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Characterization of a 13th-century Tibetan birch bark manuscripts: investigating utilization and craftsmanship

Qingle Chen^{1,2}, Tsomo Tashi³, Shan Wang⁴, Saerji⁵, Yimin Yang² & Hongen Jiang²✉

Paper has become the world's predominant writing medium since its invention. However, non-paper writing materials have also played a significant role in human civilization, serving purposes beyond mere text transmission. Despite their importance, research about craftsmanship and utilization of these alternative materials remain limited. In this study, we employed non-destructive and micro-destructive analytical techniques—including THM-Py-GC/MS, p-XRF, ATR-FTIR, and hyperspectral imaging (HIS) to examine fragments excavated from Taklung Monastery in Tibet. Results identified birch bark as the writing material and revealed that ink was prominently gold (Au). This discovery reports a rare case of the utilization of gold ink on birch bark, offering valuable insights into 13th-century Tibetan writing material production. Furthermore, HIS enabled text extraction from the fragments. Combined with the unique excavation context, we suggest that birch bark also possesses religious significance. This study enhances our understanding of the diverse applications of writing materials of ancient Tibet.

Manuscript materials have played an irreplaceable role in the dissemination of human civilization. Since its formal invention during the Eastern Han Dynasty (25–220 AD), paper has gradually become the most widely used writing medium worldwide. However, even before the advent of paper, a variety of writing materials existed, including organic substrates such as bark, leaves, silk, sheepskin, donkey hide, and wooden tablets, as well as inorganic materials such as clay tablets, gold, silver, bronze plates, and stone slabs¹. These materials also served as crucial vehicles for information transmission and exchange, significantly contributing to the formation and advancement of early human civilizations. Among them, writing materials such as palm leaves manuscripts and birch bark were extensively used in northwestern India and Kashmir until the Mughal Empire (1526–1857 AD), when they were gradually replaced by paper^{2,3}. Even today, certain religious scriptures continue to be written on these materials, indicating that non-paper manuscripts held an essential and enduring role in ancient societies, serving not only as text carriers but also fulfilling diverse functional and symbolic purposes.

The Tang-Tubo Road and the Tubo-Nepal Road, as branches of the Silk Road across the Qinghai-Tibet Plateau, served as vital corridors connecting central China with China Tibet, Nepal, and India since the Tang Dynasty (618–907 AD), facilitating trade, religious transmission, and tributary exchanges⁴. *The Old Book of Tang* (*Jiu Tang Shu* 舊唐書), the earliest

systematic historical record of the Tang Dynasty, contains detailed accounts of political figures, legal systems, major events, and foreign affairs, making it an essential primary source for Tang historiography. A notable passage states: “Tubo (633–842 AD, represents the Tibetan regime in ancient China), requested silkworm eggs, as well as artisans skilled in brewing, milling, papermaking, and ink production, all of which were granted”. This indicates that papermaking technology had been introduced into Tubo by at least 650 AD. Lhasa, as a key hub along the Tang-Tubo and Tubo-Nepal routes, became a center of cultural and technological exchange. With the spread of papermaking, paper production rapidly expanded across Tubo, particularly in Lhasa and Shannan city⁵. Numerous studies have been applied on the materials^{6–10}, pigments, and writing media^{11,12}, as well as crafts¹³ of Tibetan manuscripts across different periods, laying a foundation for understanding the development of manuscript craftsmanship of ancient Tibetans.

However, due to geographical constraints and limited transportation, external materials were rarely accessible to Qinghai-Tibet Plateau in large quantities. Before the introduction of paper, local communities utilized various alternative writing substrates, including bark, wooden tablets, and bamboo slips⁵. Even after the adoption of paper, materials such as palm leaves and birch bark remained in widespread use for Buddhist scripture transcription. Understanding how these multi-material manuscripts were produced and utilized is key to reconstructing Tibetan manuscript

¹Key Laboratory of Vertebrate Evolution and Human Origins of Chinese Academy of Sciences, Institute of Vertebrate Paleontology and Paleoanthropology, Chinese Academy of Sciences, Beijing, China. ²Department of Archaeology and Anthropology, University of Chinese Academy of Sciences, Beijing, China.

³Cultural Relics Preservation Institute, Tibet Autonomous Region, Lhasa, China. ⁴China Academy of Cultural Heritage, Beijing, China. ⁵School of Foreign Languages, Peking University, Beijing, China. ✉e-mail: jianghongen@ucas.ac.cn

production system. Yet, research in this area remains scarce, highlighting an urgent need for further investigation.

In 2023, during the restoration of a stupa at Taklung Monastery in Lhundrup County, Lhasa, Tibetan Autonomous Region (TAR), two fragmentary bark-like pieces bearing inscriptions were discovered. These samples provide rare and valuable material evidence for studying the utilization and production techniques of historical Tibetan manuscripts. This study employs non-destructive and minimally invasive analytical methods, including Thermally assisted Hydrolysis and Methylation Pyrolysis-gas chromatography/mass spectrometry (THM-Py-GC/MS) and Attenuated Total Reflection Fourier Transformed Infrared Spectroscopy (ATR-FTIR), to identify the material composition of the manuscript fragments. Additionally, hyperspectral imaging (HSI) and portable X-ray fluorescence (p-XRF) are utilized to recover textual content and characterize the ink. These findings offer new insights into the diverse material applications and craftsmanship of historical Tibetan manuscripts.

Methods

Site and sample information

Taklung Monastery is located in Lhasa, TAR (Fig. 1). As a principal monastery of the Kagyu Sect of Tibetan Buddhism, it holds significant religious and historical importance. Founded in 1180 AD, the monastery became a center for Buddhist teachings, attracting disciples and establishing the Taklung Kagyu lineage, which remains influential within Tibetan Buddhism.

The monastery complex covers an irregularly shaped area of approximately 87,500 m², with monastic quarters in the northern section and temple structures in the southern section. The manuscript samples were excavated from the ruins of ChoKhang Marbo (the red temple) (Fig. 1b) within the monastery, which underwent archaeological investigation between April and June 2023. The site yielded a variety of artifacts, including statues of diverse materials, ritual conch shells, stupas, fragmented ancient texts, religious implements, and *Tsha-tshas*. *Tsha-tshas* are small, molded clay votive tablets depicting Buddhas or stupas, regarded in Tibetan Buddhism as sacred objects for dispelling misfortune and invoking blessings.

The two manuscript fragments (sample number was designated as XZDL-1 and XZDL-2, respectively) were originally folded and embedded within a *tsha-tsha*, placed inside a statue (Fig. 2). These samples provide critical material evidence for studying the craftsmanship and utilization diversity of Tibetan manuscripts.

Radiocarbon dating

A small fragment (~1 mg) from sample XZDL-1 was submitted to the Chronology Laboratory of Lanzhou University for radiocarbon dating. Accelerator mass spectrometry (AMS) was performed using a MICADAS system, and the age result was calibrated using OxCal v4.4 with the IntCal 20 atmospheric curve.

Sample observation and imaging

Length, width, and thickness of the fragments were measured using a digital caliper. Surface morphology was examined under a Leica S9D stereo-microscope. Macroscopic images were captured with a Nikon D610 camera. To improve the readability of faded text, a handheld hyperspectral imager (SPECIM-IQ) was applied for data acquisition, followed by processing with a multispectral imaging system (Nuance EX, Cambridge Research & Instrumentation, Inc. (Cri)).

The multispectral images were tested using VNIR visible near-infrared band range from 450 to 720 nm with a spectral sampling of 10 nm. The ink and blank area spectra were selected as endmembers from the images, and the hyperspectral images were unmixed through the unmixing module accompanying Nuance EX. Fifteen images were taken for each of the two fragments separately, after which the images were spliced by PS 2018 software.

Thermally assisted hydrolysis and methylation pyrolysis-gas chromatography/mass spectrometry (THM-Py-GC/MS)

Samples were taken from blank areas with a mass of about 0.5 mg. Subsequently, they were placed in the sample cup. Derivatization was performed by adding 2 μ L of 25% tetramethylammonium hydroxide (TMAH) in

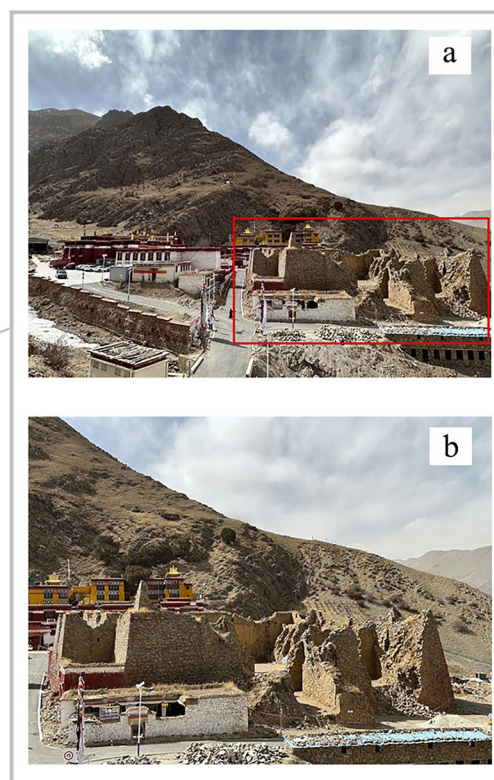
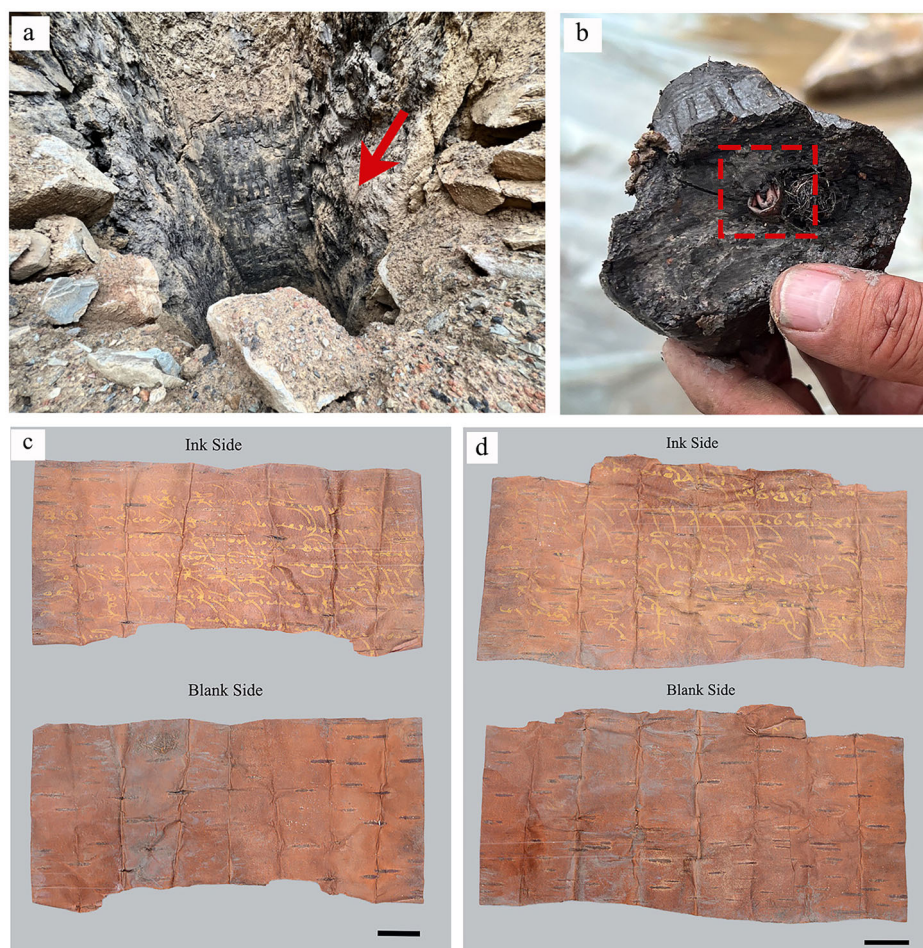


Fig. 1 | The location of the Taklung Monastery. a Exterior appearance of Taklung Monastery (the red box shows the location of ChoKhang Marbo), **b** Exterior view of ChoKhang Marbo (the red temple).

Fig. 2 | The excavation site of the manuscript samples. a Location of the *tsha-tsha* containing manuscripts fragments, **b** samples set inside the *tsha-tsha*, with the fragments shown in the red box, **c** picture of XZDL-1, **d** picture of XZDL-2 (scale bar = 1 cm).



methanol to the cup. Then, put the sample cup into the pyrolyzer (PY3030D, Frontierlab) for pyrolysis with a temperature of 500 °C. GC/MS instrument model was QP2030 NX, Shimadzu; inlet temperature was set at 300 °C in GC; samples were transferred by split injection technique, with a ratio of 20:1; the temperature program for the column was set as follows: initially maintained at 40 °C for 3 min, then increased to 350 °C at a rate of 10 °C per minute, and finally held at 350 °C for 5 min. Helium was utilized as carrier gas with a flow rate at 1 ml/min. The mass spectrometer was operated in electron ionization (EI) mode with an ionization energy of 70 eV, and the mass spectra were acquired over a range of m/z 45–550. NIST 2017 Libraries was used in compound identification.

Attenuated total reflectance fourier-transform infrared spectroscopy (ATR-FTIR)

Non-invasive surface analysis was performed using an Agilent 4300 handheld FTIR spectrometer (Agilent Technologies). Spectra were acquired in the 4000–650 cm^{-1} range with 4 cm^{-1} resolution and 64 scans. Data were normalized before visualization.

X-ray fluorescence (XRF) analysis

Qualitative and semi-quantitative X-ray fluorescence (XRF) measurements were performed on samples using a Bruker TRACER 5 g handheld spectrometer under a helium (He) atmosphere. The instrument utilized a detector equipped with a 1 μm graphene window, enabling the detection of elements ranging from Na ($Z = 11$) to U ($Z = 92$). The precious metal mode from the instrument was selected to test. The working parameters were 40 kv for excitation voltage; 11.5 μA for current; test time was 30 s. Tests were carried out for comparison between the ink area and the blank part of each sample, respectively.

Results

Radiocarbon dating

The radiocarbon dating results of the manuscript fragments are presented in Table 1. Sample XZDL-1 yielded a radiocarbon age of 787 ± 18 BP, which calibrates to 1224–1273 cal AD (95.4% confidence interval). Historical records indicate that Taklung Monastery was established in the late 12th century. The dating results place the fragments within the 13th century, align well with the monastery's construction and early usage period.

Information on the text of the fragments

The contents recorded on the two fragments primarily consist of Sanskrit dhāraṇīs transcribed in Tibetan cursive script, along with one Tibetan-written prayer. Dhāraṇīs generally refer to longer mantras with diverse content forms. Collectively, these two manuscript fragments express devotion to various Buddhist figures and convey aspirations for a blessed life.

The specific details revealed by hyperspectral imaging are as follows (Fig. 3):

XZDL-1

1. ... namo ma(ni)ratna ...
2. gu(h)y(a)ratna ma ... um̐ namo ratna .. ratna ..
3. thra vaṃ dmaṃ chu sa myed bu a ra sa ya sras dang d... dang ..
4. ri .. ru ma vya sa smyod (tsh)i(g) gsung bar sa grus cing rang sems
5. 'khrul pa dag pa dang | 'gro ba'i yon tan 'dus par shog | om̐
6. hriḥ ha ha hūm hūm phaṭ | om̐ om̐ om̐ sa(r)ba(buddha)ḍākiniye
7. vajravarm̐aniye vajrabhairaconiye(vajravairocaniye?)
8. .. bharimi ...
9. | om̐ bhāi ya | stem̐ ṇa rna ra .. man
10. ... | om̐ ...

Table 1 | Results of XZDL-1 radiocarbon dating

Lab. no.	Sample	14 C age (years BP)	Calibrated age, 2 σ -range (years AD)
LZU24369	XZDL-1	787 $\pm$ 18	1224–1273 (95.4%)

**Fig. 3 | Hyperspectral imaging of two manuscripts samples. a XZDL-1, b XZDL-2.****XZDL-2**

1. ...
2. ma ma ba bud re | .. vaṃ hūṃ hūṃ
3. svā (hā) || oṃ ḍākani ḍākani | recini recini | re
4. ṭani reṭani | trasani trasani | srarirana srarira |
5. sa | (ma)d sa ba ra ṇa saraṃ saraṇime guru svāhā ||
6. oṃ sarmaduṣṇīṣavi(ja)ya(par)isuddhe | hūṃ hūṃ svāhā
7. oṃ sa(rma)duṣṇīṣa(vija)ye hūṃ phaṭ || oṃ maṇi
8. padme hūṃ | oṃ bu svāhā ||

Note: ‘...’: multiple unrecognisable syllables; ‘..’: one indecipherable syllable; ‘.’: part of an indecipherable syllable; ‘()’: reconstructed syllable; ‘|’: separator.

The manuscript XZDL-1 contains two distinct genres: mantra and prayer. Notably, the mantra section demonstrates particular veneration for three key Buddhist deities: Sarvabuddhaḍākini, Vajravārṇanī, and Vajravairocanī. In contrast, XZDL-2 consists exclusively of mantra texts, featuring invocations to Ḍākini and Uṣṇīṣavijaya, both significant figures in Buddhist tradition. This fragment concludes with the auspicious six-syllable mantra, a particularly renowned and symbolically important mantra within Buddhist practice. Both fragments consistently reference objects of worship that exhibit strong connections to esoteric Buddhist traditions historically prevalent in the TAR.

Microscopic examination

The manuscript fragments XZDL-1 (89.42 × 43.30 × 0.18 mm) and XZDL-2 (94.90 × 48.24 × 0.13 mm) exhibit an irregularly shaped, brownish-yellow appearance. The upper and lower edges show clean, straight cuts indicating deliberate trimming, while the irregular lateral edges with abruptly terminated text suggest the complete manuscript was torn vertically (Fig. 4).

**Fig. 4 | Microscopic morphology of sample XZDL-1. Lenticels indicated by arrows.**

Multiple distinct east-west oriented creases indicate repeated folding prior to deposition. Combined with the observed surface creases and irregular central fracture patterns, this suggests intentional fragmentation to facilitate insertion into the narrow cavity of the statue. The crude tearing patterns imply rough handling during this process.

The rough surface texture displays 0.5–1.0 cm long black striations resembling the lenticels characteristic of birch bark. The reddish-brown coloration corresponds well with the active deeper cork layers (phelloderm) of birch. However, these morphological features alone are insufficient for definitive species identification, necessitating complementary analytical approaches.

ATR-FTIR analysis

Comparative analysis was conducted using modern birch bark (*Betula utilis*) samples as reference. The infrared spectra of the manuscript fragments showed remarkable similarity to the birch bark reference samples. The spectral features were characterized as follows (Fig. 5). The presence of characteristic peaks for lignin, hemicellulose, and carbohydrate components confirms the preservation of original organic components in the historical material. The close spectral match between the manuscript fragments and modern birch bark samples, particularly in the fingerprint region (1800–800 cm⁻¹), provides strong evidence for the bark origin of the writing substrate. Identification of vibration type of peaks and their origins was displayed in Table 2. Furthermore, the ancient samples exhibit high morphological and compositional similarity to modern counterparts, suggesting their well-preserved condition. These samples were found deeply compacted within *tsha-tsha*, which may have provided a unique environment conducive to their preservation.

ATR-FTIR spectroscopy offers a viable method for identifying ink components, including binders, pigments, and adhesives^{14,15}. However, in this study, the spectral signals corresponding to these compounds were

notably weak. Comparative analysis of blank and inked areas revealed a high degree of spectral similarity, suggesting minimal detectable differences. This

limitation likely arises from matrix effects caused by the substrate, compounded by the extreme thinness of the ink layer.

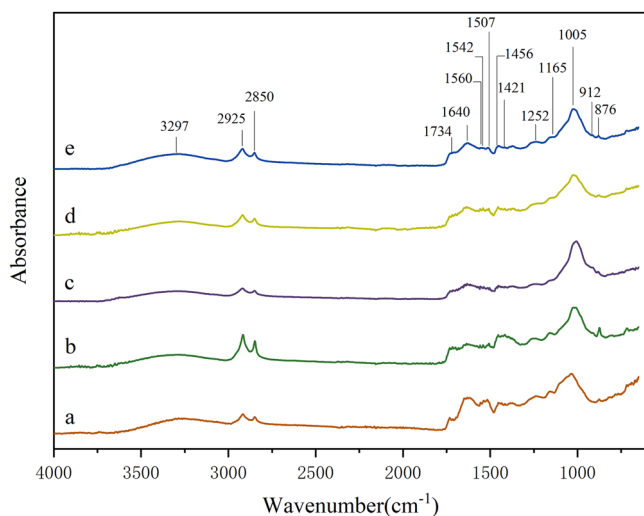


Fig. 5 | Infrared spectral results of samples. a modern birch bark (*Betula utilis*), **b** XZDL-1, **c** XZDL-2, **d** ink area of XZDL-1, **e** ink area of XZDL-2.

Table 2 | Positions of peaks in infrared spectra and corresponding vibration types

Wave number(cm^{-1})	Assignment	Reference
3286	O–H stretching of aromatic and aliphatic compounds	
2917	Asym. CH_2 stretching	
2844	Sym. CH_2 stretching	
1734	C=O stretching vibration in acetyl groups	45
1640	Adsorbed H_2O	46
1425–1560	Aromatic skeletal vibrations	47,48
1252(peak in literature: 1266–1270)	G ring plus C=O stretching	45,46
1165(peak in literature: 1160)	Aromatic C–H in plane deformation; typical for G units	45,46
1005	C–O stretching of carbohydrate	
912	Asym. out-of-phase ring stretching	46
<900	Out of plane CH_2 deformation	

THM-Py-GC/MS analysis

THM-Py-GC/MS analysis identified multiple triterpenoid compounds eluting between 30.00 and 37.00 min (Fig. 6; Table 3). Comparative analysis with reference literature^{16,17} and the NIST 2017 mass spectral library confirmed the presence of lupane-type, oleanane/ursane-type, and other pentacyclic triterpenoids.

The mass spectrum exhibited a characteristic high-abundance fragment ion at m/z 189 (Fig. 7a), diagnostic for lupane-type triterpenoids. This signature fragment originates from C-ring cleavage at the C9–C11 and C8–C14 bonds, followed by elimination of a water molecule from the C3-hydroxyl group. Three prominent compounds (29, 24, and 27) showed distinctive fragmentation patterns at m/z 262, 203, and 189, characteristic of methyl oleanolate derivatives (Fig. 8). Specifically: m/z 262 results from retro-Diels–Alder (RDA) cleavage of the D/E rings. m/z 203 derives from A/B ring demethoxylation. m/z 189 arises through D/E ring demethylation.

Furthermore, compounds 33 and 36 demonstrated concurrent fragment ions at m/z 189 and 203, confirming their pentacyclic triterpenoid nature. The analysis also revealed substantial quantities of co-eluting compounds, including fatty acid esters, aromatic methyl ethers, and aliphatic hydrocarbons (Table 3).

It is widely recognized that birch bark is primarily rich in a series of lupane-type derivatives, and minor amounts of oleanane- and ursane-type triterpenoids^{18–22}. These terpenoids exhibit high chemical stability and can be detected not only in fresh birch bark but also in archaeological samples subjected to prolonged burial^{23,24}, making them crucial biomarkers for determining the plant origin of such materials. Py-GC/MS analysis of ancient birch bark tar readily yields a characteristic series of lupane-type triterpenoids^{16,17}, which share a compositional profile similar to that of birch bark itself²⁴.

In this study, a significant abundance of lupane-type triterpenoids, along with trace amounts of oleanane-type triterpenoids, was detected, strongly supporting a close association with the genus *Betula*. However, in addition to terpenoids, birch bark also contains suberin, procyanidins, lignin, and other macromolecular constituents. Further analysis of these additional components could provide more definitive evidence for identifying the precise material source of the manuscript fragments.

The TMAH derivatization coupled with Py-GC/MS proves highly effective in detecting components containing polar functional groups such as esters. This method facilitates the cleavage and methylation of macromolecules at polar functional groups while minimizing the fragmentation of alkyl C–C bonds, thereby preserving alkyl chain length information to the greatest extent. The TMAH derivatization typically converts hydroxyl groups into methoxy groups, yielding derivatives such as ethers and esters.

Fig. 6 | Total Ion Chromatogram (TIC) of sample XZDL-1.

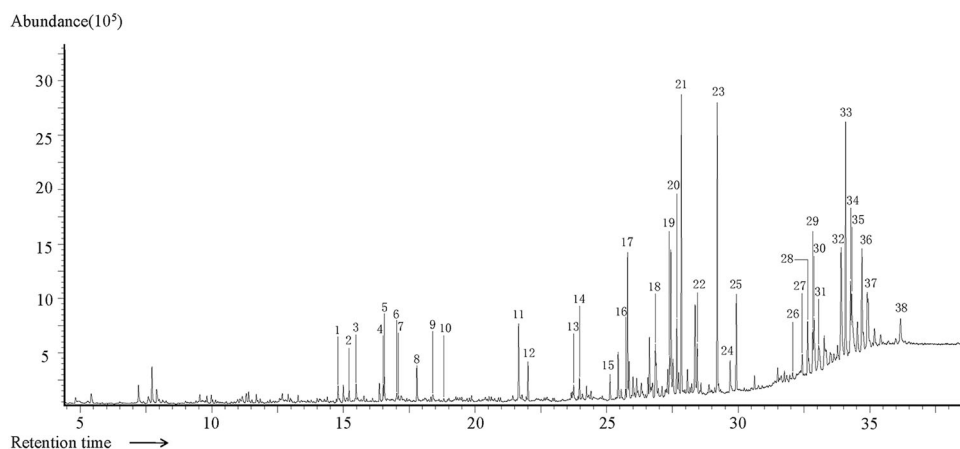
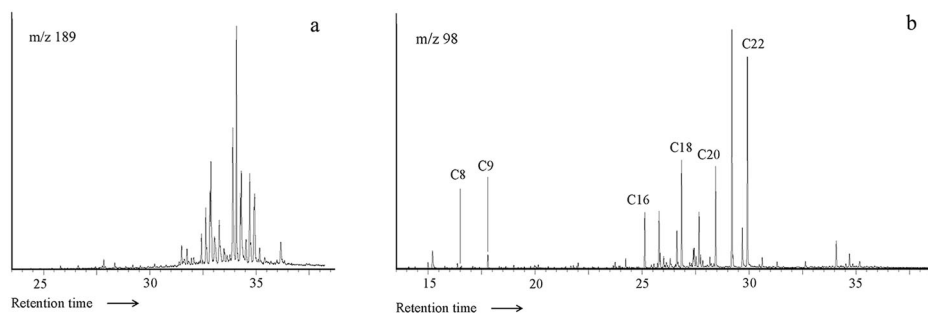


Table 3 | Pyrolysate of ancient fragments of XZDL-1 (No. corresponds to Fig. 6)

No.	Retention Time/min	Compound	Fragment ions (ranked by decreasing order of intensity)	MW
1	14.79	2-Methoxy-4-vinylphenol	150, 135, 77, 107, 79	150
2	15.21	8-Methoxyoctanoic acid, methyl ester	45, 55, 74, 124, 96	188
3	15.48	Benzene, 4-ethenyl-1,2-dimethoxy-	164, 91, 77, 149, 103	164
4	16.51	Octanedioic acid, dimethyl ester	69, 55, 74, 97, 129	202
5	16.56	5-Nonenoic acid, methyl ester	45, 74, 55, 138, 87, 171	170
6	17.03	Benzaldehyde, 3,4-dimethoxy-	166, 95, 77, 51, 79	166
7	17.09	3-Octadecene	55, 69, 83, 97, 111	252
8	17.79	Nonanedioic acid, dimethyl ester	55, 74, 83, 152, 111	216
9	18.39	Benzoic acid, 3,4-dimethoxy-, methyl ester	165, 196, 79, 51, 125	196
10	18.81	1,2-Dimethoxy-4-(2-methoxyethenyl) benzene	194, 151, 179, 91, 119	194
11	21.66	2-Propenoic acid, 3-(3,4-dimethoxyphenyl)-, methyl ester	222, 191, 91, 77, 207	222
12	22.01	Hexadecanoic acid, methyl ester	74, 87, 55, 143, 69, 270	270
13	23.75	7-Octadecenoic acid, methyl ester	55, 69, 81, 96, 74	296
14	23.97	Methyl stearate	74, 87, 55, 143, 69, 298	298
15	25.13	Hexadecanedioic acid, dimethyl ester	98, 55, 74, 84, 69	314
16	25.72	Methyl 9-eicosenoate	55, 74, 69, 83, 97	324
17	25.79	3,13-Octadecadien-1-ol	55, 45, 81, 67, 95	266
18	26.85	Octadecanedioic acid, dimethyl ester	98, 74, 55, 84, 69	342
19	27.39	Methyl 11-docosenoate	55, 69, 74, 83, 97, 352	352
20	27.67	11-Eicosenoic acid, methyl ester	45, 55, 74, 87, 97, 324	324
21	27.84	Unknown	74, 81, 201, 45, 67	
22	28.44	Eicosanebioic acid, dimethyl ester	98, 74, 55, 69, 84, 368	370
23	29.20	13-Docosenoic acid, methyl ester	45, 55, 74, 69, 83, 352	352
24	29.69	Methyl 22-hydroxydocosanoate	55, 74, 98, 87, 69	370
25	29.93	Docosanedioic acid, dimethyl ester	98, 74, 55, 69, 84, 397	398
26	31.75	Lupane-type triterpenoids	93, 189, 107, 121, 81	
27	32.43	Lupane-type triterpenoids	189, 91, 105, 119, 134	
28	32.64	Lupane-type triterpenoids	95, 109, 119, 393, 189	
29	32.83	Oleanic acid, methyl ester derivatives	203, 262, 189, 133, 119	
30	32.88	Lupane-type triterpenoids	189, 93, 107, 119, 121	
31	33.05	Lupane-type triterpenoids	93, 107, 189, 121, 119	
32	33.91	Lupane-type triterpenoids	189, 95, 107, 119, 81	
33	34.08	Pentacyclic triterpenoids	95, 203, 189, 81, 71	
34	34.26	Oleanic acid, methyl ester derivatives	203, 262, 133, 189, 119	
35	34.31	Lupane-type triterpenoids	189, 81, 93, 55, 107	
36	34.70	Pentacyclic triterpenoids	203, 95, 81, 189, 69	
37	34.90	Oleanic acid, methyl ester derivatives	203, 262, 133, 119, 69	
38	36.16	Lupane-type triterpenoids	207, 95, 81, 69, 189	

Fig. 7 | Extracted ion chromatogram (EIC) of sample XZDL-1. a lupane-type triterpenoids, **b** dimethyl esters.

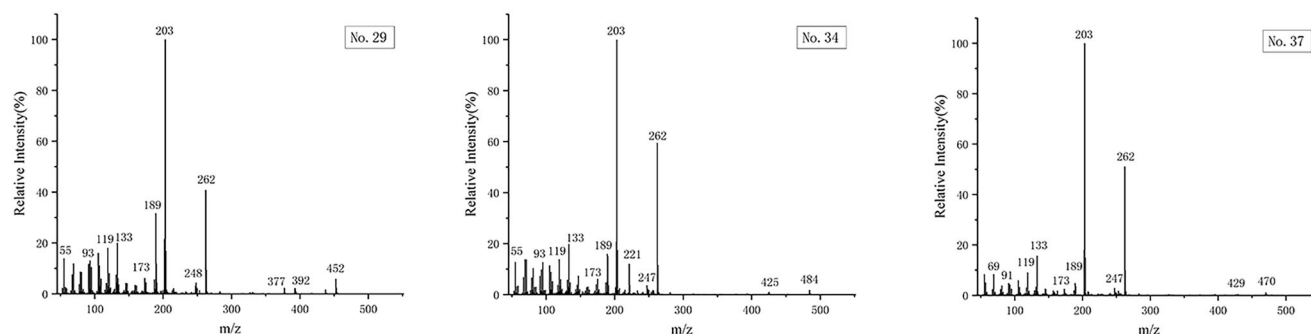


Fig. 8 | Mass spectra of three oleanane-type methyl ester derivatives (numbering corresponds to Table 3 and Fig. 6).

The analytical results revealed that the birch bark excavated from Taklung Monastery contains a substantial abundance of methyl esters and methyl ether derivatives, including saturated and unsaturated fatty acids, as well as methyl esters of ω -hydroxy fatty acids. Additionally, a series of long-chain dicarboxylic acids were identified. Previous studies have demonstrated that long-chain dimethyl esters, formed through derivatization of dicarboxylic acids, typically produce characteristic fragment ions at m/z 98 during mass spectrometric cleavage (Fig. 7b)^{25,26}. The ion chromatograms obtained in this study confirmed the presence of multiple dimethyl esters of dicarboxylic acids (peaks 4, 8, 15, 18, 22, and 25), with carbon chain lengths predominantly ranging from C8 to C22 and showing an even-numbered carbon preference. Among these, compounds with C16, C18, and C22 carbon chains exhibited the highest peak intensities. In addition to carboxylic acid derivatives, the results also indicated the presence of unsaturated aliphatic alcohols (peak 17) and linear alkenes (peak 7).

Multiple studies have demonstrated that birch bark tar contains not only a series of terpenoids but also homologous linear saturated/unsaturated mono- and dicarboxylic acids, n -alkenes, n -alkanes, and ω -hydroxy fatty acids^{16,17,27}. These compounds are likely derived from suberinic biopolymers and may serve as diagnostic criteria for birch bark identification.

In this study, the detected carboxylic acid derivatives exhibited remarkable structural similarity to the monomeric constituents of suberin—a biopolyester primarily composed of hydroxy, epoxy, and dicarboxylic acids. Upon derivatization and depolymerization, suberin typically yields C16, C18, C22, and C24 ω -hydroxy fatty acids and dicarboxylic acids as dominant components^{28,29}. The abundant presence of suberin-derived compounds in our pyrolysis results aligns with previous findings on birch bark tar, further validating the reliability of our analytical approach.

Notably, several aromatic dimethyl ether derivatives (peaks 3, 6, 9, 10, 11) were identified. These compounds are characteristic pyrolysis products of guaiacyl (G)-type lignin, originating from residual lignin in the bark. The detection of G-type lignin is consistent with the ATR-FTIR results. Unlike the xylem of most angiosperms where syringyl (S)-type lignin predominates, birch bark has been reported to contain significantly higher proportions of G-type lignin²⁸, likely reflecting tissue-specific physiological differences within the same plant. The predominance of G-type lignin in our samples provides additional evidence supporting the compositional consistency between the manuscript fragments and birch bark.

Composition analysis of manuscript inscriptions

Combined with spectral feature analysis, two samples primarily contain five main elements ($>0.1\%$): Au, Fe, Cu, Rh, and Pd. Among these, Rh and Pd are elements generated by the instrument itself during testing and can thus be excluded as contributors to the sample composition.

In these two samples, the content of Au is significantly elevated in the ink areas, with spectral results showing that the energies of Au La and Au Ma are markedly higher than those in blank regions. In contrast, the peak energies of Fe Ka and Cu Ka exhibit no significant variation, indicating similar concentrations in both the ink and blank areas (Fig. 9; Table 4). This suggests that the written portions contain a higher content of Au. Naturally

grown birch bark is primarily composed of organic matter and typically contains minor amounts of metallic elements. The presence of these Fe and Cu elements may be associated with the burial environment of the samples.

Discussion

Birch bark, as a writing material with a long history, has been documented across various cultures worldwide. During the 19th century, several birch bark manuscripts were discovered in Central Asia, including the Bower Manuscript, the Bajaur Collection, the Gāndhārī Dharmapada (Kharoṣṭhī script), and the Gilgit Manuscripts. Among these, the Bower Manuscript was first unearthed in Kucha, Xinjiang Uygur Autonomous Region, China, and later acquired by Lieutenant Hamilton Bower of the British Indian Army in the late 19th century. Currently housed in the Bodleian Library at the University of Oxford, this manuscript comprises 56 birch bark folios inscribed with ancient Sanskrit in Brāhmī script. Dating to the 4th–6th centuries AD, it preserves invaluable content on early Indian medicine, divination, and other subjects, holding significant historical and scholarly importance.

Since the 1990s, numerous fragments and scrolls of Kharoṣṭhī-script birch bark manuscripts (1st century BC–3rd century AD) have been recovered, predominantly containing Buddhist texts³⁰. Beyond religious purposes, birch bark served diverse functions—recording letters, contracts, legal agreements, debt records, and legal codes³¹, highlighting its versatility as a writing medium. Its utilization persists into modern times, with documented examples from India, Northeastern China, Afghanistan, Pakistan, the North American Great Lakes region, Novgorod (Russia), and Mongolia^{30,32,33}, typically surviving as fragments or bound codices.

In India, birch bark itself was regarded as sacred. In addition to its role as a writing substrate, it was fashioned into amulets enshrined in stupas or worn as personal talismans³⁴. Excavations in Kashmir, Afghanistan, and Pakistan have yielded abundant birch bark fragments, often stored in clay jars or stupas³⁵. This deliberate deposition reflects a ritual practice aimed at preserving sacred Buddhist scriptures. Some fragments were even placed within the hands of Buddha statues. Paleographic analysis of Kharoṣṭhī fragments reveals that their contents predominantly feature Buddhist texts in varied literary forms, distinguishing their ritual function from intact sutra scrolls.

The birch bark manuscript from Taklung Monastery was discovered inside a small *tsha-tsha*—a clay votive stupa prevalent in Tibetan Buddhism, typically used as filler material within larger stupas³⁶. The bark had been intentionally folded and stored within the figurine, inscribed with Buddhist hymns and mantras. This depositional context parallels ancient practices in Gandhara, underscoring a shared religious intentionality. The Taklung manuscript thus exemplifies not only textual transmission but also the symbolic significance of its materiality, reflecting the multifaceted cultural perceptions and utilitarian diversity of writing materials in ancient TAR.

The Qinghai-Tibet Plateau is rich in birch (*Betula* spp.) resources. As a genus of deciduous trees widely distributed across the boreal and temperate zones of the Northern Hemisphere, *Betula* comprises approximately 100 species, many of which thrive in high-altitude and high-latitude regions.

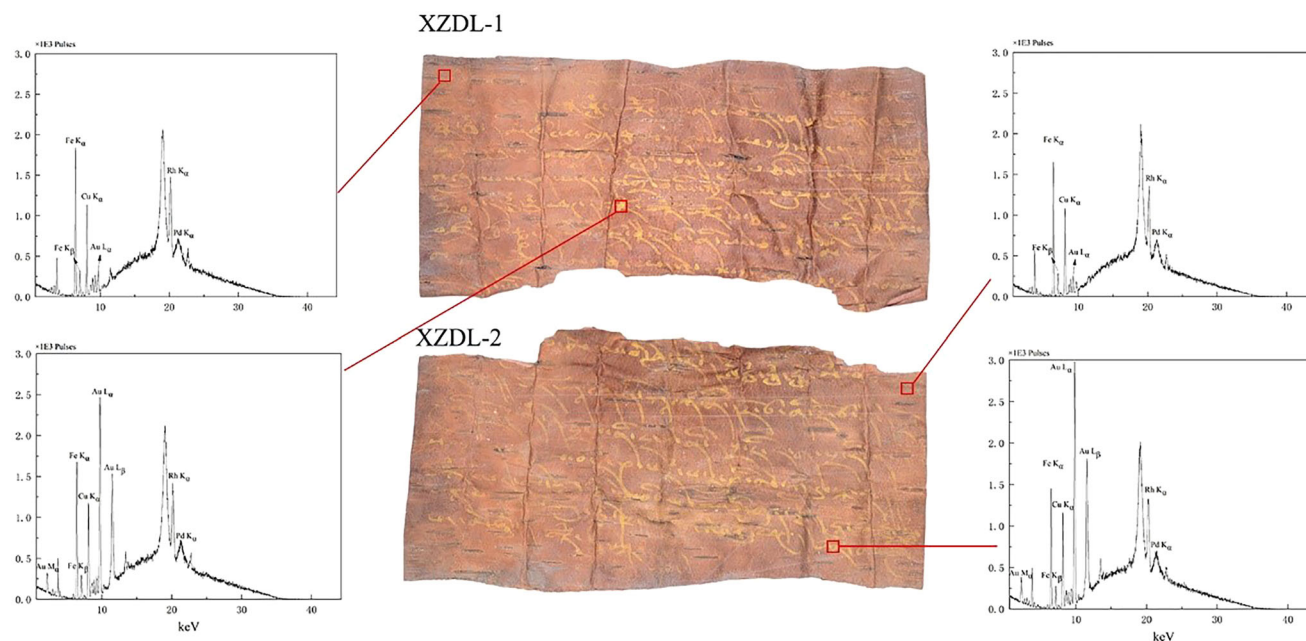


Fig. 9 | XRF spectral data of sample XZDL-1 and XZDL-2.

Table 4 | Percentage of main metallic elements of ink and blank areas in two samples

Elements	Relative amounts in different parts of the sample(wt/%)			
	XZDL-1		XZDL-2	
	Ink	Blank	Ink	Blank
Au	26.79	5.14	32.56	5.22
Cu	8.14	8.02	7.05	8.88
Fe	12.39	15.49	11.77	15.71
Rh	18.78	24.85	17.20	24.79
Pd	11.7	15.88	10.94	15.21

Within the alpine vegetation zone of the Qinghai-Tibet Plateau, 12 birch species have been documented, including *Betula alnoides*, *Betula cylindrostachya*, *Betula utilis*, and *Betula platyphylla*^{37,38}. Notably, *Betula utilis* (Himalayan birch) is widely distributed across the Himalayan range at elevations of 2700–4500 m³⁹. Given the region's geographical constraints and limited access to external resources, locally abundant birch species likely served as the primary raw material for producing manuscript fragments.

The Himalayan orogeny endowed Qinghai-Tibet Plateau with abundant mineral resources, including typical gold deposits and gold-bearing ore belts⁴⁰. Historical records indicate that gold mining and utilization flourished during the Tubo Dynasty. *The Old Book of Tang* notes that Tubo abounds in gold, silver, copper, and tin and all of comparable quality. A document unearthed in Dunhuang recounts that in the summer of the Dog Year (746 AD), the King hosted a banquet at the *Gserkhung* (gold mine). These accounts confirm gold mining activities in Tubo prior to the 7th century.

Tibetan metalworking technology was equally advanced. *The Cefu Yuanguai* (冊府元龜), a Song Dynasty encyclopedic historical text, documents that Tibetans had mastered quenching techniques for metal processing. A gilded forged copper bowl excavated from a Tibetan tomb in Tzethang, Shannan City⁴¹, further attests to sophisticated metallurgical skills during the Tubo Dynasty³³. *The Old Book of Tang* also records that in 736 AD, Tubo King sent envoys to the Tang court bearing “hundreds of gold and silver artifacts of extraordinary craftsmanship.” These evidences collectively

demonstrate advanced capabilities in mining, metallurgy, and metal artistry in Tubo Dynasty.

Within this well-established mining and processing system, the gold ink employed in the Taklung manuscript was likely produced locally. While pure gold represented the most prestigious material for gold-like inks, its prohibitive cost led to the development of alternative preparation methods as documented in historical Tibetan texts. One such method involved blending ‘equal parts gold or glue, thickened sesame oil, and copper’ to create a more affordable substitute⁴². In this study, the Taklung manuscript’s gold-like ink consists predominantly of gold. Comparative analysis between ink and blank area showed no significant variation in Cu. The notably high gold concentration further attests to the manuscript’s exceptional cultural and material value.

Gold-like ink is commonly observed in Buddhist scriptures, typically applied to dark-colored paper (e.g., indigo or black), like dark-blue paper, to enhance visual contrast through the interplay of dark backgrounds and luminous script. Dark-blue paper was traditional Tibetan writing material and produced through an elaborate manufacturing process. When combined with gold ink, it was considered as deluxe edition and was precious material symbolizing great sanctity and highly cherished⁴³. While numerous Tibetan literary sources document the use of gold ink in manuscript production, detailed descriptions of the accompanying writing materials remain conspicuously absent from these records. In particular, the question of whether all such manuscripts employed dark-blue paper as their substrate remains unresolved in current scholarship^{42,44}. In this study, we provide the evidence for the use of gold ink on birch bark in Tibetan manuscript production. This discovery offers new insights into the diversity of Tibetan manuscript production techniques.

Through a comprehensive analytical approach involving radiocarbon dating, morphological examination, ATR-FTIR, and THM-Py-GC/MS, this study has successfully identified the manuscript fragments excavated from Taklung Monastery as birch bark, dating to approximately the 13th century. Furthermore, p-XRF analysis revealed that the ink used in the manuscripts was predominantly composed of gold (Au). The manuscript’s content and archaeological context indicate that these birch bark manuscripts served religious purposes. The availability of local resources and a well-developed metal production system provided the foundation for local production. Notably, this study reports the utilization of gold ink on birch bark, which offers significant insights into the manuscript craft of ancient Tibetan during the 13th century.

Data availability

The datasets used in this study are available from the corresponding author upon reasonable request.

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Author contributions

Conceptualization: Q.C., H.J.; Methodology: Q.C., S.W., Y.Y.; Formal analysis, Writing-original draft: Q.C.; Writing -review and editing: H.J., T.T.; Resources: T.T.; Text information analysis: E.S.; Project administration, Supervision: H.J. All authors reviewed and approved the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to Hongen Jiang.

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