

Supplementary Material

Technological affinities between qinghui and carbonaceous mortars from Baocheng and Yaotai walls at Xianling Mausoleum

Fig. S1 Representative mortar samples, acid treatment and recovered acid-insoluble residues.

(a) Representative fragments of the seven mortar samples before laboratory preparation. (b) Representative stages of HCl treatment and recovery of the acid-insoluble fraction. (c) Representative acid-insoluble residues from the seven mortars, arranged in the same sample order as in panel (a). Dark particles are conspicuous in the residues from Q-G, Y-G, H-G and H-M but are not comparably observed in those from Q-Z, Y-Z and H-Z. Acid treatment was used to concentrate insoluble constituents and was not interpreted as a quantitative measurement of carbonaceous matter.

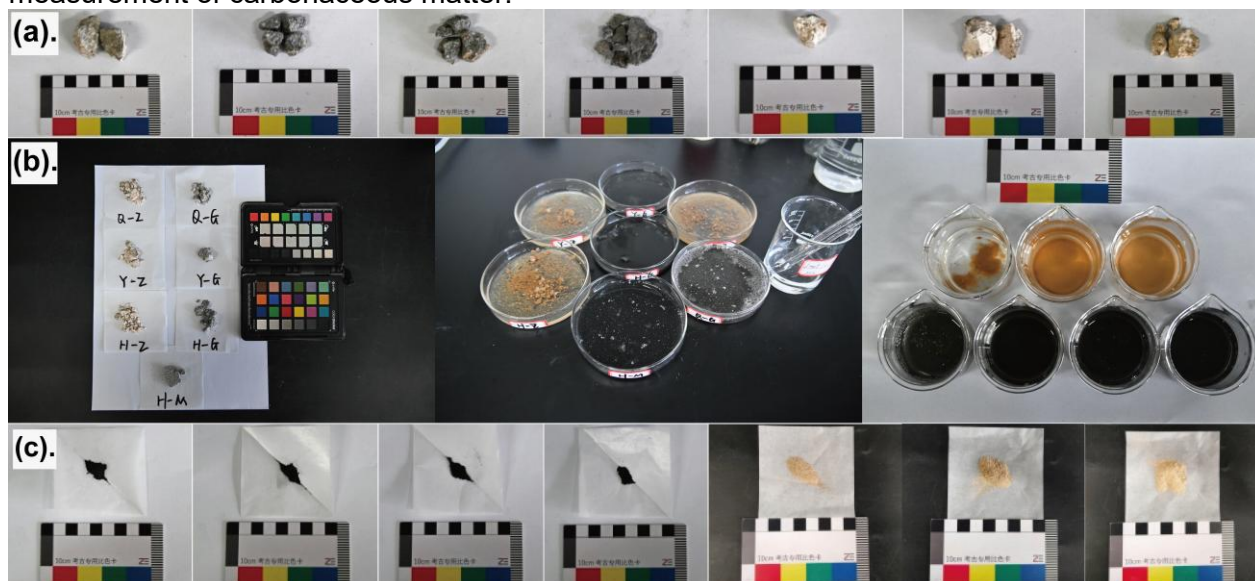


Fig. S2 Polished cross-sections, acid-insoluble residues and representative black agglomerates of the seven Xianling mortar samples.

The first two columns show representative polished cross-sectional views. “AT” denotes microscopic images of acid-insoluble residues, and “A1” denotes representative millimetre-scale black agglomerates where present.

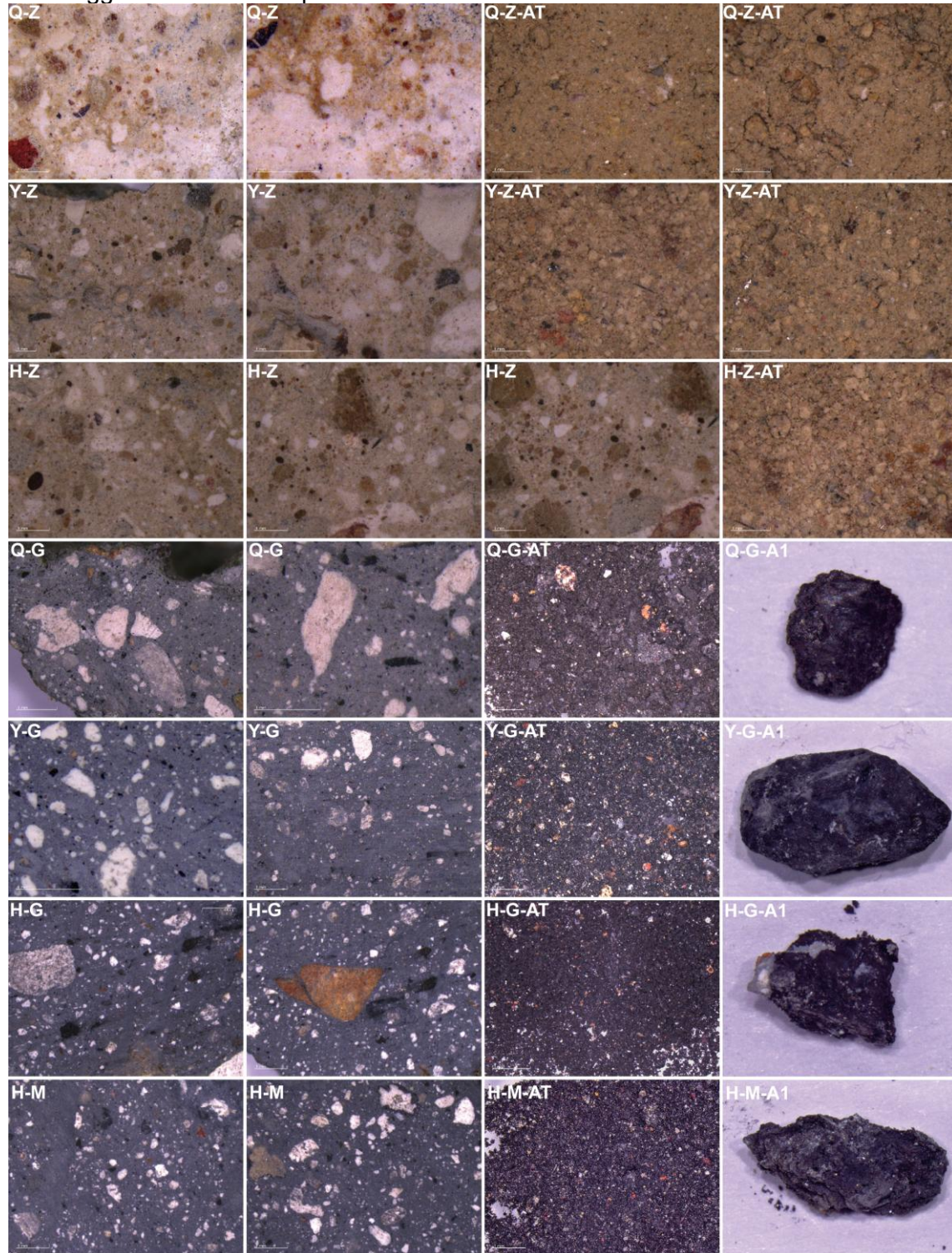


Fig. S3 Thin-section petrographic observations of the seven Xianling mortar samples.

(a) Q-G; (b) Y-G; (c) H-G; (d) H-M; (e) Q-Z; (f) Y-Z; and (g) H-Z. DP, dark particle; Agg., aggregate.

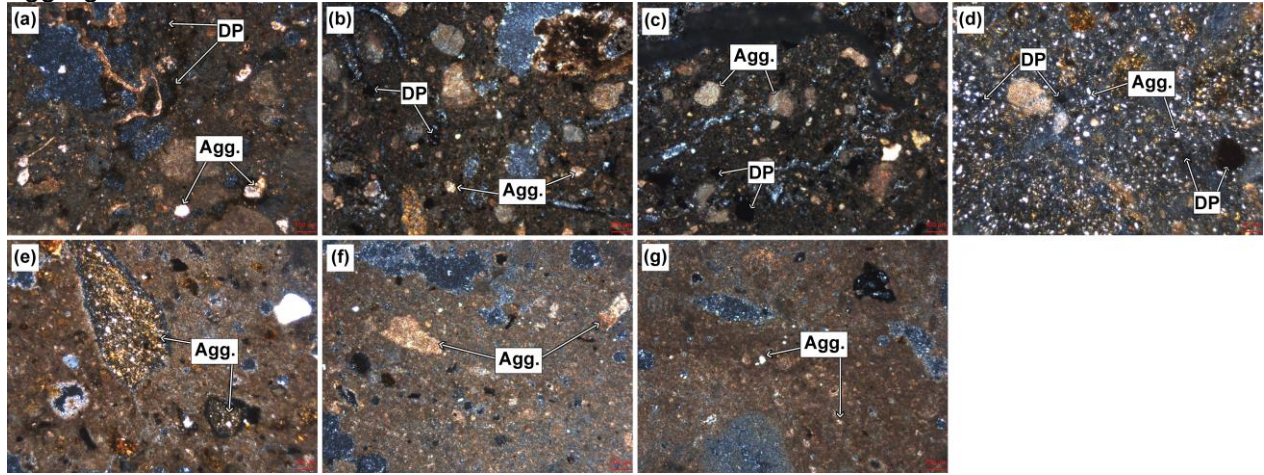


Fig. S4 Raman screening of the pale bedding mortars and darker pointing and finishing mortars.

(a) Representative Raman spectra from Q-Z, Y-Z and H-Z. No comparable broad D-G response was detected within the 1200–1750 cm^{-1} region under the present screening protocol. (b) Representative spectra from visually black particles in Q-G, Y-G, H-G and H-M, showing broad D- and G-region responses characteristic of poorly ordered carbonaceous matter. (c) Representative spectra from optically inconspicuous regions of the darker mortars showing weaker but detectable D-G responses. Spectra are vertically offset for clarity. D and G labels denote first-order carbon-band regions and do not imply source-specific identification.

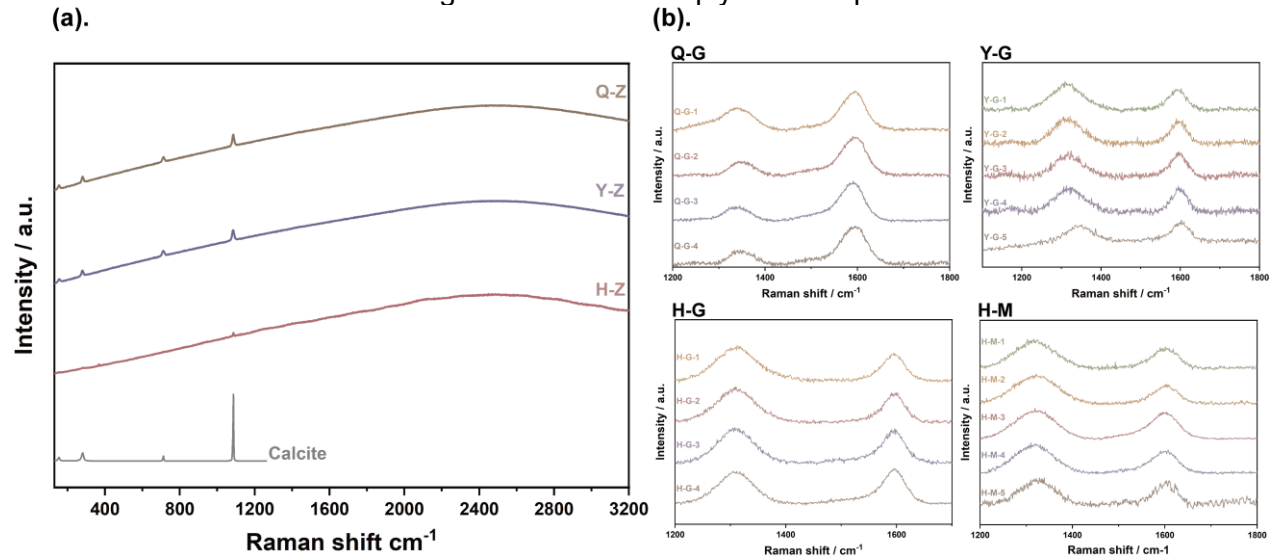
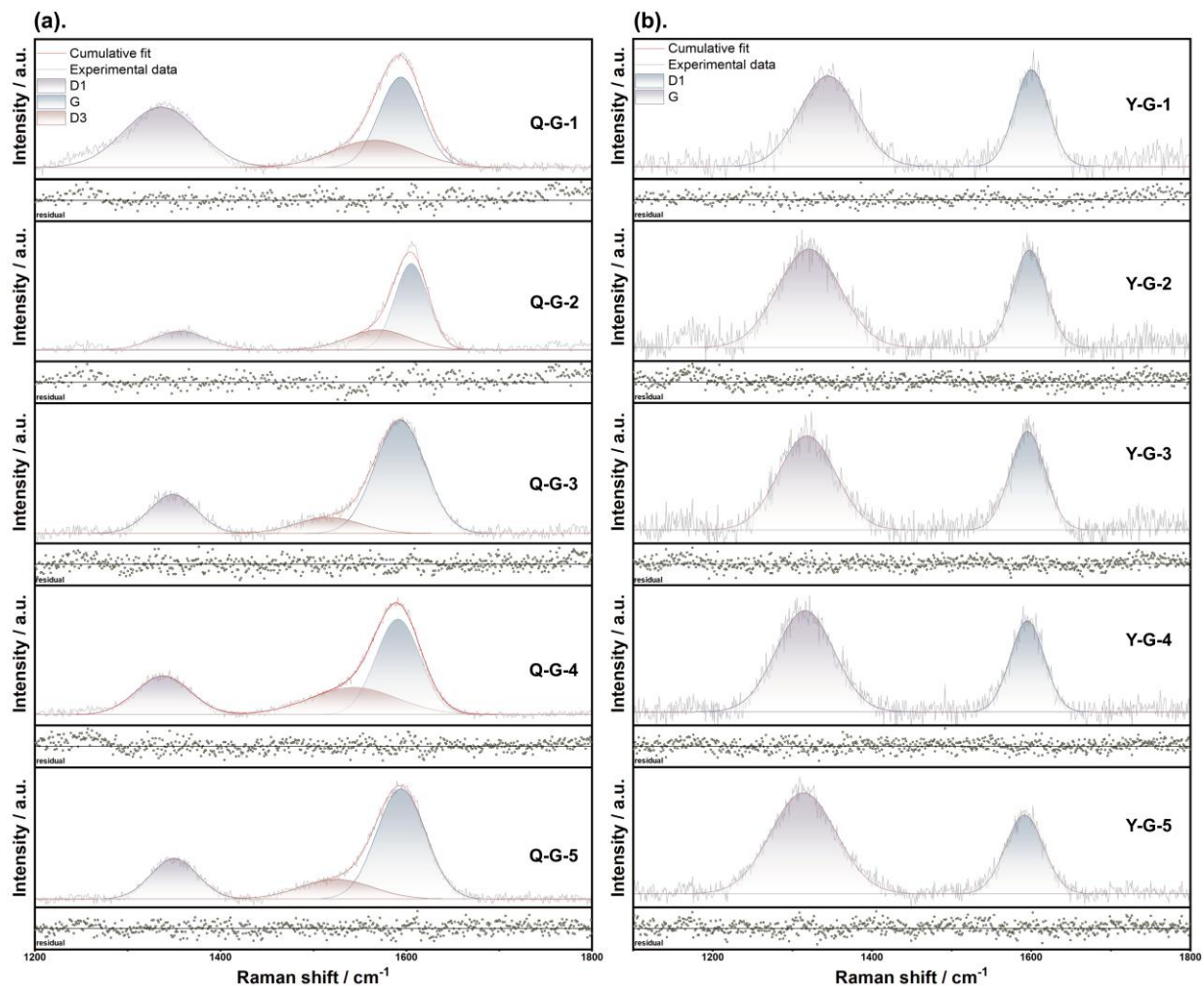


Fig. S5 Individual first-order Raman envelope fits and residuals for representative carbon-positive spectra from Q-G, Y-G, H-G and H-M.

Five representative carbon-positive spectra are shown for each darker mortar. Where fitting met the acceptance criteria, the experimental spectrum, cumulative fit, fitted Gaussian components and residual are presented. D+G or D+D3+G models were applied according to spectral complexity. Fits reaching parameter boundaries or otherwise judged unstable were not retained for quantitative interpretation. Complete spectral descriptors and fitting results are reported in Table S2.



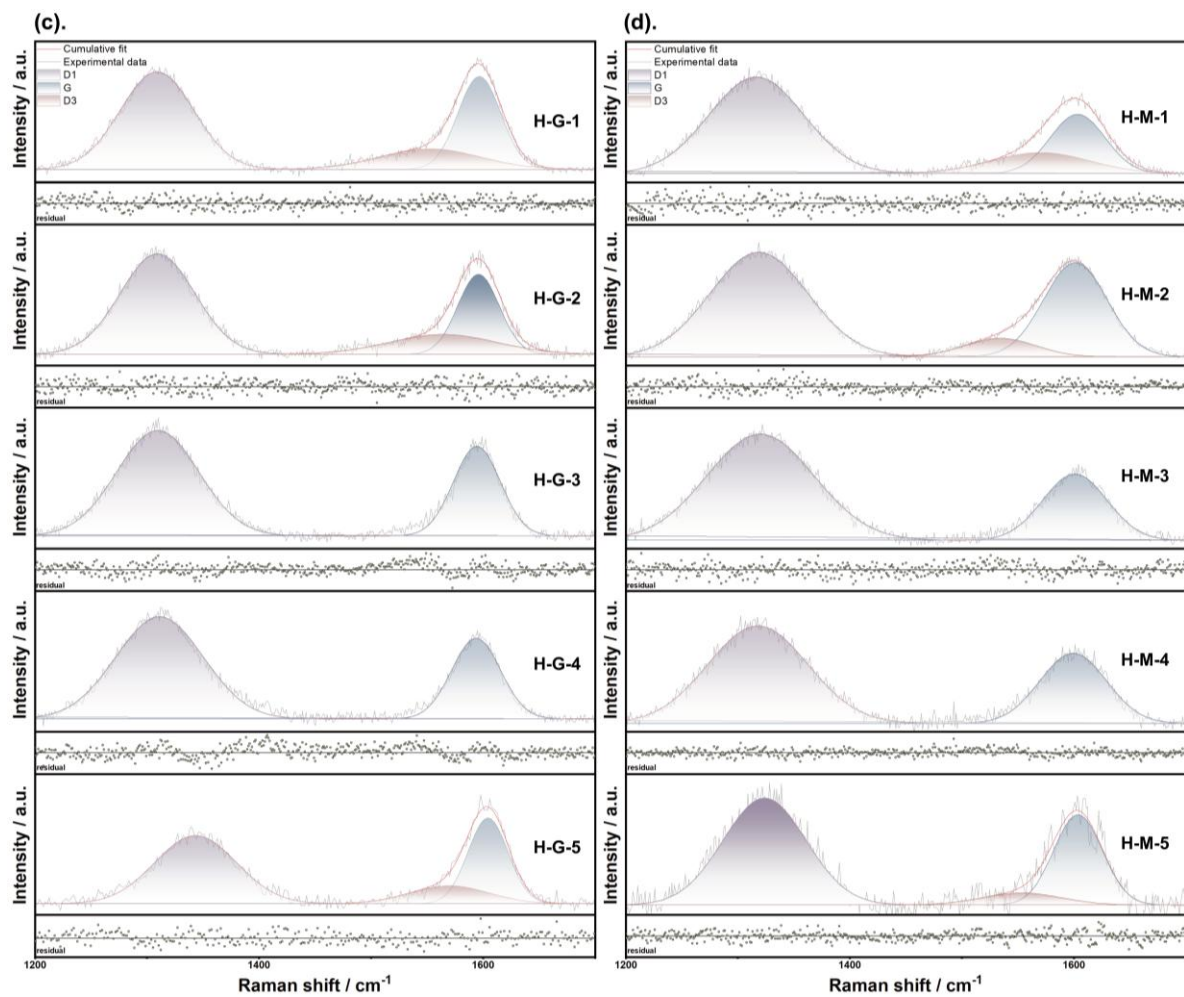
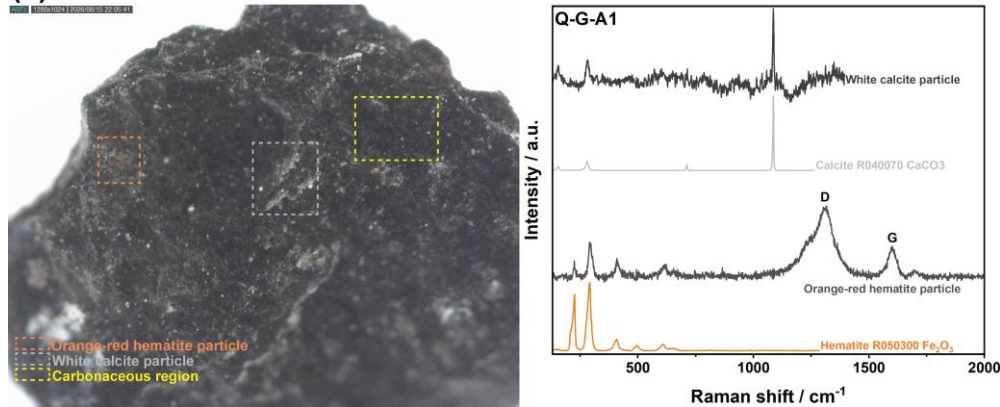


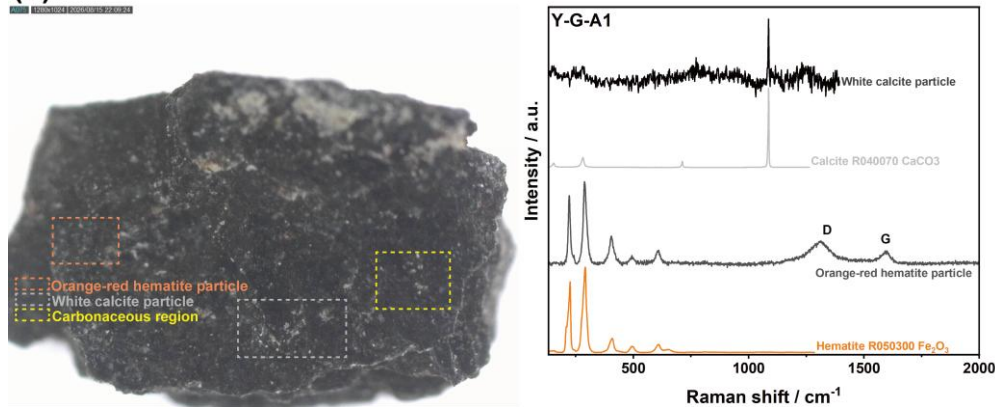
Fig. S6 Raman examination of representative millimetre-scale black agglomerates from the three darker mortars.

Representative sectioned agglomerates Q-G-A1, Y-G-A1, H-G-A1 and H-M-A1, with maximum dimensions of approximately 3, 2, 4 and 2 mm, respectively, are shown together with Raman measurement positions and representative spectra. For each agglomerate, three points within black regions were identified as poorly ordered carbonaceous matter, two points on white crystalline inclusions as calcite and two points on orange-red inclusions as hematite. The images document the recurring carbonaceous–calcitic–hematitic association within the interiors of the representative agglomerates. H–G–A1 is shown in Fig. 5 of the main text. Complete point assignments are summarised in Table S4.

(a).



(b).



(c).

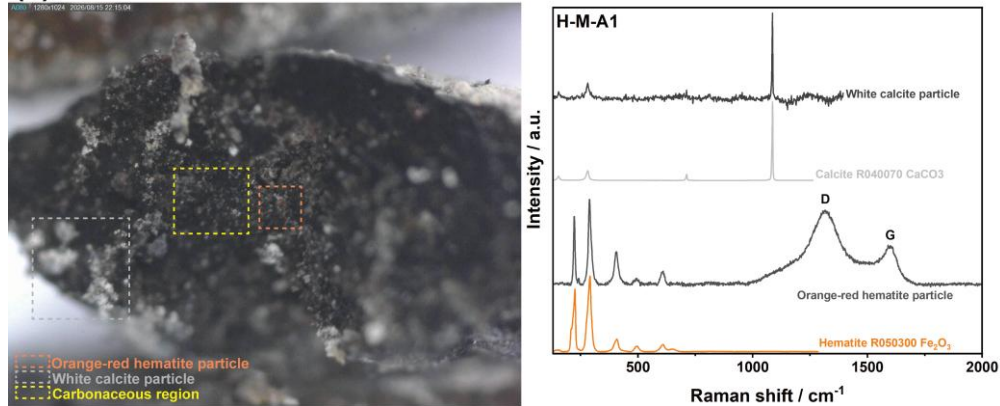


Fig. S7 Multi-field Raman mapping of carbon-related signals in Q-G.

Three spatially distinct cross-sectional fields are shown: Q-G-M1 (10×10 grid, $25 \mu\text{m}$ step), Q-G-M2 (nominal 8×7 grid, $25 \mu\text{m}$ step) and Q-G-M3 (8×8 grid, $25 \mu\text{m}$ step). For each field, the optical image, baseline-corrected D+G integrated-area map and fixed-window A_D / A_G ratio map are presented. Missing or invalid pixels were not spatially interpolated. A pixel was classified as carbon-positive only when both $\text{SNR}_D \geq 3$ and $\text{SNR}_G \geq 3$.

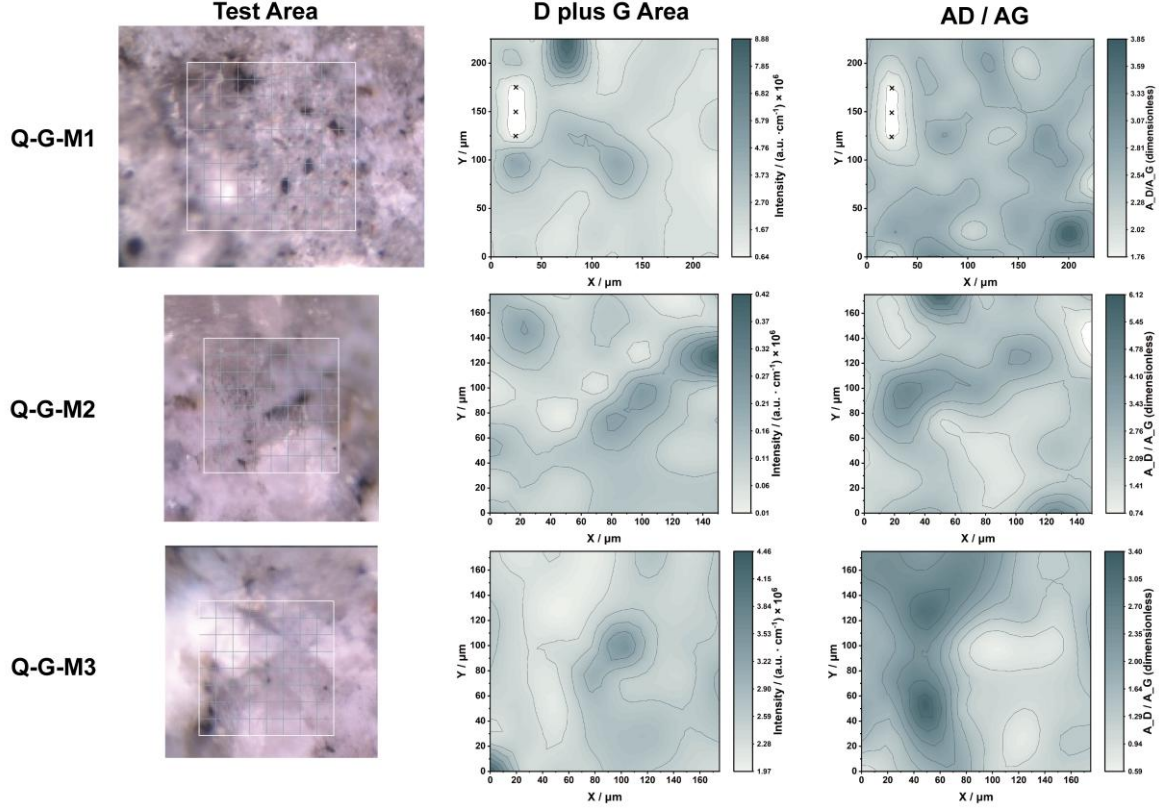


Fig. S8 Multi-field Raman mapping of carbon-related signals in Y-G.

Three spatially distinct cross-sectional fields are shown: Y-G-M1 (10 × 10 grid, 25 μm step), Y-G-M2 (nominal 8 × 8 grid, 25 μm step) and Y-G-M3 (8 × 8 grid, 25 μm step). For each field, the optical image, baseline-corrected D+G integrated-area map and fixed-window A_D / A_G ratio map are presented. Missing or invalid pixels were not spatially interpolated. A pixel was classified as carbon-positive only when both $SNR_D \geq 3$ and $SNR_G \geq 3$.

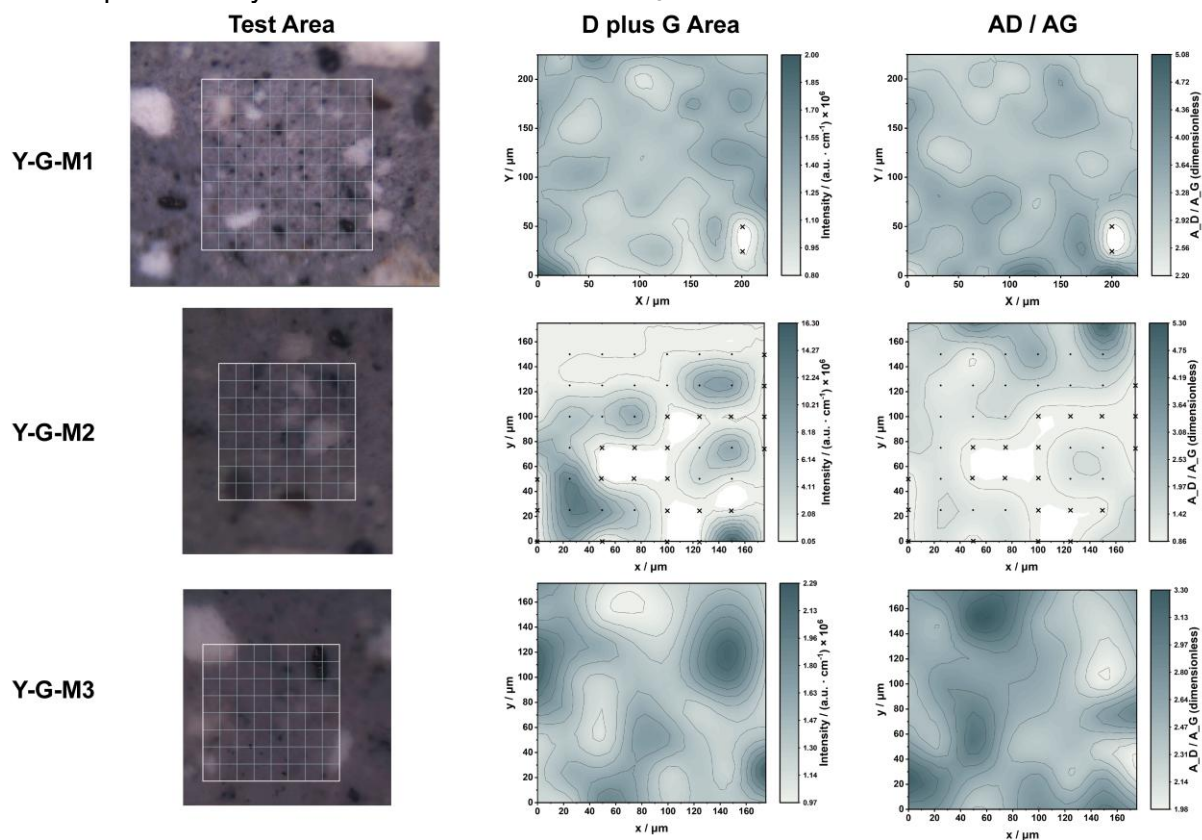


Fig. S9 Multi-field Raman mapping of carbon-related signals in H-G.

Three spatially distinct cross-sectional fields are shown: H-G-M1 (10×10 grid, $25 \mu\text{m}$ step), H-G-M2 (nominal 8×8 grid, $25 \mu\text{m}$ step) and H-G-M3 (8×8 grid, $25 \mu\text{m}$ step). For each field, the optical image, baseline-corrected D+G integrated-area map fixed-window A_D / A_G ratio map are presented. Missing or invalid pixels were not spatially interpolated. A pixel was classified as carbon-positive only when both $\text{SNR}_D \geq 3$ and $\text{SNR}_G \geq 3$.

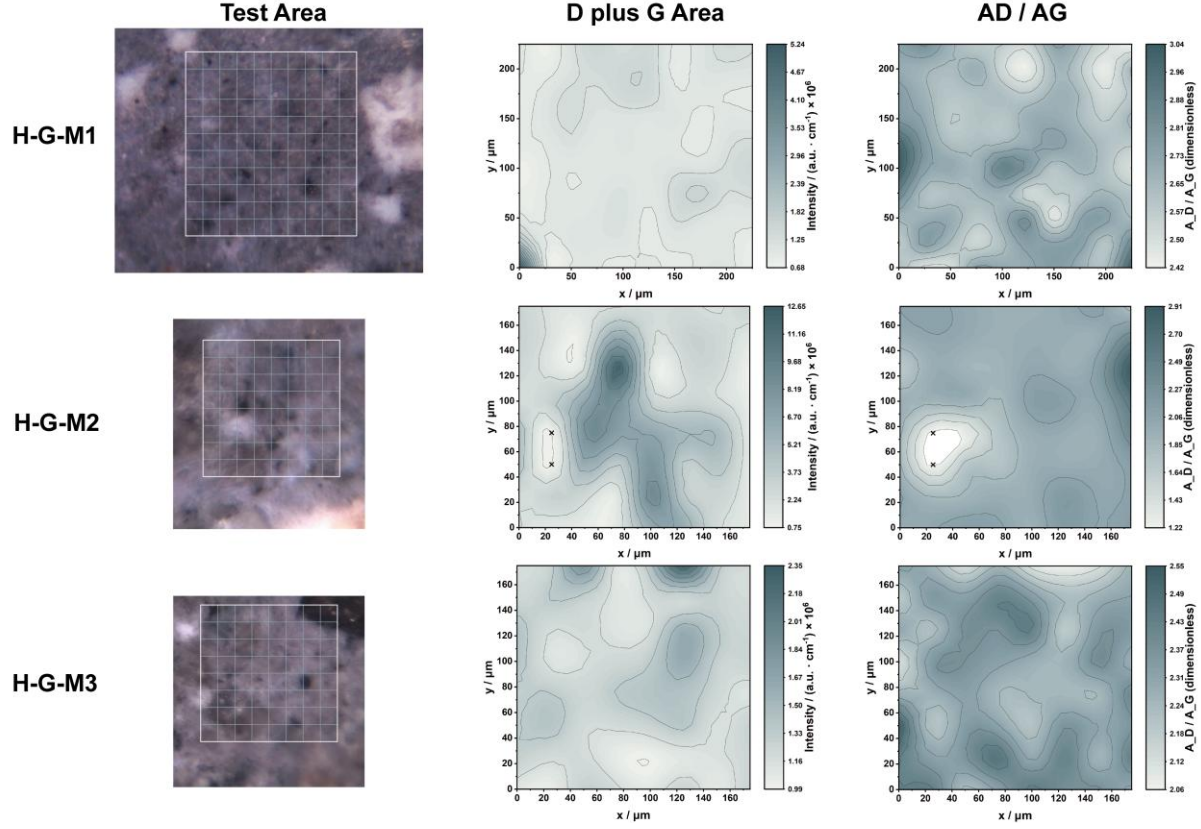


Fig. S10 Multi-field Raman mapping of carbon-related signals in H-M.

Three spatially distinct cross-sectional fields are shown: H-M-M1 (10×10 grid, $25 \mu\text{m}$ step) and H-M-M3 (8×8 grid, $25 \mu\text{m}$ step). For each field, the optical image, baseline-corrected D+G integrated-area map fixed-window A_D / A_G ratio map are presented. Missing or invalid pixels were not spatially interpolated. A pixel was classified as carbon-positive only when both $\text{SNR}_D \geq 3$ and $\text{SNR}_G \geq 3$.

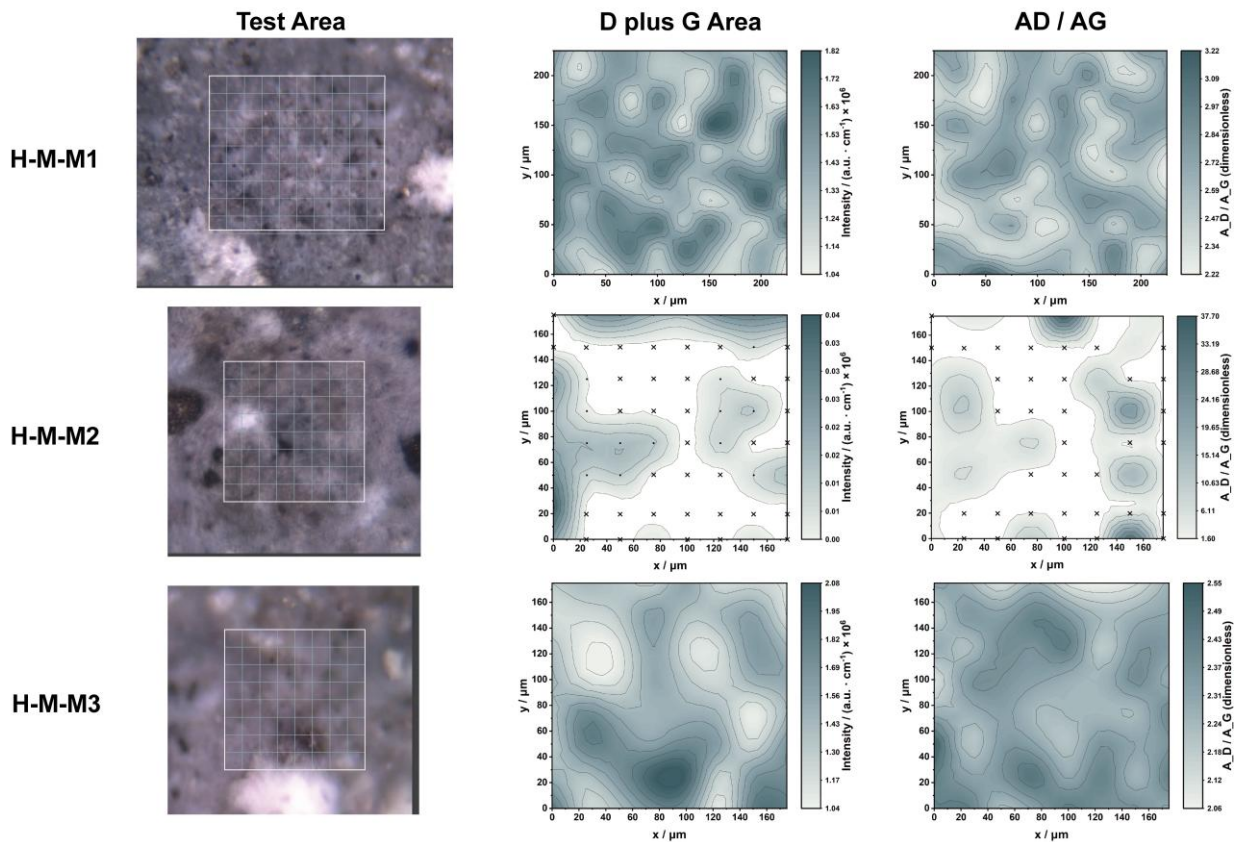


Fig. S11 Complete TG–DTG–DSC curves of the darker pointing and finishing mortars.

TG, DTG and DSC curves of Q–G, Y–G, H–G and H–M acquired independently under nitrogen and air. Atmosphere-dependent differences are most pronounced within the broad 500–800 °C interval, which also encompasses the principal carbonate-decomposition process. Measurements under the two atmospheres were performed on separate small aliquots without independent archaeological replicates; the differences are therefore interpreted descriptively as bulk thermal behaviour and were not converted into carbon contents.

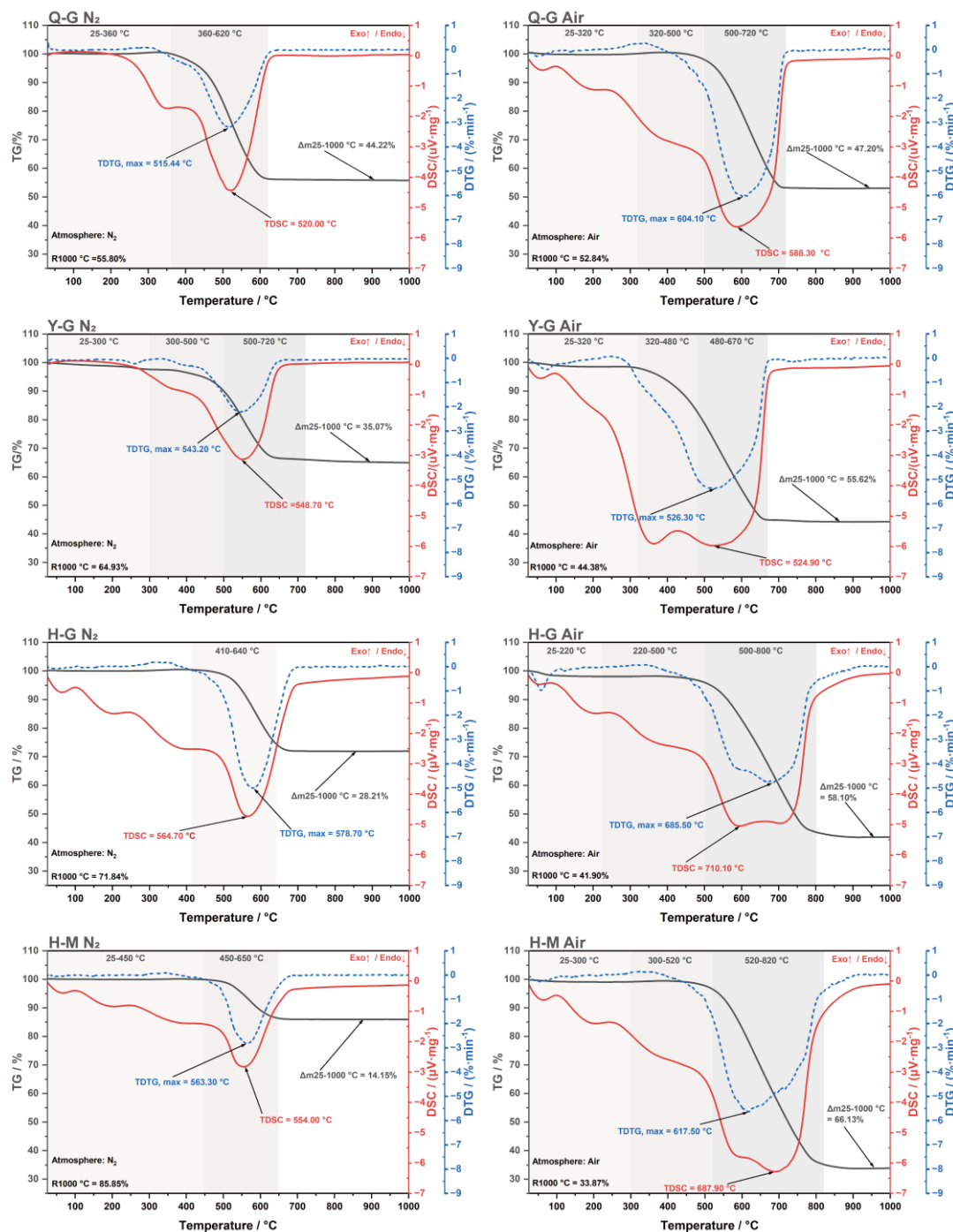
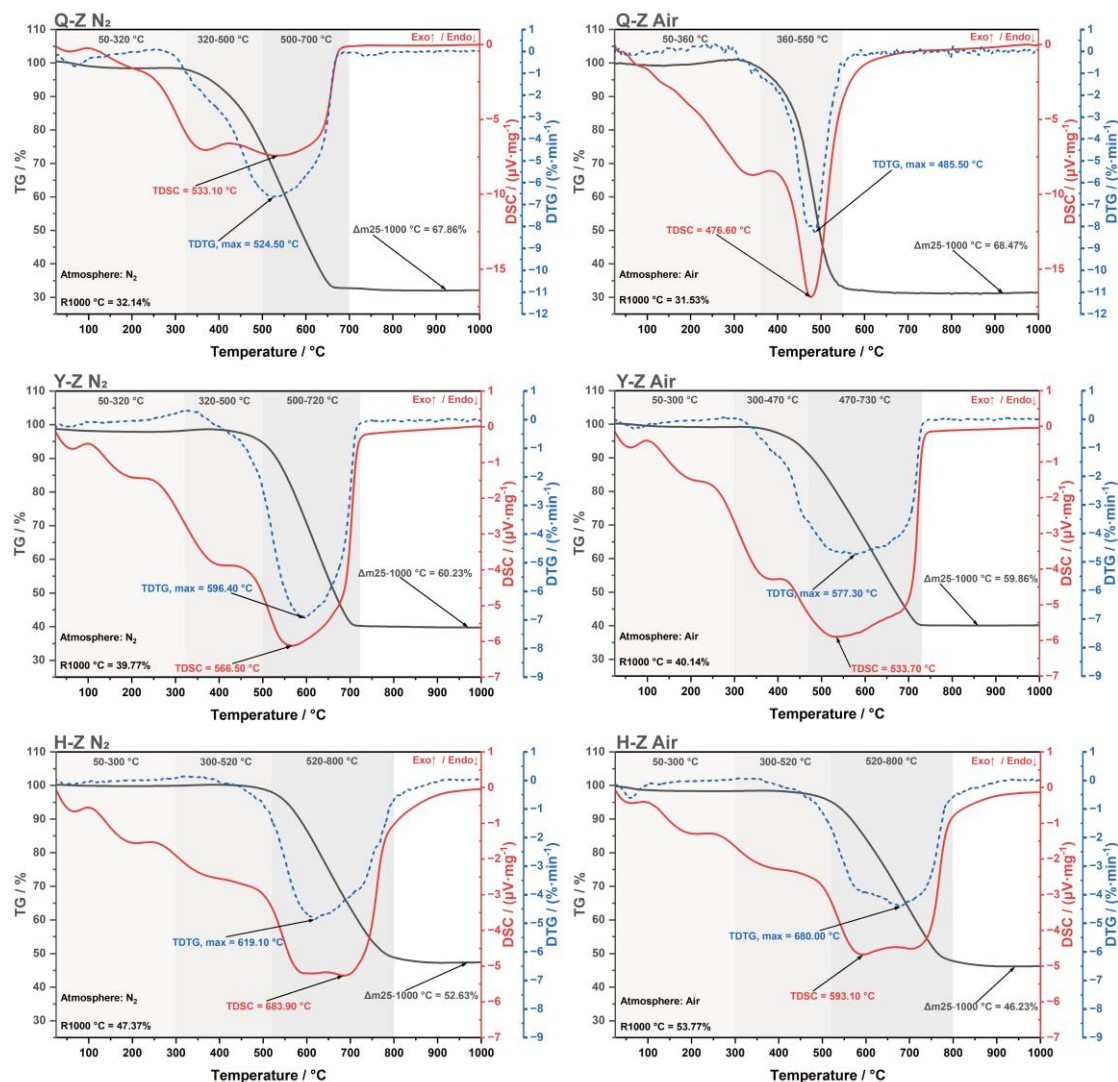


Fig. S12 Complete TG–DTG–DSC curves of the pale bedding mortars.

TG, DTG and DSC curves of Q–Z, Y–Z and H–Z acquired independently under nitrogen and air. Compared with several darker mortars, the bedding mortars show smaller atmosphere-dependent differences in total mass loss. The thermal data are used as supporting bulk-material information and not as independent molecular evidence for the presence or absence of carbonaceous matter.



Tab S1 Acid-insoluble residue measurements for the seven Xianling mortar samples.

Sample	Replicate	Initial mass (g)	Residue mass (g)	Residue yield (%)	Mean residue yield (%)	SD (%)
Q-G	1	0.5000	0.0874	17.48	18.14	1.45
	2	0.5000	0.0857	17.14		
	3	0.5000	0.0990	19.80		
Y-G	1	0.5000	0.0578	11.56	11.67	0.59
	2	0.5000	0.0557	11.14		
	3	0.5000	0.0615	12.30		
H-G	1	0.5000	0.0504	10.08	10.90	0.91
	2	0.5000	0.0594	11.88		
	3	0.5000	0.0537	10.74		
H-M	1	0.5000	0.0524	10.48	11.15	0.60
	2	0.5000	0.0568	11.36		
	3	0.5000	0.0581	11.62		
Q-Z	1	0.5000	0.1908	38.16	37.05	0.97
	2	0.5000	0.1830	36.60		
	3	0.5000	0.1819	36.38		
Y-Z	1	0.5000	0.2058	41.16	41.29	0.95
	2	0.5000	0.2115	42.30		
	3	0.5000	0.2021	40.42		
H-Z	1	0.5000	0.2213	44.26	44.17	0.55
	2	0.5000	0.2179	43.58		
	3	0.5000	0.2233	44.66		

Note: Residue yield was calculated relative to the initial dry mortar mass. Mean and SD were calculated from three independent acid-treatment replicates for each sample. Acid-insoluble residue yield includes quartz, silicate and lithic components and was not interpreted as carbonaceous-matter content.

Table S2 Individual first-order Raman spectral descriptors and fitting results for representative carbon-positive spectra from the darker mortars.

Spectrum ID	Model	D maximum (cm ⁻¹)	G maximum (cm ⁻¹)	A _D / A _G	Fitted D (cm ⁻¹)	Fitted G (cm ⁻¹)	Fitted D3 (cm ⁻¹)	FWHM _D (cm ⁻¹)	FWHM _G (cm ⁻¹)	FWHM _{D3} (cm ⁻¹)	Adj. R ²	Boundary	QC
Q-G-1	complex	1356.52	1605.42	1.28	/	/	/	/	/	/	/	3-peak boundary hit	Fixed-window only
Q-G-2	D+D3+G	1348.77	1593.39	1.35	1348.77	1593.39	1516.06	59.84	81.67	64.06	0.9918	No	Accept
Q-G-3	D+D3+G	1338.14	1591.07	1.43	1338.14	1591.07	1543.42	68.38	110.39	56.25	0.9897	No	Accept
Q-G-4	D+D3+G	1350.21	1594.28	1.35	1350.21	1594.28	1524.54	58.87	92.00	61.83	0.9838	No	Accept
Q-G-5	D+D3+G	1336.20	1594.01	1.79	1336.20	1594.01	1565.67	93.59	104.35	55.12	0.9091	No	Accept
Y-G-1	D+G	1344.73	1600.46	2.56	1344.73	1600.46	/	85.61	/	50.41	0.9103	No	Accept
Y-G-2	D+G	1320.81	1597.82	2.92	1320.81	1597.82	/	93.04	/	49.28	0.9064	No	Accept
Y-G-3	D+G	1318.49	1595.37	2.54	1318.49	1595.37	/	84.24	/	51.80	0.9389	No	Accept
Y-G-4	D+G	1315.82	1595.10	2.89	1315.82	1595.10	/	85.75	/	50.38	0.9650	No	Accept
Y-G-5	D+G	1313.94	1591.61	3.19	1313.94	1591.61	/	96.85	/	56.30	0.9924	No	Accept
H-G-1	D+D3+G	1308.97	1596.66	2.30	1308.97	1596.66	1552.44	77.52	105.69	45.20	0.9867	No	Accept
H-G-2	D+D3+G	1309.37	1595.91	2.50	1309.37	1595.91	1564.01	78.72	112.90	43.83	0.9825	No	Accept
H-G-3	D+G	1309.63	1594.46	2.97	1309.63	1594.46	/	86.58	/	49.47	0.9827	No	Accept
H-G-4	D+G	1311.12	1593.79	3.25	1311.12	1593.79	/	92.35	/	51.46	0.9649	No	Accept
H-G-5	complex	1343.38	1604.40	1.17	/	/	/	/	/	/	/	3-peak boundary hit	Fixed-window only
H-M-1	complex	1316.58	1603.29	2.76	/	/	/	/	/	/	/	3-peak boundary hit	Fixed-window only
H-M-2	D+D3+G	1318.84	1601.25	2.45	1318.84	1601.25	1534.13	103.13	74.49	67.16	0.9835	No	Accept
H-M-3	D+G	1320.22	1600.91	3.58	1320.22	1600.91	/	113.33	/	67.93	0.9762	No	Accept
H-M-4	D+G	1317.84	1599.34	3.05	1317.84	1599.34	/	105.32	/	70.30	0.9072	No	Accept
H-M-5	D+D3+G	1323.94	1603.65	1.68	1323.94	1603.65	1553.73	87.24	82.97	51.30	0.9828	No	Accept

Note: Experimental D- and G-band maxima and fixed-window area ratios were determined directly from the processed spectra and are independent of the peak-fitting model. Gaussian D+G or D+D3+G models were applied according to spectral complexity. Fitting parameters from boundary-limited or otherwise unstable fits were not retained. Adjusted R² is reported only for accepted fits. A slash (/) indicates that the corresponding fitting parameter was not retained or was not applicable. Fixed-window ratio values were not interpreted as universal indicators of structural disorder, thermal history or carbon source.

Table S3 Acquisition parameters, quality control and dual-band SNR classification for the Raman mapping fields.

Sample	Field ID	Grid	Step (μm)	Intended points	Measured spectra	Missing	Invalid	Valid	SNR positive	Positive fraction (%)
Q-G	Q-G-M1	10×10	25	100	100	0	3	97	96	99
Q-G	Q-G-M2	8×7	25	56	56	0	0	56	44	78.6
Q-G	Q-G-M3	8×8	25	64	64	0	0	64	64	100
Y-G	Y-G-M1	10×10	25	100	100	0	2	98	98	100
Y-G	Y-G-M2	8×8	25	64	64	0	21	43	37	86
Y-G	Y-G-M3	8×8	25	64	64	0	0	64	64	100
H-G	H-G-M1	10×10	25	100	100	0	1	99	99	100
H-G	H-G-M2	8×8	25	64	64	0	2	62	59	95.2
H-G	H-G-M3	8×8	25	64	64	0	0	64	64	100
H-M	H-M-M1	10×10	25	100	100	0	0	100	99	99
H-M	H-M-M2	8×8	25	64	64	0	0	64	11	17.2
H-M	H-M-M3	8×8	25	64	64	0	0	64	64	100

Note: A pixel was classified as carbon-positive only when both $SNR_D \geq 3$ and $SNR_G \geq 3$. SNR_D and SNR_G were calculated from the maximum baseline-corrected intensities within 1280–1450 and 1560–1650 cm^{-1} , respectively, using the larger standard deviation of the 1000–1100 and 1900–2000 cm^{-1} baseline regions as the noise estimate. Positive fractions were calculated relative to valid spectra only. Missing or invalid pixels were excluded and were not spatially interpolated. Positive fractions describe individual mapped fields and were not interpreted as bulk carbon contents.

Table S4 Raman identification results for representative millimetre-scale black agglomerates.

Agglomerate	Approx. maximum size	Carbon points	Calcite points	Hematite points
Q-G-A1	~3mm	3 / 3	2 / 2	2 / 2
Y-G-A1	~2mm	3 / 3	2 / 2	2 / 2
H-G-A1	~4mm	3 / 3	2 / 2	2 / 2
H-M-A1	~2mm	3 / 3	2 / 2	2 / 2

Note: Q-G-A1, Y-G-A1, H-G-A1 and H-M-A1 are representative sectioned agglomerates selected from the four darker mortars. For each agglomerate, three points were analysed within black regions, two on white crystalline inclusions and two on orange-red inclusions. Entries such as 3/3 or 2/2 indicate the number of points yielding the reported identification relative to the total number analysed. Agglomerate morphology was variable and was not used for classification or source attribution.

Table S5 Analytical methods applied to the seven Xianling mortar samples.

Sample	Wall section	Function	O M	Petrography	XRD	FTIR	SEM- EDS	Acid treatment	Raman cross- section	Raman residue	Raman agglomerate	Raman mapping	TG- DSC
Q-G	Qian Bao cheng	Pointing	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Y-G	Yaotai	Pointing	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
H-G	Hou Bao cheng	Pointing	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
H-M	Hou Bao cheng	Finishing	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Q-Z	Qian Bao cheng	Bedding	✓	✓	✓	✓	✓	✓	✓	—	—	—	✓
Y-Z	Yaotai	Bedding	✓	✓	✓	✓	✓	✓	✓	—	—	—	✓
H-Z	Hou Bao cheng	Bedding	✓	✓	✓	✓	✓	✓	✓	—	—	—	✓

Note: A check mark (✓) indicates that the analysis was performed; an em dash (—) indicates that the analysis was not performed or was not applicable to the corresponding sample. OM, optical microscopy; SEM-EDS, scanning electron microscopy with energy-dispersive X-ray spectroscopy; TG-DSC, thermogravimetry-differential scanning calorimetry. Raman cross-sectional screening was performed on all seven mortars. Raman analysis of acid-insoluble residues targeted conspicuous dark particles recovered from Q-G, Y-G, H-G and H-M; no comparable dark particles were observed in the residues of Q-Z, Y-Z or H-Z. Raman analysis of millimetre-scale black agglomerates and Raman mapping were restricted to the four darker pointing and finishing mortars.