

Non-invasive pigment identification at the Yungang Grottoes (Caves 7–8): a chemically corroborated spectral library

Bo Ning

Yungang Academy

Lihong Li

Yungang Academy

Wenxiu Wan

wanwx3@mail2.sysu.edu.cn

Sun Yat-sen University

Ziru Yu

Sun Yat-sen University

Xiangyang Yu

Guangzhou Guangxin Technology Co., Ltd.

Yuchen Guo

Guangzhou Guangxin Technology Co., Ltd.

Shuqiang Lyu

Beijing University of Civil Engineering and Architecture

Kunxi Qu

Guangdong University of Technology

Article

Keywords: Yungang Grottoes, hyperspectral technology, three-tier spectral library, spectral matching, chemical corroboration

Posted Date: September 29th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11060674/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Non-invasive pigment identification at the Yungang Grottoes (Caves 7–8): a chemically corroborated spectral library

Bo Ning¹, Lihong Li¹, Wenxiu Wan^{2,*}, Ziru Yu^{3,**}, Xiangyang Yu⁴, Yuchen Guo⁴,
Shuqiang Lyu⁵, Kunxi Qu⁶

¹Yungang Academy, Datong 037007, China.

²School of Physics, State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-sen University, Guangzhou 510275, China.

³School of Electronics and Communication Engineering, Sun Yat-Sen University, Shenzhen 518107, China.

⁴Guangzhou Guangxin Technology Co., Ltd., Guangzhou 510300, China.

⁵School of Geomatics and Urban Spatial Informatics, Beijing University of Civil Engineering and Architecture, No. 15 Yongyuan Road, Daxing District, Beijing 102616, China.

⁶School of Physics and Optoelectronic Engineering, Guangdong University of Technology, Guangzhou 510006, China.

Contributing authors: ningbo007@163.com; wanwx3@mail2.sysu.edu.cn; yuziru@mail.sysu.edu.cn;

Abstract

Cultural relics constitute a precious part of human cultural heritage, making the early and comprehensive recording of their digital information increasingly urgent. Pigment identification on painted relics, however, remains hampered by scarce reference spectral databases, by library construction and validation protocols ill-suited to the task, and by the absence of site-specific pigment libraries. Here we construct a three-tier reflectance spectral library for Caves 7 and 8 of the Yungang Grottoes (Datong, China), combining commercial pigment standards, references migrated from public libraries and a Yungang-specific archive. In situ point spectra are matched within colour families against the library using a weighted score combining spectral angle mapping (SAM) and Euclidean distance, converted into a graded decision via two thresholds. Migrating the reference spectra increased gypsum re-identification from 0/15 to 14/15. On chemically confirmed reference points, pigment-group accuracy under leave-one-out re-fitting was 88.0% (95% confidence interval (CI) 78.7–93.6%), and the high-confidence zone covered 40.0% of points with no errors. Raman spectroscopy and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) revealed later interventions, including repainting containing emerald green. We thus establish a pigment classification and distribution survey of Caves 7–8, yielding a unified pigment inventory, and complete the application by transferring from point spectra to wall-scale hyperspectral imagery. This three-tier library framework is readily transferable to other painted heritage sites and provides a spectroscopic basis for long-term conservation monitoring and informed restoration decisions.

Keywords: Yungang Grottoes; hyperspectral technology; three-tier spectral library; spectral matching; chemical corroboration

1 Introduction

Pigments are the material basis of polychrome relics: what the paints are made of bears on two distinct questions — how the caves were decorated and redecorated over time, and how what survives should now be conserved. The Yungang Grottoes (Datong, Shanxi Province, China) were carved mainly in the fifth century CE and inscribed on the UNESCO World Heritage List in 2001; they preserve one of the world’s largest ensembles of polychrome stone sculpture, but centuries of weathering, dust deposition and repeated repainting have blurred the palette, and the sandstone beneath it is chemically active: salt crystallisation and sulphation are documented deterioration processes at the site [1]. Once pigments degrade or flake off, the information they carry is unrecoverable. Building a pigment spectral library and recording the pigments over the long term is therefore an urgent task.

Sampling-based analysis has long supplied the reference picture of grotto polychromy [2, 3], and its authority is hard to match: a micro-sample submitted to Raman spectroscopy or electron microscopy identifies a phase outright. But every extraction is irreversible, and on surfaces that may have been renewed many times, sampling can never approach the spatial scale on which the paint actually varies. Non-invasive in-situ identification makes the opposite trade, accepting lower specificity per measurement in return for full-surface coverage and no damage [4–7]. Among non-invasive techniques, visible–shortwave-infrared (VNIR–SWIR) reflectance spectroscopy occupies the complementary position [8, 9]: one spectrum carries both the electronic transitions diagnostic of chromophores and the vibrational overtones of hydroxyl, structural water and carbonate, it is acquired in seconds at arm’s length, and the same measurement principle scales from single points to imaging. What a reflectance spectrum does not carry is an intrinsic identification: it names a pigment only by comparison with a reference.

That comparison is only as good as the collection behind it, and such collections have been assembled for three decades, mostly for point-based techniques: the Raman libraries of Bell et al. [10] and of Burgio and Clark [11]

remain standard references in conservation science. Reflectance and imaging collections have multiplied more recently, abroad and in China alike. Cosentino’s FORS database offers downloadable spectra of 54 historical pigments in four binders but stops at the near-infrared [12]; the INFRA-ART open-access library integrates ATR-FTIR, Raman, XRF and shortwave-infrared reflectance for over 900 reference materials [13]; and the HYPERDOC dataset provides 1681 hyperspectral datacubes of historical documents and ink mock-ups over 400–1700 nm [14]. In China, the Dunhuang Academy established a standard multispectral image database of 29 paint materials used in the Dunhuang murals [15], and the online TPP spectral library of typical pigments used in Chinese paintings was built at the Beijing University of Civil Engineering and Architecture [16]. None of these, however, was built as a reflectance matching library for the materials of Yungang.

Existing collections share three limitations, and each shapes one part of the present design. The first is coverage: standards are mostly laboratory pure materials, not cross-anchored against micro-analysis of the site itself, so the commercial mineral pigments used in modern restoration at Yungang and the site’s own alteration products are absent, and real aged surfaces are poorly represented [12, 13]. The second is reliability: existing collections do not grade their answers, so on aged, dust-covered and intimately mixed paint, forcing every measurement into a best-match label returns assignments more confident than the evidence warrants, a concern also raised by recent reliability-graded work on sooty murals [17]; what is needed is a decision that carries a grade and can decline to name. The third is chronology: existing collections do not screen candidates by period either, yet where overpaintings of different periods share one wall, a spectrally plausible candidate may be historically impossible, so candidates must be screened for chronological plausibility before they are named.

The main work of this paper is as follows. (1) A tiered and transferable construction method for a pigment spectral library is proposed, which combines commercial standards, public-library references migrated under an explicit

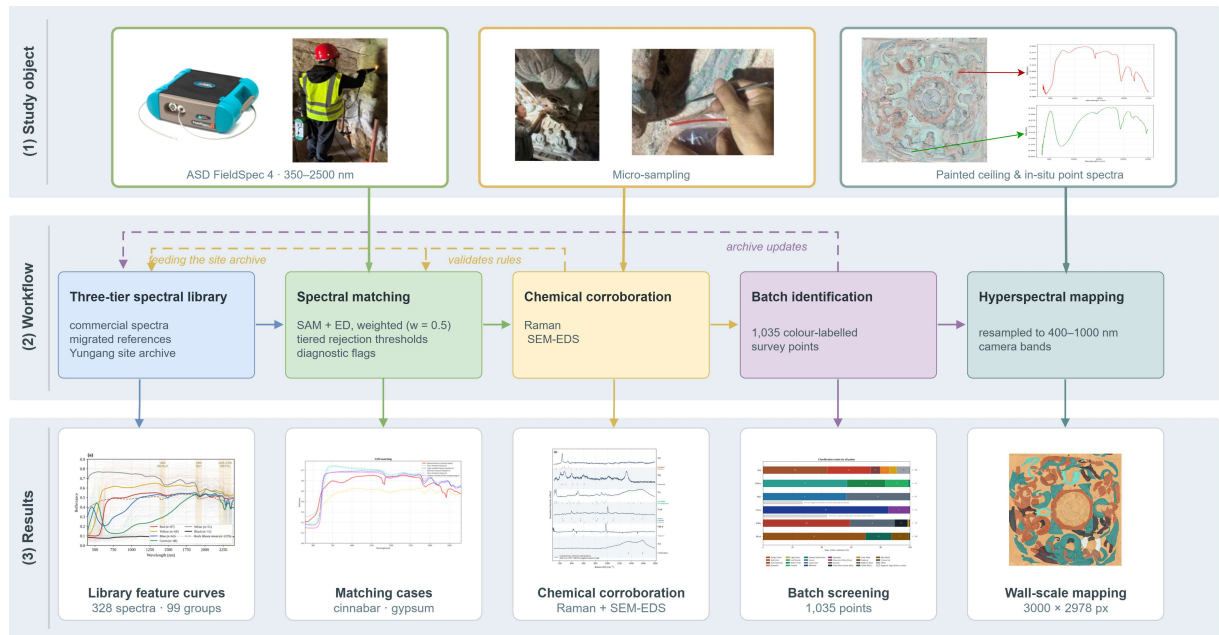


Fig. 1 Overall study design: the painted surfaces of Caves 7–8, measured by in-situ point reflectance spectra and representative micro-sampling, pass through the workflow from the three-tier spectral library to chemical corroboration (Raman, SEM-EDS), identification of the 1035 survey points and wall-scale hyperspectral mapping, with representative outputs of each module shown below; dashed links mark feedback into the site archive.

shape check and dual validation, and a Yungang-specific archive anchored by Raman and SEM-EDS micro-analysis. (2) Pigments are identified by weighted spectral matching of the spectral angle mapper and Euclidean distance, with fitted rejection thresholds converting match scores into graded decisions and a reference that post-dates the site raising a chronological-anomaly flag instead of a name. (3) The procedure is applied to all 1035 colour-labelled survey points of the two caves, yielding the unified pigment inventory of Caves 7–8. (4) The application is completed by a transfer path from point spectra to wall-scale hyperspectral imagery. Figure 1 summarises the design.

2 Materials and methods

2.1 Study site and painted surfaces

The survey plan follows the architecture. Each of the two caves comprises a front and a rear chamber, with domed ceilings, arched doorways, attic storeys and numerous niches, and surviving polychromy occurs on sculpted figures, architectural members and ceiling coffers. Measurements were

therefore organised by structural unit — front chamber, rear chamber, arch, dome, attic and key niches — so that every colour family was covered, with important niches and domes sampled at higher density. Numbered layers cited below, such as arch layer 3, refer to the working levels of the scaffolding erected from bottom to top inside the caves (six levels in each cave), on which the instruments were positioned during acquisition.

2.2 Instrumentation and data acquisition

Point reflectance spectra were collected in situ with an ASD FieldSpec 4 portable field spectrometer covering 350–2500 nm (Table 1), which yields 2151 channels at 1 nm spacing from three detectors: a silicon photodiode array and two thermoelectrically cooled InGaAs detectors. The ASD FieldSpec 4 uses a holographic diffraction grating for spectroscopic analysis. When composite light from the sample strikes the grating, light of different wavelengths is diffracted and reflected at different angles, thereby spatially separating it into a series of monochromatic beams of different wavelengths, which are then precisely measured

Table 1 Specifications of the instruments

Parameter	ASD FieldSpec 4	GX-0410H
Spectral range	350–2500 nm	400–1000 nm
Spectral resolution	3 nm	2.8 nm
Channels	2151	300
Acquisition	Point measurement	Push-broom line scan, 1920 pixels per line

by a three-detector system optimized for different wavelength bands. The instrument measures $12.7 \times 35.6 \times 29.2$ cm, weighs 5.44 kg, and the acquisition probe carries an internal halogen lamp. Acquisition followed a fixed routine: 20 min warm-up; white-reference calibration at each acquisition session and whenever the illumination changed; multiple spectra per point acquired and averaged, with positions marked on colour photographs; and immediate re-measurement whenever wavelength drift, abnormal reflectance or excessive noise appeared. Ambient illumination was kept as low as practicable to suppress stray light. Representative points were micro-sampled for corroborative Raman and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) analysis. Sampling points were chosen to cover the six colour families across the main structural units and scaffold levels, with priority given to points representative of the principal identifications. Wall-scale mapping uses a push-broom hyperspectral camera (GX-0410H, Guangzhou Guangxin Technology Co. Ltd) operating as a grating line scanner over 400–1000 nm, with 2.8 nm spectral resolution (FWHM) in 300 channels, 1920 spatial pixels per line (Table 1).

2.3 A tiered, transferable reflectance spectral library

The unified library is organised in three tiers. The first is a commercial standard set collected in the laboratory: 60 commonly used pigments, mainly mineral with a few plant-based and synthetic products, from three Chinese suppliers (Jiangsixutang, Tianya and Jinyuan Sunshine), comprising 269 spectra in 90 brand-grade groups. The second consists of mineral references migrated from

public libraries: 55 spectra from the USGS splib-derived rock library (gypsum, celestite, haematite and nano-haematite, goethite, limonite and malachite) and 4 from the ECOSTRESS/JPL library (anglesite SO-10A and atacamite H-4A in three grain sizes) [18, 19], totalling 59 migrated spectra in 9 groups. The unified identification library thus comprises 328 spectra in 99 groups. A full rock library of 1276 common rock-forming mineral spectra is kept separately, for recognising bare stone and weathering crusts.

The third tier is the Yungang-specific archive, built from the results of chemical detection and spectral matching: whenever micro-analysis confirms a pigment group or a characteristic mixture on in-situ points, the mean spectrum of those points enters the archive as an identification entry. The archive therefore grows as the chemical work proceeds, and its composition as established here is reported together with the micro-analytical evidence.

Candidate spectra from outside enter the unified library only through a three-step admission process, which applies both to references migrated from public libraries and to new archive entries added as the chemical corroboration campaign proceeds. In step 1, shape screening, a candidate’s value range and absorption features must be consistent with the target mineral, so that mislabelled, overly noisy or instrument-incompatible spectra are removed before they can participate in matching. In step 2, import with dual validation, admitted candidates take effect only if neither re-identification accuracy on the chemically confirmed reference points (Sect. 3.2) nor library leave-one-out cross-validation (LOOCV) accuracy degrades; if either does, the whole batch is rolled back, so that performance cannot silently decline as the library grows. In LOOCV, each library entry is held out in turn and reclassified against the remainder. In step 3, size balancing, each import is limited to about ten spectra per group, so that identification reflects spectral fit rather than group size.

2.4 Spectral matching and graded decision rules

Raw spectra are splice-corrected, replicate-averaged and truncated to 400–2400 nm to remove

noisy instrument edges. The spectral angle mapper (SAM) treats spectra as n -dimensional vectors X and Y and measures their included angle (Eq. 1); depending only on spectral shape, it is robust to illumination and albedo changes [20]. Euclidean distance (ED) measures the straight-line distance between two spectra (Eq. 2) and is amplitude-sensitive, so it complements SAM. The combined score normalises both measures to $[0, 1]$ over the candidate set and averages them with weight w (Eq. 3); scores closer to 0 indicate closer matches. The weight is selected by grid search over $w \in [0, 1]$ on the chemically confirmed reference points, the optimum forming a plateau at $w = 0.4$ – 0.6 from which $w = 0.5$ was adopted. Scores are aggregated from spectra to brand-grade groups by keeping each group’s best-scoring spectrum.

$$\text{SAM}(X, Y) = \arccos \frac{X \cdot Y}{\|X\| \|Y\|} \quad (1)$$

$$\text{ED}(X, Y) = \|X - Y\|_2 \quad (2)$$

$$S = w \frac{\text{SAM} - \text{SAM}_{\min}}{\text{SAM}_{\max} - \text{SAM}_{\min}} + (1 - w) \frac{\text{ED} - \text{ED}_{\min}}{\text{ED}_{\max} - \text{ED}_{\min}} \quad (3)$$

Unlike conventional spectral matching, which accepts the best candidate as the result, the combined score S of Eq. 3 is here passed through two graded decision layers, both fitted on the chemically confirmed reference points (Sect. 3.2): one judges the reliability of the match, the other judges chronological plausibility. The first layer is a graded rejection rule. Matching ranks every library candidate by S ; writing s_1 and s_2 for the scores of the best and the runner-up candidates, the margin $\Delta s = s_2 - s_1$ measures how clearly the best candidate wins. A point falls in the *high-confidence* zone when $s_1 \leq 0.15$ and $\Delta s \geq 0.05$, in the *tentative* zone when $s_1 \leq 0.30$, and in the *to-review* zone otherwise, so that mixed and aged material is flagged for review instead of being forced into a label. The two thresholds were selected on a candidate grid ($s_1 \in \{0.05, 0.10, 0.15, 0.20\}$, $\Delta s \in \{0.00, 0.02, 0.05\}$) by maximising high-confidence-zone correctness first and coverage second, with ties broken towards the stricter threshold.

The second layer handles chronology. The Yungang Grottoes were built in the Northern Wei

period, so a pigment that does not belong to that period is flagged as chronologically anomalous rather than identified. On this basis the legacy Prussian-blue indicator competes in matching but never returns a name: a point whose best overall candidate is the indicator is flagged as chronologically anomalous, and its in-library decision is read at indicative level. The complete procedure runs from acquisition and preprocessing through SAM, ED and weighted matching, graded rejection and diagnostic flagging to chemical corroboration (Fig. 1).

3 Results

3.1 Composition and internal separability of the library

Figure 2a shows the mean characteristic curve of each colour family, averaged over the 328 library spectra (99 groups), with the mean of the 1276 rock-library spectra as bedrock reference. Black stays below 0.1 reflectance over the full range. White is bright at 0.41–0.77. Yellow and red peak at 0.55–0.65 and show the S-shaped reflectance rise between 550 and 700 nm typical of iron-family pigments. Green peaks near 500 nm with the visible-range absorptions of copper compounds, and blue peaks at 450–500 nm. The SWIR absorptions near 1400, 1900 and 2200–2350 nm, arising from overtones and combinations of hydroxyl, structural water and carbonate, provide the key bands for separating pigments within a family. The rock mean approaches white and yellow in amplitude but lacks the visible-range feature edges, so amplitude alone cannot separate pigment from substrate; this is the direct reason for keeping a shape measure in the matching procedure. That the families separate is a property of the data. In the feature space spanned by the visible red-edge slope (550–700 nm) and the continuum-removed 2200–2350 nm absorption depth — two quantities read directly off each spectrum, with no training involved — the six families occupy distinct regions (Fig. 2b).

Before matching field points, the library’s internal consistency was assessed at colour-family level by LOOCV (Fig. 2c): each of the 328 entries was held out in turn and reclassified against the rest with the same preprocessing and scoring. Accuracy is reported as overall accuracy (OA =

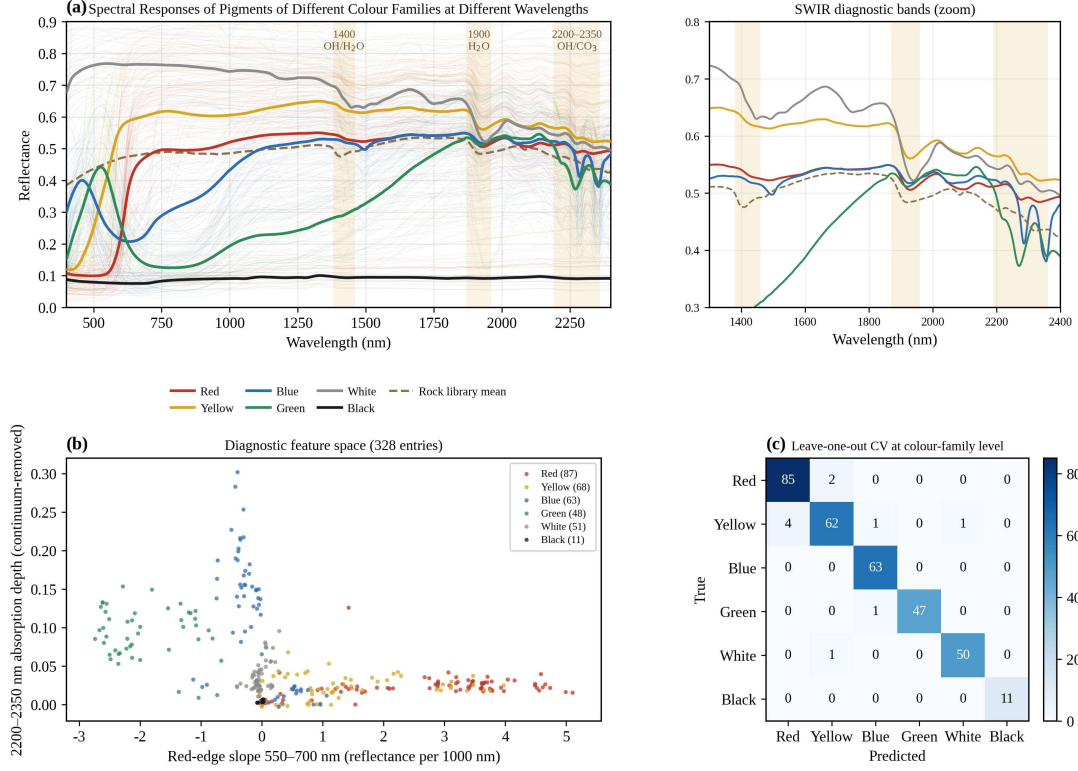


Fig. 2 Characteristics and internal consistency of the unified library. (a) Mean characteristic curves by colour family with member spectra in light lines, and the rock-library mean as bedrock reference; shaded bands mark the diagnostic SWIR absorption regions, and the 1300–2400 nm segment is magnified on the right because the hydroxyl, structural-water and carbonate absorptions that separate pigments within a family concentrate there. (b) Distribution of the 328 entries in the feature space of visible red-edge slope against continuum-removed 2200–2350 nm absorption depth, coloured by family. (c) Colour-family leave-one-out cross-validation confusion matrix of the weighted combination.

C/N , with C of N entries correctly reclassified) and Cohen’s kappa ($\kappa = (OA - p_e)/(1 - p_e)$, with p_e the chance-agreement term from the true and predicted class counts), and confidence intervals on the proportions reported in this paper are 95% Wilson score intervals. The weighted combination ($w = 0.5$) reaches $OA = 0.970$ and $\kappa = 0.962$, comparable to SAM (0.976 and 0.970, a difference of two spectra) and clearly above ED (0.939 and 0.924). The combination is adopted because ED’s amplitude term supplies independent information for distinguishing same-shape spectra of different brightness on aged surfaces, and because the two metrics together span the (score, margin) space on which the graded rule is calibrated.

3.2 Spectral matching results

This section first walks through two representative cases — cinnabar and gypsum — and then reports

the performance of the fitted rule on the chemically confirmed reference points and the decision space it defines.

The cinnabar points serve as the representative case, because red is the family in which the shape-versus-amplitude trade-off is most visible; the same behaviour appears in the other chemically confirmed pigment groups. The spectra of the 12 cinnabar reference points (Fig. 3a) share their shape, with the diagnostic red edge near 600 nm always present, while their amplitude varies between about 0.35 and 0.70 with ageing, dust and measurement geometry. Matching the mean spectrum within the red sub-library shows how the three measures respond (Fig. 3b–d). SAM, reading shape alone, admits the shape-similar red ochre among its leading candidates — the confusion risk of a pure shape measure among warm iron-family pigments. ED, which

retains amplitude, returns candidates that converge on cinnabar-type products of three brands, the only non-cinnabar entry being a carmine paste at fourth rank. The weighted combination inherits this amplitude cue and likewise converges on cinnabar-type candidates, so the first candidate is stable whether judged by amplitude alone or by the combination.

The second case demonstrates the decisive role of library completeness and the quantities to which the weighted matcher responds (Fig. 3e–g). Gypsum (CaSO_4) is chemically confirmed in the micro-samples, yet the library long lacked any gypsum reference. All 15 gypsum-group reference points failed re-identification before migration — the gypsum group never entered the candidate ranking at all — and white points were forced onto muscovite-white entries whose flat, bright near-infrared plateau contradicts the measured hydration bands at 1450, 1750, 1940 and 2200–2350 nm (Fig. 3e). After eight USGS gypsum spectra were migrated, re-identification reaches 14/15, and 54 of the 179 white points (30%) return gypsum as first candidate (Fig. 3f). No change was made to the algorithm between these two states.

The top-ranked entry is consistently the same spectrum: the only low-albedo gypsum reference among the eight, with a maximum reflectance of 0.42 against 0.85–0.95 for the other seven. It is a SWIR-only source measurement whose visible to near-infrared segment was edge-filled at migration, drawn dashed in Fig. 3f. Aged white surfaces reflect only 0.09–0.39, so the amplitude-sensitive ED component prefers this entry, whereas pure SAM, dominated by the macroscopic slope difference between bright powders and dark weathered walls, never ranks gypsum first (best rank 14). A single favourable reference is insufficient evidence for a site-scale claim, so the assignment was tested against evidence independent of the score. The gypsum-specific 1750 nm band is significantly deeper at gypsum-first points than at other white points (median 0.027 against 0.020; Mann–Whitney $z = 3.0$, $p \approx 0.002$; 1940 nm band $p \approx 0.03$); 52 of the 54 points show at least three of the four gypsum bands (Fig. 3g); and the chemically confirmed points anchor the assignment.

Under leave-one-out re-fitting, the first-candidate score s_1 assigns 88.0% of the chemically confirmed reference points to the correct pigment

group (95% CI 78.7–93.6), and the fitted parameters are entirely stable across folds: every fold re-selects $w = 0.5$ and the (0.15, 0.05) thresholds. The leave-one-out estimates are the ones quoted throughout this paper.

Figure 4 maps the re-identified reference points into the decision space spanned by s_1 and the margin, and shows where the discriminative power sits. The mean margin is 0.049 for correctly re-identified points against 0.016 for incorrect ones, a separation the first-candidate score s_1 alone does not provide: wrong assignments are not usually distant matches; they are matches with a close runner-up. The fitted rule ($s_1 \leq 0.15$ and margin ≥ 0.05) isolates a high-confidence zone of 30 points (40.0% coverage), all correct in sample and error-free under leave-one-out re-fitting (95% CI 88.6–100), and separates these near-identifications from the tentative zone, whose points require chemical corroboration before naming.

3.3 Chemical evidence and later interventions

Figure 5 redraws the chemical evidence from the tabulated and digitised micro-analytical data. In the cinnabar case (sample 7-2), the Raman bands at 250 and 336 cm^{-1} are consistent with α -HgS reference values (ca. 252 and 342 cm^{-1}) [10, 11], and SEM-EDS reports S and Pb as dominant elements: the sulphur is accounted for by HgS itself, and the lead indicates a co-occurring lead phase that the Raman spectrum identifies as minium. Across all samples, the measured band positions of the assigned pigments fall at or near the reference positions (Fig. 5a), and the elemental pattern separates the copper greens (Cu–Cl), lead whites and reds (Pb–S), iron reds (Fe) and sulphate whites (Ca–S) (Fig. 5b). At EDS resolution the Hg M and S K lines overlap near 2.3 keV, so mercury-specific confirmation rests on the Raman bands.

Mixing is ubiquitous, with minium accompanying cinnabar and emerald green accompanying atacamite. Combining the two micro-analyses, the chemically confirmed pigments are cinnabar, minium, red ochre (haematite group), carbon black, atacamite, azurite, lapis lazuli, celestite, anglesite and paper/pasting organic residue; gypsum is likewise confirmed, with one further suspected occurrence. Throughout, “red

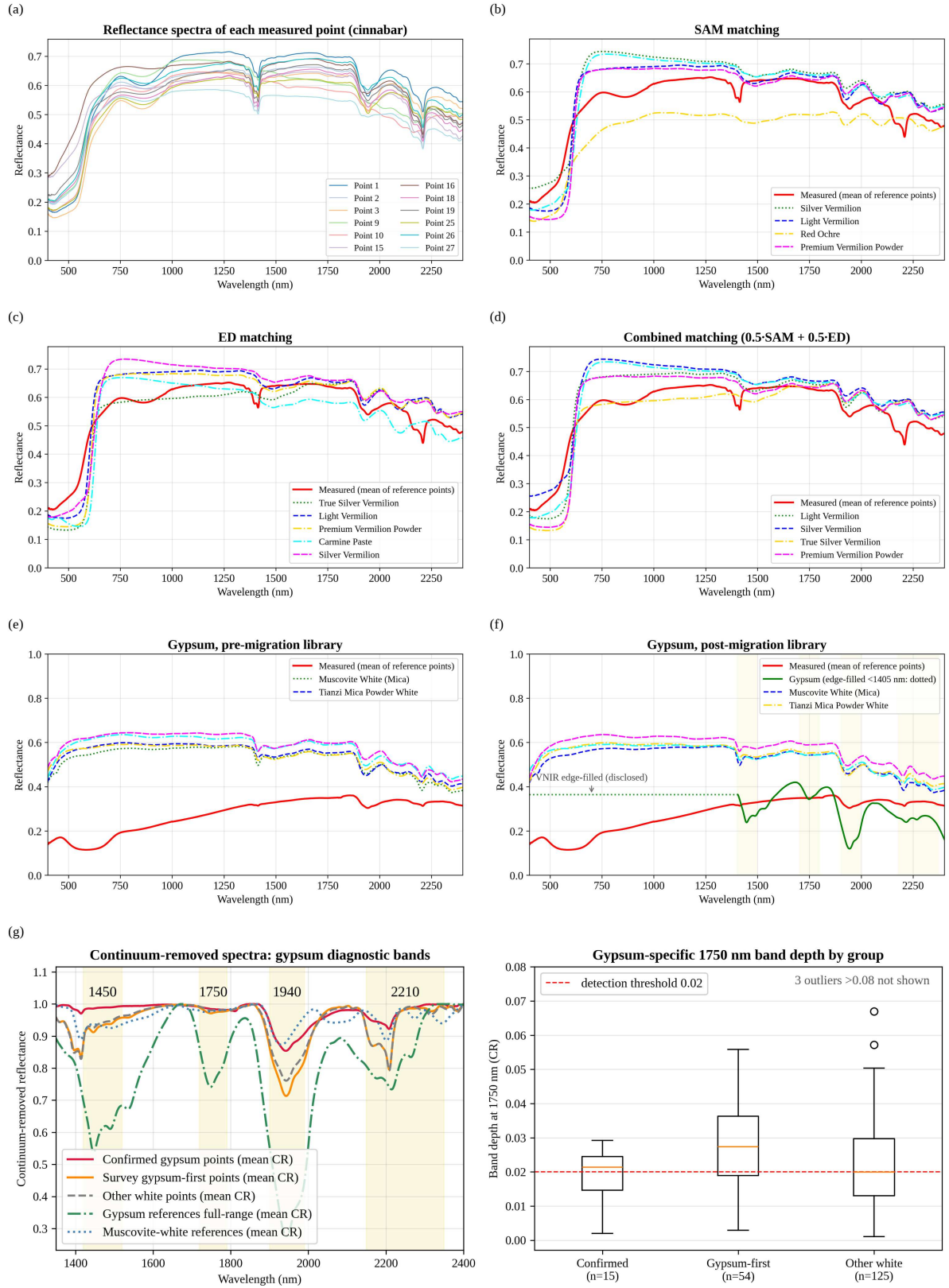


Fig. 3 Representative cases. (a) In-situ spectra of the 12 cinnabar reference points. (b–d) SAM, ED and weighted-combination ($w = 0.5$) matching of the cinnabar mean spectrum in the red sub-library. (e, f) Gypsum before and after reference migration: before, white points were forced onto muscovite-white references whose flat, bright near-infrared plateau contradicts the measured hydration bands; after migrating eight USGS gypsum spectra, the first candidate is rock-library gypsum and the measured hydration bands align (dashed: edge-filled 400–1400 nm segment of the winning SWIR-only reference). (g) Continuum-removal corroboration over four diagnostic windows (left), with the 1750 nm band depth by group (right; dashed line: 0.02 detection threshold).

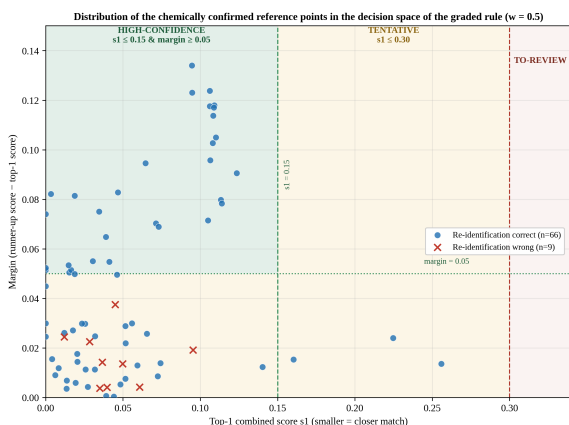


Fig. 4 Distribution of the chemically confirmed reference points in the decision space of the graded rule ($w = 0.5$, 400–2400 nm): the first combined score s_1 against the margin (runner-up minus best). Dashed lines mark the fitted thresholds ($s_1 = 0.15$, margin = 0.05), and shading marks the high-confidence, tentative and to-review zones. The high-confidence zone is error-free at 40.0% coverage in sample, and remains error-free under leave-one-out re-fitting (95% CI 88.6–100).

ochre” and “ochre” denote the earthy red pigments of hydrated iron oxide ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$); the two groups share one chemical attribution (both anchors are Raman-identified as haematite) and are separated on spectral hydration features, so their mutual discrimination reads as within-family discrimination by spectral criteria.

Three chemical findings bear on the caves’ later history, and none of them could have been reached by reflectance alone. Anglesite (lead sulphate white, PbSO_4), together with the detected paper/pasting organic residues, indicates later restoration or foreign coatings; anglesite is a sulphation product of lead white and may arise either from alteration of historical lead white or from later lead-based repainting; distinguishing these requires stratigraphic evidence, so we report it as a lead-bearing coating of uncertain date. Raman micro-analysis further indicates emerald green, synthesised only from about 1814 [21], mixed with atacamite on green surfaces (samples 7-P-1, 7-1, 8-D-6 and 8-D-7); SEM-EDS detected no As, consistent with a small emerald green fraction [22], so the finding is reported at indicative level. The mean in-situ spectrum of these samples entered the archive as the “emerald green–atacamite mixture” identification entry (Fig. 6): the in-situ single spectra of the four Raman-indicated samples agree in overall shape, and their mean forms the

entry. Comparison with a commercial malachite reference shows the mixture to be spectrally distinct from the pure copper-green entries already in the library. Finally, 8 of the 30 blue points hit the Prussian-blue indicator spectrum; since Prussian blue was synthesised only in 1704 [23], these points may indicate local later interventions and are counted at indicative level.

3.4 The full survey and the unified pigment inventory

The validated procedure was applied to the full point survey to establish the pigment distribution of Caves 7–8 as a basis for conservation planning and art-historical research. Each of the 1035 colour-labelled points was processed by weighted matching and graded rejection, and 343 points (33%) fall in the high-confidence zone. Figure 7 gives the first-candidate pigment composition of each colour family.

The red family (408 points) is dominated by iron-family reds: natural-ochre-type products take 178 first candidates and red-ochre-type products 120, followed by nano-haematite (27) and haematite (25) references. The yellow family (161 points) splits between gold-powder products (92) and yellow-ochre- and goethite-type entries (42 and 25). The white family (179 points) divides into muscovite-white products (122) and gypsum (54 of the 179 white points), the site-scale counterpart of the case in Fig. 3f, with ivory white and anglesite first at two points and one point, respectively. The blue family (30 points) divides into azurite-type (17) and lapis lazuli-type (13) candidates; 8 of these points also hit the Prussian-blue indicator and are reported as chronological-anomaly flags. The green family (115 points) is dominated by malachite-type products (98), with atacamite first at 17 points, and 50 green points are assigned to the “emerald green–atacamite mixture” entry at indicative level. The black family (142 points) divides into magnetic-black products (99), carbon-black products (26) and mica-black products (17).

The unified inventory resulting from this application is assembled in Table 2: 18 entries over the six colour families, with main compositions and occurrences. By family, the survey identifies cinnabar, minium, red ochre and ochre among the reds; yellow ochre and gold powder among the yellows; muscovite white, gypsum and anglesite

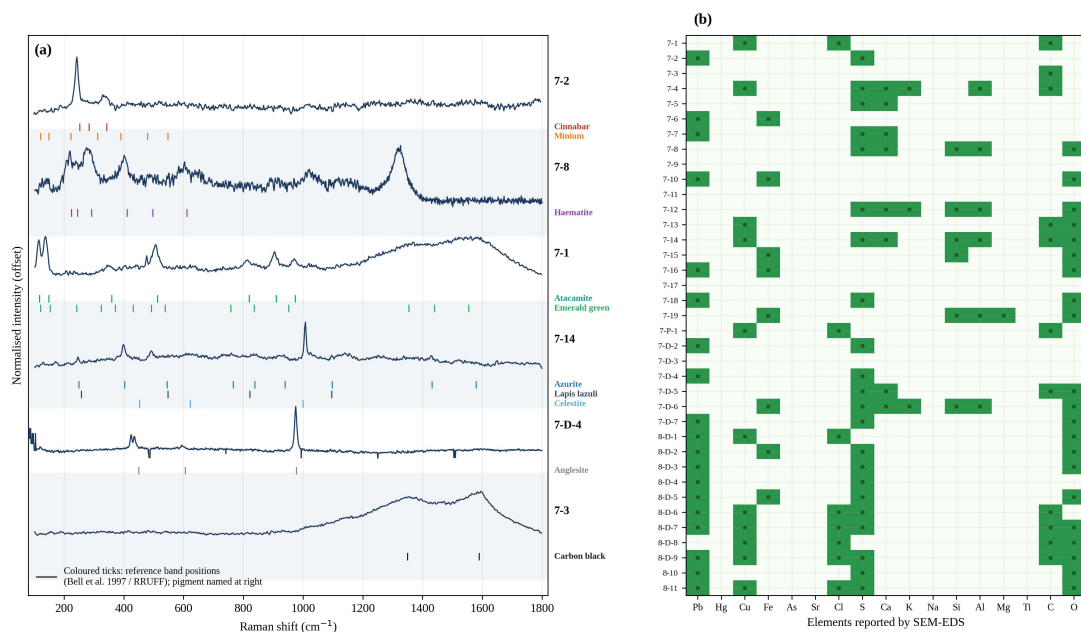


Fig. 5 Chemical corroboration from the micro-analytical data. (a) Digitised Raman traces of six representative samples, normalised and vertically offset; coloured ticks mark the reference band positions of the ten Raman-active phases, including the indicative emerald green, with lazurite being the blue mineral of lapis lazuli [10, 24]. (b) Elements reported by SEM-EDS for each sample.

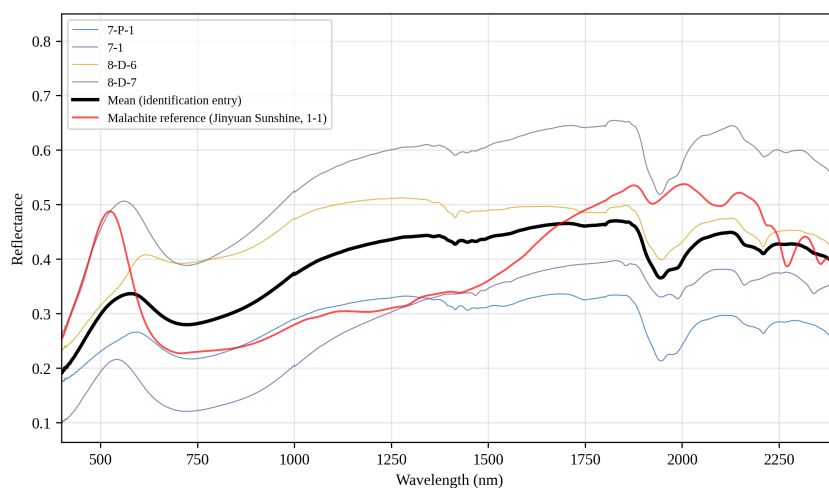


Fig. 6 Spectral composition of the “emerald green-atacamite mixture” identification entry (400–2400 nm): in-situ single spectra of the Raman-indicated samples 7-P-1, 7-1, 8-D-6 and 8-D-7 (thin lines), their mean (thick black line; the identification entry) and a commercial malachite reference (red line).

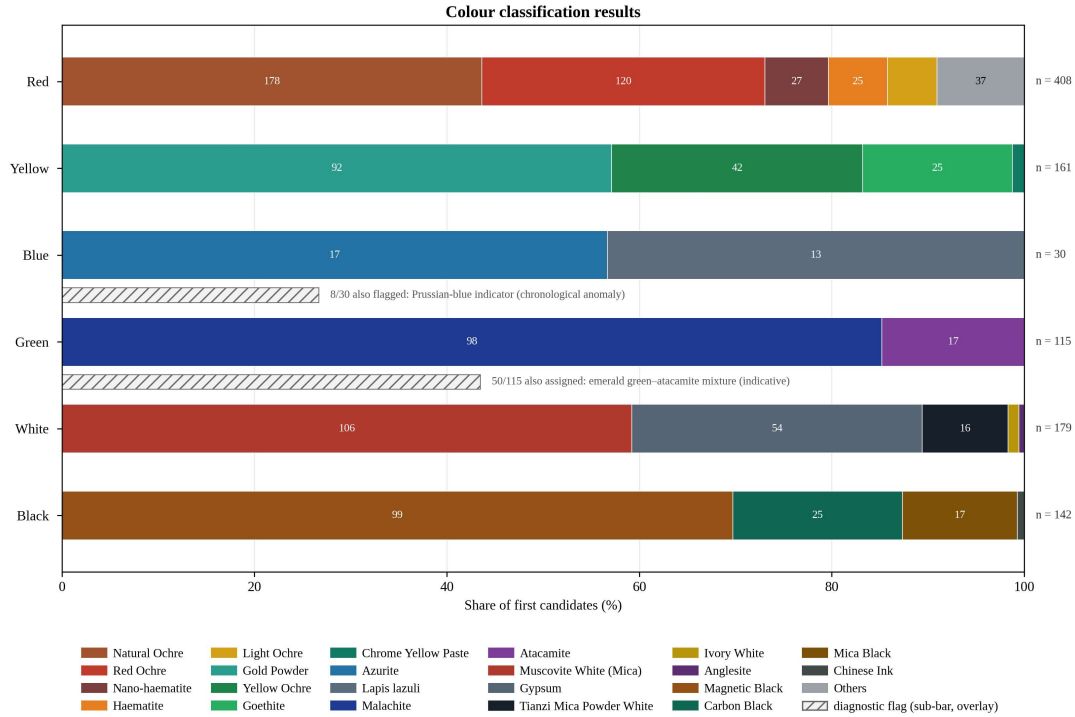


Fig. 7 Colour classification results. Each bar gives the first-candidate pigment composition of one colour family, like-named candidates merged and the remainder grouped as “Others”; hatched sub-bars mark diagnostic flags.

Table 2 Unified pigment inventory of Caves 7–8: chemical compositions and main occurrences

Colour	Pigment	Main composition	Main occurrence
Red	Cinnabar	HgS	Cave 7, arch layer 3
Red	Minium (red lead)	Pb ₃ O ₄	Cave 8, key niche
Red	Red ochre	Fe ₂ O ₃ · nH ₂ O	Cave 7, arch layer 2; dome
Red	Ochre	Fe ₂ O ₃ · nH ₂ O	Cave 7, rear chamber layer 6
Yellow	Yellow ochre	Hydrated iron oxide	Widespread (Caves 7–8)
Yellow	Gold powder	Au	Widespread (Caves 7–8)
White	Muscovite white	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	Widespread (Caves 7–8)
White	Gypsum	CaSO ₄	Cave 7, attic storey
White	Anglesite	PbSO ₄	Domes of Caves 7–8
White	Paper/pasting (substrate, not pigment)	Organic matter	Cave 7 (rear chamber and dome)
Black	Carbon black	C	Cave 7, dome
Black	Magnetic black (magnetite-type)	Fe ₃ O ₄	Mainly Cave 8 rear chamber; scattered in both caves
Green	Atacamite	Cu ₂ (OH) ₃ Cl	Green areas (Caves 7–8)
Green	Malachite	CuCO ₃ · Cu(OH) ₂	Green areas (Caves 7–8)
Green	Emerald green-atacamite mixture	Cu(CH ₃ COO) ₂ · 3 Cu(AsO ₂) ₂ + Cu ₂ (OH) ₃ Cl	Green areas (later repainting, Raman-indicated)
Blue	Azurite	2 CuCO ₃ · Cu(OH) ₂	Cave 7, rear chamber layer 6
Blue	Lapis lazuli	(Na, Ca) ₄ – 8 (AlSiO ₄) ₆ (SO ₄ , S, Cl) ₂	Cave 7, rear chamber layer 5
Blue	Celestite	SrSO ₄	Cave 7, rear chamber layer 6; Cave 8, dome

among the whites, together with paper or pasting residue on the substrate; magnetic black and carbon black among the blacks; atacamite, malachite and the emerald green-atacamite mixture among the greens; azurite, lapis lazuli and celestite among

the blues. This constitutes the pigment account of Caves 7–8 as established by this work.

3.5 Wall-scale hyperspectral inversion

The camera covers 400–1000 nm (Sect. 2.2), well short of the point spectra, but the principal colour-diagnostic features lie inside it: the S-shaped edge of iron-family pigments at 550–700 nm, the absorption edge of cinnabar near 600 nm, and the visible-range absorptions of copper greens and azurite-type minerals. Classification at colour-family and main-pigment-group level therefore remains supportable, while within-family mineral-phase discrimination weakens. Library spectra were resampled to the camera bands and the graded rejection thresholds recalibrated within 400–1000 nm; pixels are then classified by the same weighted matching and graded rejection, with sub-threshold pixels left unclassified. Spatially contiguous pixels of the same class are grouped into regions, which is what the region counts below refer to.

Figure 8 shows an inversion example for a ceiling coffer area. Colour patterns barely discernible in the true-colour composite, obscured by ageing and dust, appear clearly in the classification map. Green areas are dominated by malachite-type material, red areas by haematite-group material (red ochre and ochre) and haematite-minium-cinnabar mixtures, black outlines are carbon black, and blackened-minium areas form their own class. The emerald green areas (12 regions) and white anglesite areas (2 regions) agree with the point-level chemical evidence for later repainting, and suggest that the interventions detected at sampled points extend over whole surfaces.

4 Discussion and conclusions

This work has built a three-tier transferable reflectance spectral library for the painted surfaces of Yungang Caves 7–8 and an identification procedure that reports graded decisions rather than bare similarity scores. The library combines commercial standards with public-library references migrated under a shape check and dual validation (328 spectra in 99 groups), and a Yungang-specific archive anchored by micro-analysis. On chemically confirmed reference points the first-candidate score s_1 reaches 88.0% accuracy under leave-one-out re-fitting (95% CI 78.7–93.6), the high-confidence zone stays error-free

at 40.0% coverage, and library LOOCV reaches OA 0.970 at colour-family level. Applied to all 1035 colour-labelled survey points, the procedure yields the unified pigment inventory of Caves 7–8 (Table 2); chemical evidence reveals later interventions that a purely spectral survey could not reach, including lead-sulphate coatings of uncertain date, emerald green-bearing repainting and eight blue points flagged as chronological anomalies by the Prussian-blue indicator; and the transfer path from point spectra to wall-scale hyperspectral imagery is established (Fig. 8). Compared with current practice, the library is built for the site and extended under explicit quality control that can and did reject a batch; identification returns a graded decision and declines on two thirds of the survey rather than a name for every measurement; and anchoring the archive in micro-analysis turns identification and validation into a single loop in which each confirmed point improves the next round of matching.

Nevertheless, this study has limitations. First, the treatment of mixed pigments remains coarse, no general unmixing method has been established. Second, spectral data have so far been collected only from Caves 7–8, not from the remaining caves. Third, no time-series of in-situ spectral records has been accumulated, so the ageing state of the pigments and its spectral signature remain unquantified. These limitations define the next steps: (1) build a pigment database spanning different particle sizes and mixing ratios to support spectral unmixing of mixtures; (2) extend spectral acquisition and chemical corroboration to the whole cave complex, progressively enriching the pigment spectral library; and (3) accumulate in-situ spectral time-series and, combined with gradient-aged spectra from artificial ageing experiments, develop a model to invert for the degree of ageing. When transferring to other sites, the combination weight and rejection thresholds must be re-fitted on local chemically confirmed reference points rather than adopting the values reported here. Accumulating a site-specific archive from chemically confirmed points and feeding it back into the identification library offers a reproducible framework for the long-term digital documentation of a site’s pigments, and will benefit the digital conservation of cultural relics.



Fig. 8 Wall-scale hyperspectral inversion example. Left: true-colour composite. Right: per-pixel pigment classification map. Library spectra were resampled to the camera bands (400–1000 nm) and pixels classified by weighted matching ($w = 0.5$) with re-calibrated graded rejection thresholds, leaving sub-threshold pixels unclassified; the legend gives the per-class counts of spatially contiguous same-class regions (263 in total).

List of abbreviations

SAM: spectral angle mapper; ED: Euclidean distance; VNIR: visible–near-infrared; SWIR: short-wave infrared; XRF: X-ray fluorescence; SEM-EDS: scanning electron microscopy with energy-dispersive X-ray spectroscopy; LOOCV: leave-one-out cross-validation; OA: overall accuracy; CI: confidence interval.

Declarations

Ethics approval and consent to participate

This article does not contain any studies with human participants or animals performed by any of the authors.

Consent for publication

The consent for the publication of details and images in the manuscript are obtained from all participants.

Availability of data and materials

Data sharing is not applicable to this article as some of the data were collected on the surface of real cultural relics.

Competing interests

The authors declare that they have no competing interests.

Funding

This work was supported by the National Natural Science Foundation of China [grant number: 62605497], the Key R&D Program of Jiangxi Province, China [grant number: S202595331], and the Sun Yat-sen University [grant number: 74130-71010028].

Authors' contributions

Conceptualization: YZR, WWX, NB, LLH, YXY, and LSQ. Methodology: YZR, WWX, and LSQ. Validation: YZR, WWX, QKX, GYC. Formal analysis: YZR, WWX, LSQ. Resources: NB, LLH, YZR, YXY. Writing–original draft preparation and writing–review: all authors. The paper was approved by all authors. All authors read and approved the final manuscript.

References

- [1] Zhang Y, Cao C, Du H, Huang J, Guo X, Luo Q, et al. Investigation into the gaseous SO_2 attack on sandstone in the Yungang Grottoes. *Minerals*. 2023;13(1):123.

- [2] Zhou GX, Cheng HW. Study on the pigments in ancient murals in Yungang Grottoes. *Kaogu (Archaeology)*. 1994;(10):948–951. [in Chinese].
- [3] Fan X, Cui J, Wang S, Tai L, Guo J, Yan H. Analysis of pigments unearthed from the Yungang Grottoes archaeological excavations. *Minerals*. 2024;14(3):221.
- [4] Fischer C, Kakoulli I. Multispectral and hyperspectral imaging technologies in conservation: current research and potential applications. *Studies in Conservation*. 2006;51(Suppl. 1):3–16.
- [5] Liang H. Advances in multispectral and hyperspectral imaging for archaeology and art conservation. *Applied Physics A*. 2012;106(2):309–323.
- [6] Ma C, Dou H, Zhao Z, Qiu X, Li H, Wang X. Review of in-situ non- and micro-destructive techniques for pigment analysis in architectural heritage. *npj Heritage Science*. 2025;13:222.
- [7] Harth A. The study of pigments in cultural heritage: a review using machine learning. *Heritage*. 2024;7(7):3664–3695.
- [8] Aceto M, Agostino A, Fenoglio G, Idone A, Gulmini M, Picollo M, et al. Characterisation of colourants on illuminated manuscripts by portable fibre optic UV–visible–NIR reflectance spectrophotometry. *Analytical Methods*. 2014;6(5):1488–1500.
- [9] Cucci C, Delaney JK, Picollo M. Reflectance hyperspectral imaging for investigation of works of art: old master paintings and illuminated manuscripts. *Accounts of Chemical Research*. 2016;49(10):2070–2079.
- [10] Bell IM, Clark RJH, Gibbs PJ. Raman spectroscopic library of natural and synthetic pigments (pre- $\approx$ 1850 AD). *Spectrochimica Acta Part A*. 1997;53(12):2159–2179.
- [11] Burgio L, Clark RJH. Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. *Spectrochimica Acta Part A*. 2001;57(7):1491–1521.
- [12] Cosentino A. FORS spectral database of historical pigments in different binders. *e-Conservation Journal*. 2014;2:54–65.
- [13] Cortea IM. Towards FAIR data management in heritage science research: updates and progress on the INFRA-ART spectral library. *Heritage*. 2024;7(5):2569–2585.
- [14] López-Bal-domero AB, Nieves JL, Moronta-Montero F, Martínez-Domingo MÁ, Fernández-Gualda R, Hernández-Andrés J, et al. Hyperspectral dataset of historical documents and mock-ups from 400 to 1700 nm (HYPERDOC). *Scientific Data*. 2025;12:1248.
- [15] Chai BL, Su BM, Zhang WY, Wang XW, Li LZ. Standard multispectral image database for paint materials used in the Dunhuang murals. *Spectroscopy and Spectral Analysis*. 2017;37(10):3289–3306. [in Chinese].
- [16] Lyu S, Liu Y, Hou M, Gao Z, Yang X, Gu M. Designing and construction of the spectral library for typical pigments used in Chinese paintings. *International Archives of the Photogrammetry, Remote Sensing and Spatial Information Sciences*. 2019;XLII-2/W15:703–708.
- [17] Sun P, Lyu S, Hou M, Wang W. A reliability-oriented decision-support framework for pigment indication on sooty murals from VNIR–SWIR reflectance spectra. *npj Heritage Science*. 2026;14(1):286.
- [18] Clark RN, Swayze GA, Wise R, Livo E, Hoeffen T, Kokaly R, et al.: USGS digital spectral library splib07a. US Geological Survey. US Geological Survey Data Series 303.
- [19] Meerdink SK, Hook SJ, Roberts DA, Abbott EA. The ECOSTRESS spectral library version 1.0. *Remote Sensing of Environment*. 2019;230:111196.

- [20] Kruse FA, Lefkoff AB, Boardman JW, Heidebrecht KB, Shapiro AT, Barloon PJ, et al. The spectral image processing system (SIPS)—interactive visualization and analysis of imaging spectrometer data. *Remote Sensing of Environment*. 1993;44(2–3):145–163.
- [21] Fiedler I, Bayard MA. Emerald green and Scheele’s green. In: FitzHugh EW, editor. *Artists’ Pigments: A Handbook of Their History and Characteristics*, vol. 3. Washington: National Gallery of Art; 1997. p. 219–271.
- [22] Cheng X, Xia Y, Ma Y, Lei Y. Three fabricated pigments (Han purple, indigo and emerald green) in ancient Chinese artifacts studied by Raman microscopy, energy-dispersive X-ray spectrometry and polarized light microscopy. *Journal of Raman Spectroscopy*. 2007;38(10):1274–1279.
- [23] Berrie BH. Prussian blue. In: FitzHugh EW, editor. *Artists’ Pigments: A Handbook of Their History and Characteristics*, vol. 3. Washington: National Gallery of Art; 1997. p. 191–217.
- [24] Lafuente B, Downs RT, Yang H, Stone N. The power of databases: the RRUFF project. In: Armbruster T, Danisi RM, editors. *Highlights in Mineralogical Crystallography*. Berlin: De Gruyter; 2015. p. 1–29.