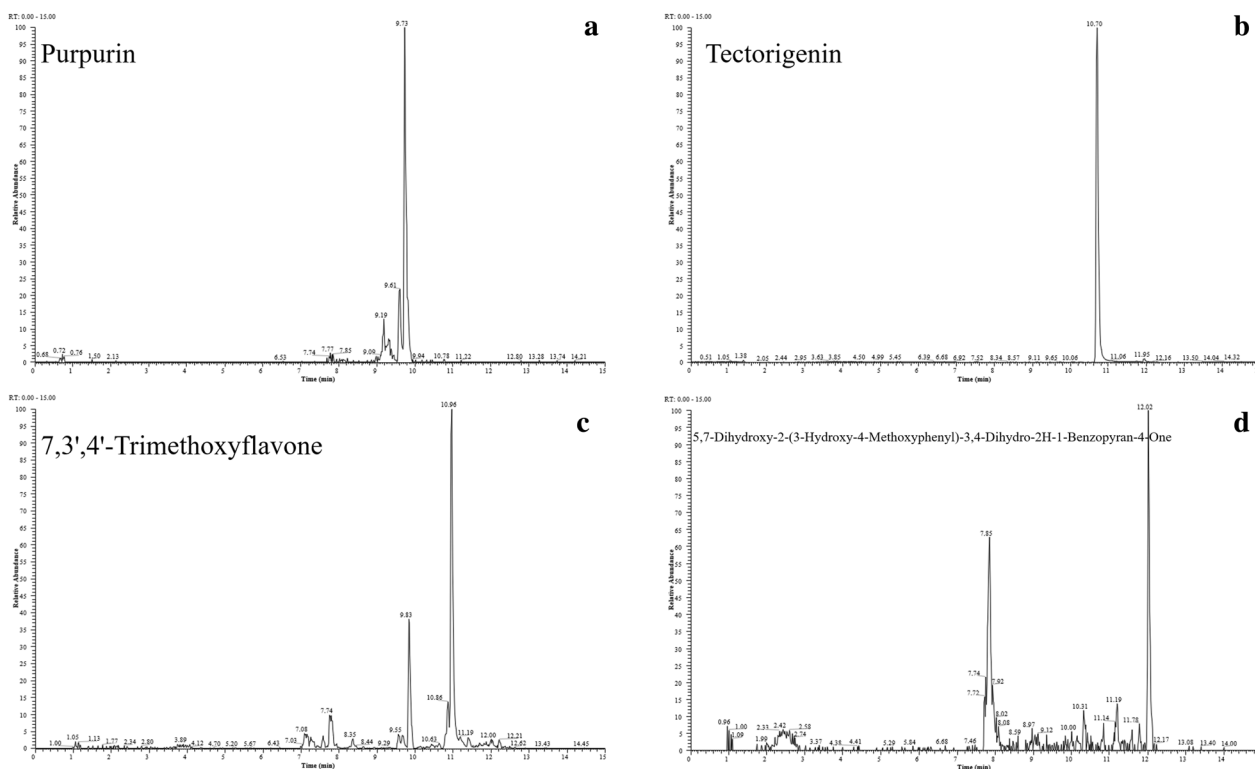


Fig. 8 a Secondary mass spectra of purpurin in T1; b Secondary mass spectra of isoflavones in T1; c Secondary mass spectra of 7-O-methylated flavonoids in T1; d Secondary mass spectra of chalcones in T1

Considering that sample T1 is the silk fabric wrapped around the leather on the DieXie belt of No. 1 Liao Tomb, the analytical results align with the descriptions in ancient literature, suggesting that the color of T1 fabric is indeed yellow-red.

Discussion

Our integrated analysis has revealed that T1 is a three-layer overlapping plain fabric made of *Bombyx mori* silk, and its original color is yellow-red. *Khitan Rituals and Customs*, an ancient book states that "Khitan belts can be categorized into three types according to their materials: metal belts used as funeral objects; leather belts, and silk belts used in real life." The silk-wrapped leather structure in this study indicates that this DieXie belt was intended for daily use as well as interred with the tomb owner as a funeral object. In both scenarios, leather was prone to wear and tear during use, moisture, distortion, and mold growth. Plain woven silk, known for its smooth and flat texture, offers several advantages when used to wrap leather. According to the original characteristics of silk, it can protect the leather, and acts as padding to offer cushioning, and the overlapping of multiple layers helps absorb sweat and keep softness. These result in excellent belt strength and great comfort for the wearer. This type of silk and leather combination was unique and is found in ancient Chinese belts for the first time, with only one similar previous case reported as a belt attached to a harness [50]. During the Liao Dynasty, natural white silk was considered a highly decorative material compared to leather. With highly developed dyeing techniques, people could dye the silk fabric to enhance the belt's appearance. X1 consists of three layers of plain fabric and has Four-end-Complex gauze embroidery, all of which were made of *Bombyx mori* silk. It is the external decoration of the leather pouch hanging on the DieXie belt. An embroidery pouch is one of the objects often worn on the belt in addition to currency or small items such as a bow, sword, handkerchief, and knife. The DieXie belt not only serves functional and aesthetic purposes but also acts as an identifier of the tomb owner [39]. The presence of silver and copper materials, the intricate fabric, and the embroidered pouch suggests that the tomb owner was a Khitan nobleman holding an official position above the seventh rank.

Since the Wei-Jin and North-South Dynasties, the Khitan, one of the ancient tribes of northern China, have maintained contact with the Han and other ethnic groups of the Central Plains. Khitan had the textile industry before Liao's formation, according to *The History of Liao*: "The people of the country raised

mulberry trees and learned textile technology". After the founding of the Liao state, the Liao Dynasty inherited the system of the Tang and Song dynasties based on the original textile industry and established official silk institutions in various places, leading to the development and spread of the silk weaving industry [41]. After a long period of systematic domestication on a large scale, *Bombyx mori* silk has become the primary silk product in all dynasties due to its superior quality, even in Liaoning province, which is known as the main region of *Antheraea pernyi* silk. Moreover, the Liao government set up the "Embroidery Institute" and "Dyeing Institute", responsible for the management of fabric embroidery and dyeing. The Khitan people created and excelled in the art of embroidery with fusion and ethnicity, which was the most advanced embroidery among the nomadic peoples in the north at that time. Moreover, the yellow-red belt examined in this study indicates the advanced silk dyeing technology of the Liao Dynasty, elevating the silk dyeing technology of ancient China to a new peak.

Conclusion

The analytical results and discussion lead us to the following conclusions: The DieXie belt discovered in the Liao tomb at Zhangjiayao Forest is made of three overlapping layers of plain silk fabrics, and its original color of yellow-red corresponds to that described in the literature. This special color was over-dyed, with the red color coming from madder and the yellow color coming from plants containing flavonoid dyeing tissues. The textile on the pouch is a plain silk fabric with Four-end-complex gauze embroidery. A combination of proteomics and ELISA analyses reveals that both silk fabrics are from *Bombyx mori* silk. Additionally, the silk fabric covering the leather was designed to protect the leather, enhance wearing comfort, and improve the appearance of the belt, reflecting the Liao people's dual pursuit of practicality and decoration for clothing. Through a meticulous analysis of the belt's form, material, animal origin of silk, and dyestuff using various methods, this study sheds light on the weaving, embroidery, and dyeing techniques employed during that period, and the findings serve as physical evidence of the exquisite silk products and advanced handicraft industry that existed during the Liao Dynasty, validating the accounts documented in numerous ancient texts.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-023-01064-6>.

Additional file 1. Supplementary material.

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Author contributions

RG, LY and BW designed the research; LC, YF and GS provided archaeological samples and background; RG, BX, MH, HY and JZ performed analyses; and all authors helped drafting/revising the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declarations

Competing interests

The authors declare no competing interests.

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