

Synergistic chemical and structural colorations in early polychromic ceramic glazes over 1000 years ago

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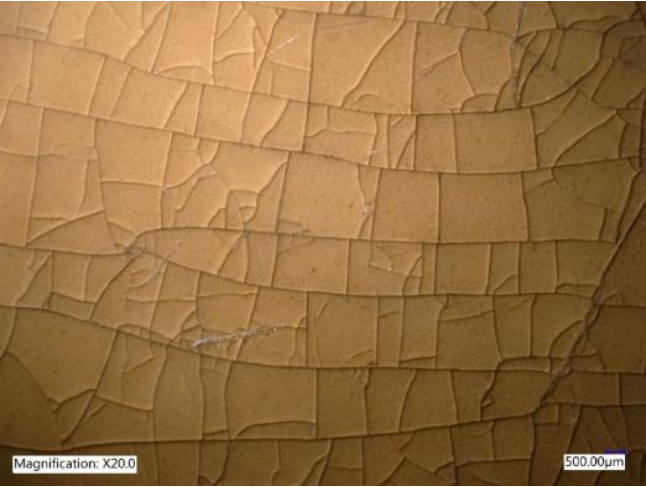
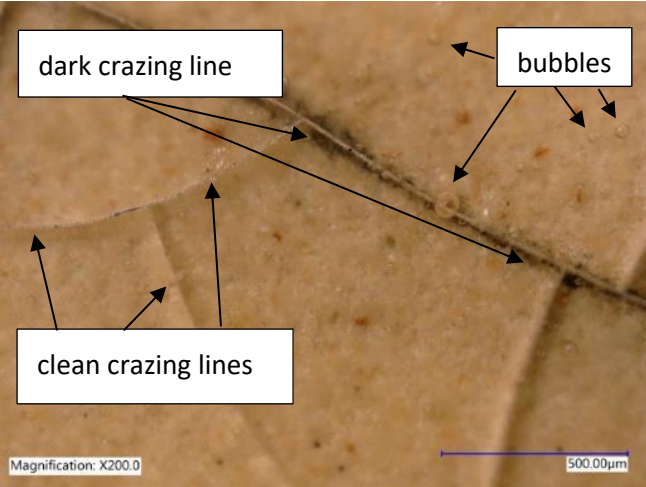
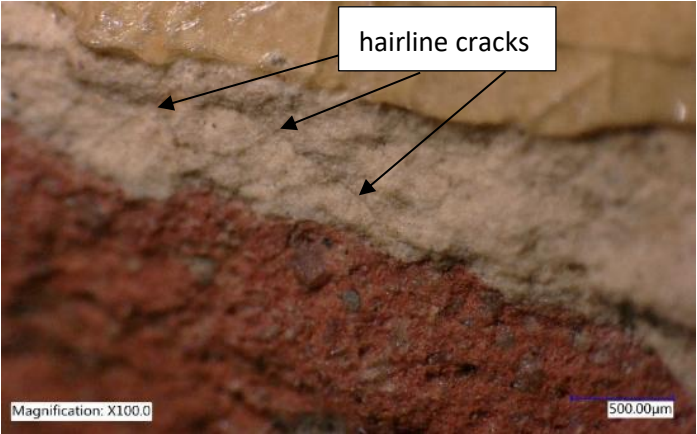
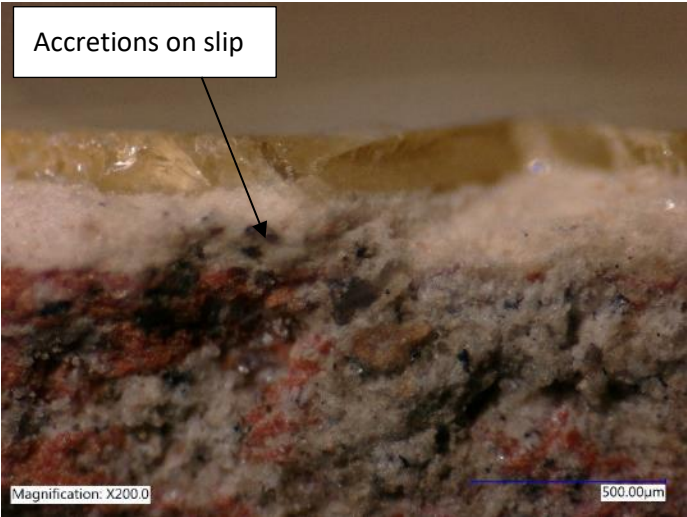
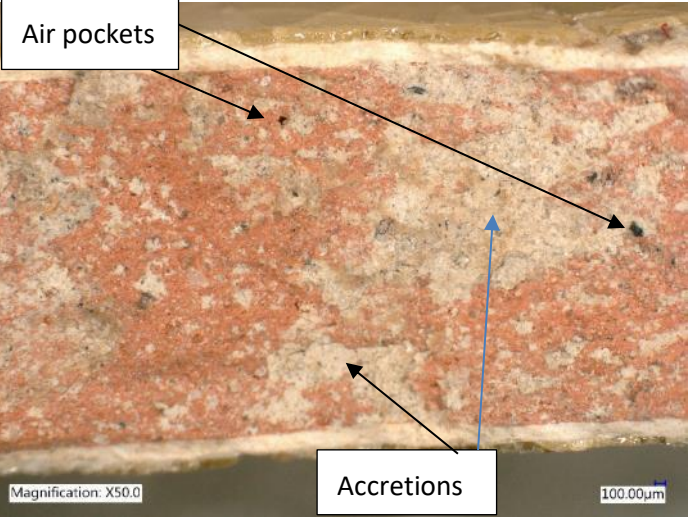
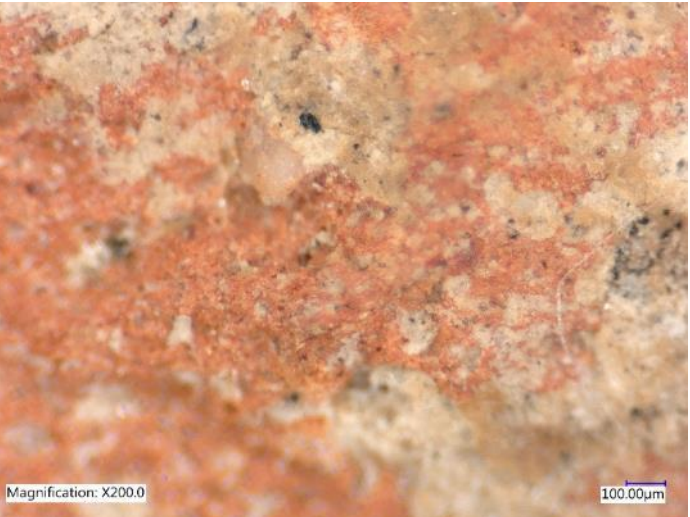
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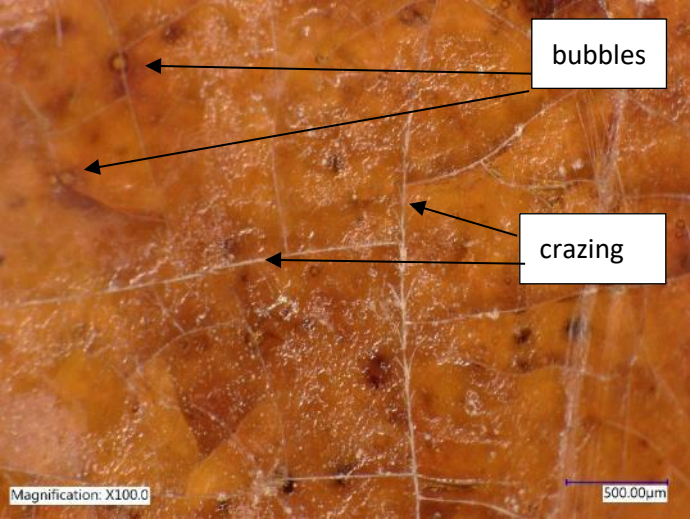
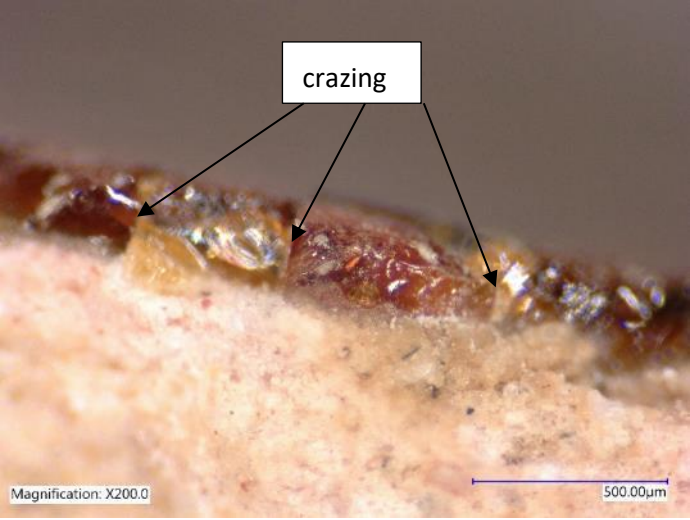
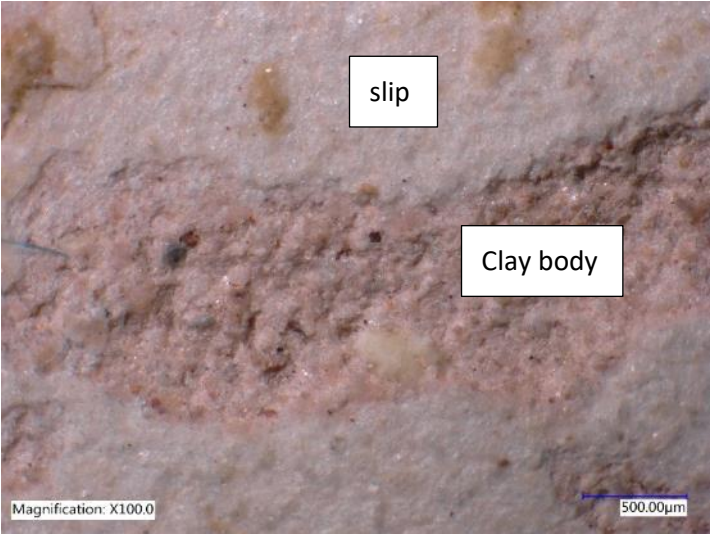
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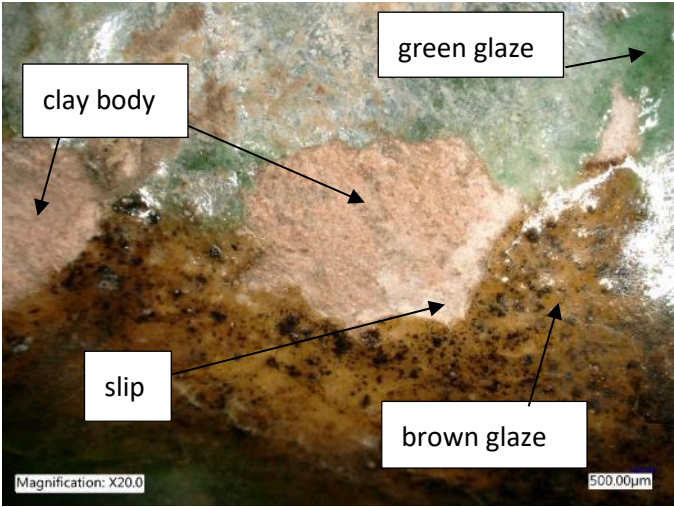
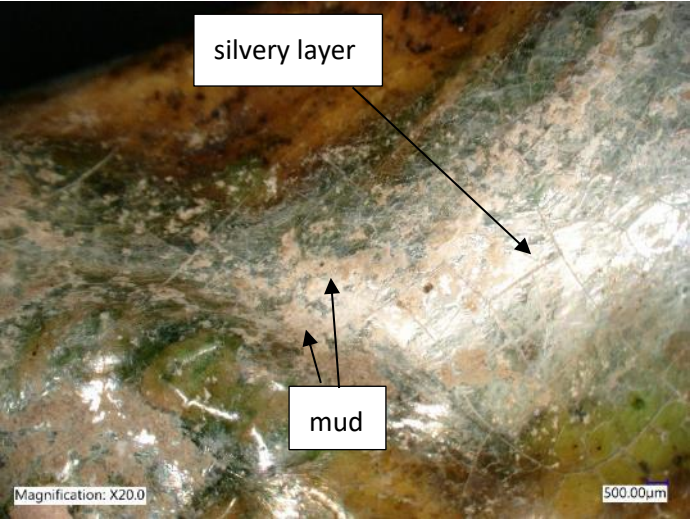
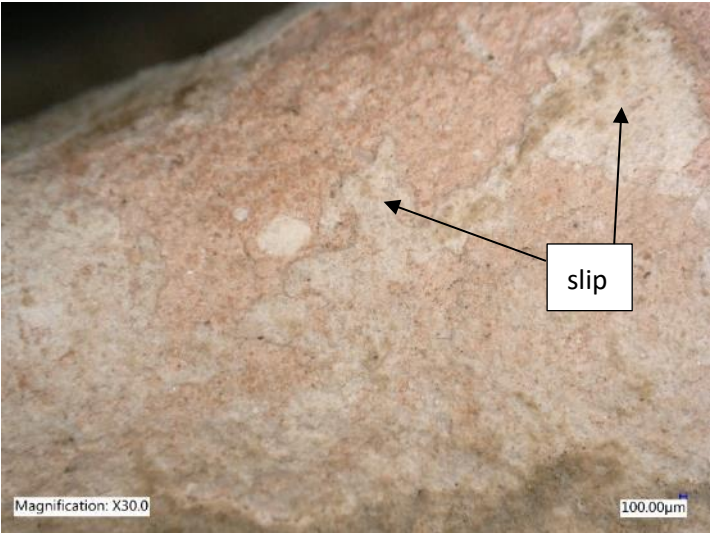
Supplementary Tables S1-S3 and Figs. S1 and S2

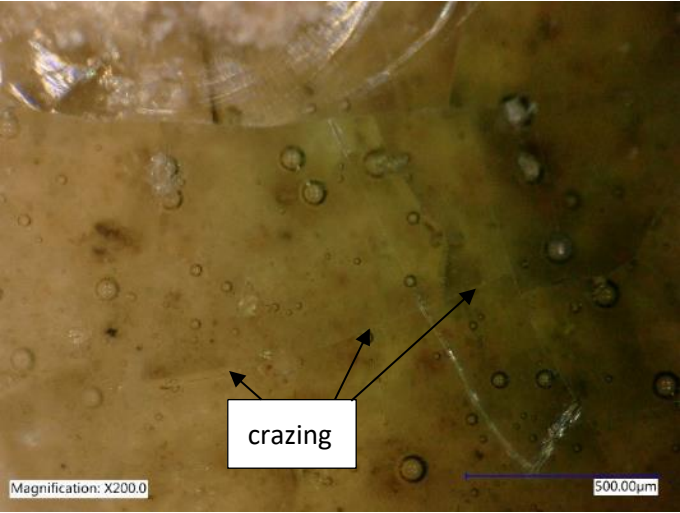
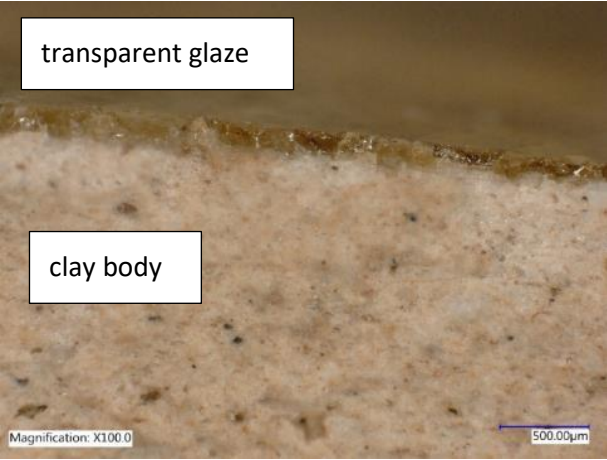
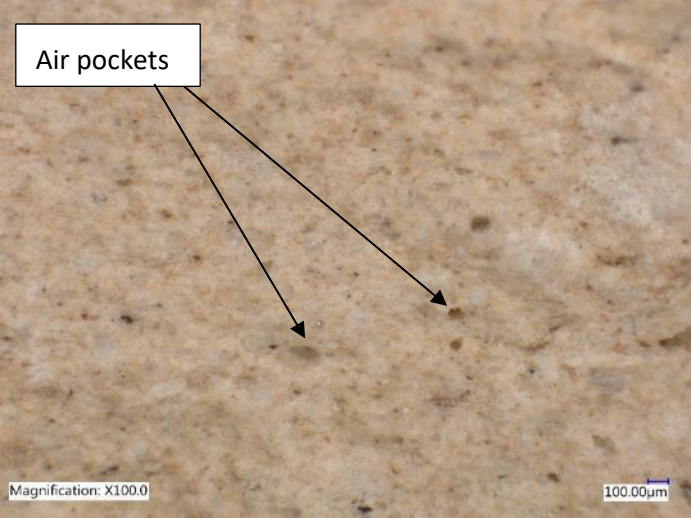
Supplementary Table S1. Description of samples.

Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
T1	Provenance: Qiong kiln, Sichuan city site General description: shard of 6.5 x 4.3 x 0.3 cm, slipped and glazed on both sides. Many accretions on clay and slip from the burial site, only affecting the exposed areas, not the interior of the shard. Glaze: light-yellow translucent glossy glaze applied on both sides of the ceramic. One coat of glaze of 0.1mm in thickness applied by immersion. Slip: white-creamy 0.2mm thick slip applied on both sides of the ceramic. Clay: red stoneware of 3mm thick.	<u>Light yellow glaze (interior and exterior):</u> Good adhesion to the slip layers on both sides. Crazing¹ resulting in different shapes and dimensions on both sides of the shard.  Some crazing lines are dark while most are clean, indicating alterations from infiltrations during burial or development of biological growth. Small bubbles, not visible to the naked eye, at different levels within the glaze formed during manufacturing process. 	<u>White slip (interior and exterior):</u> Strong and good adhesion to clay and glaze. Some vertical and oblique hairline cracks.  Some accretions on the slip from the burial site. 	<u>Red stoneware clay body:</u> Compact, hard and good adhesion to slip. No visible cracks. Few small air pockets Many accretions from the burial site.  

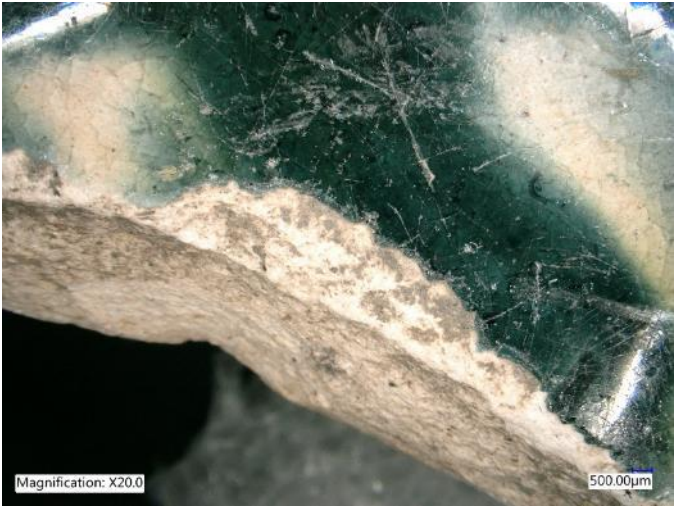
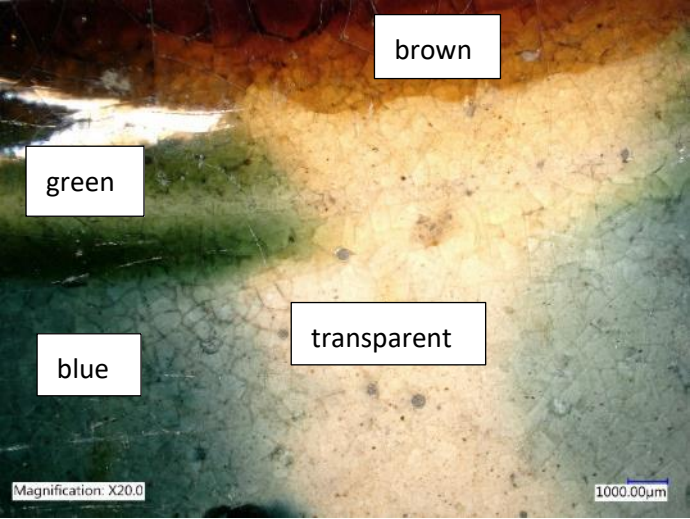
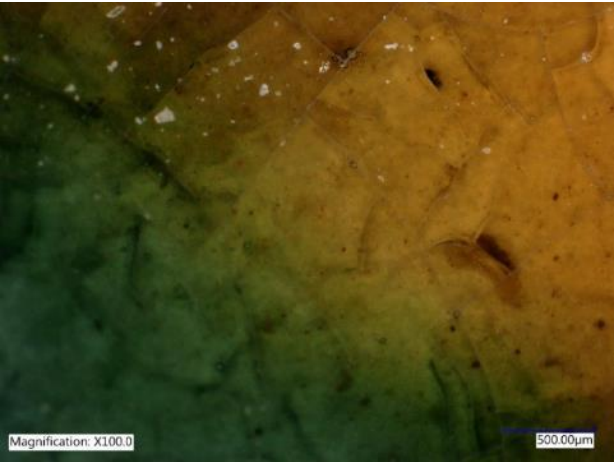
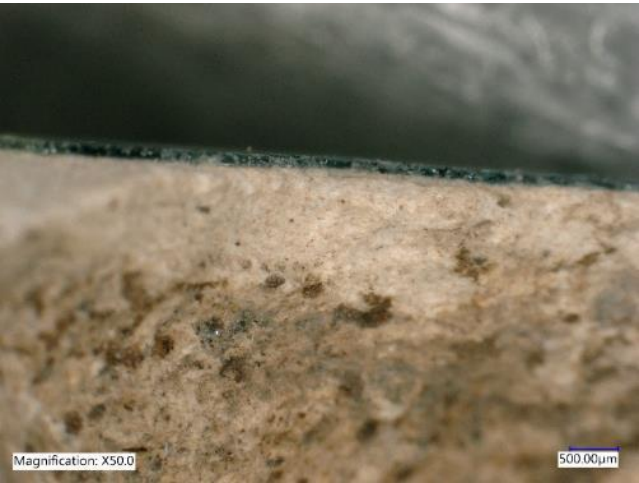
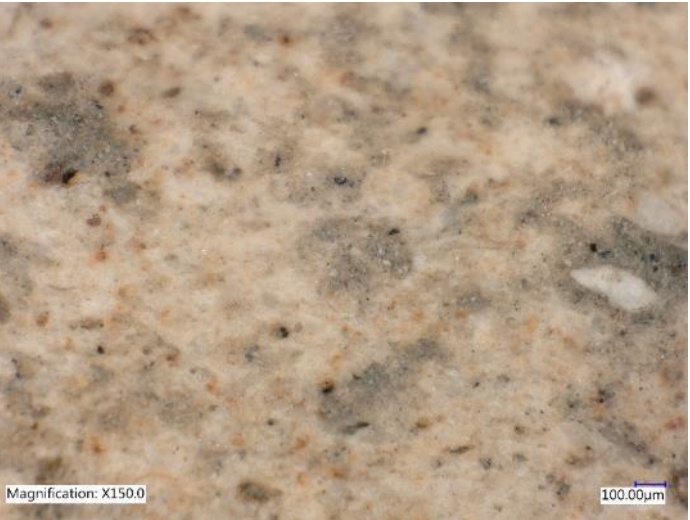
¹ Hairline cracks of various lengths due to the stresses cause during the clay/slip and glaze cooling.

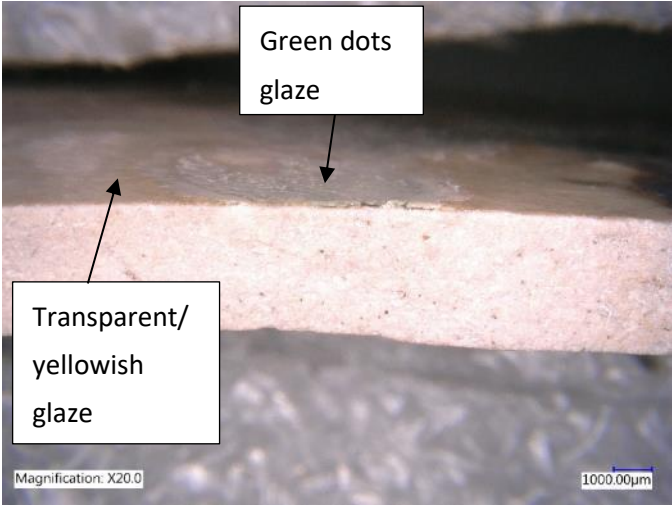
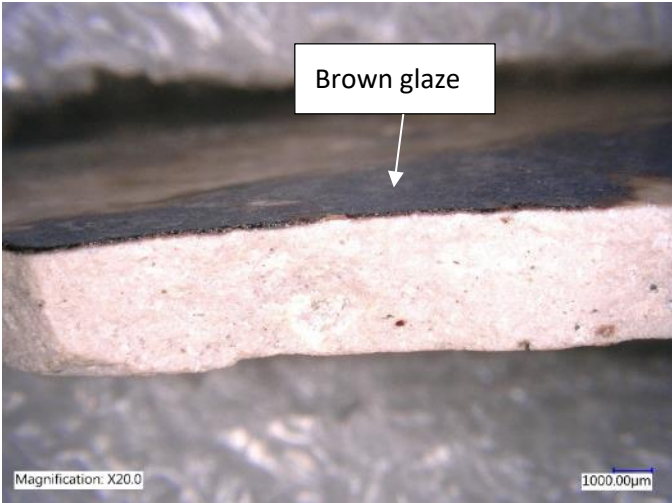
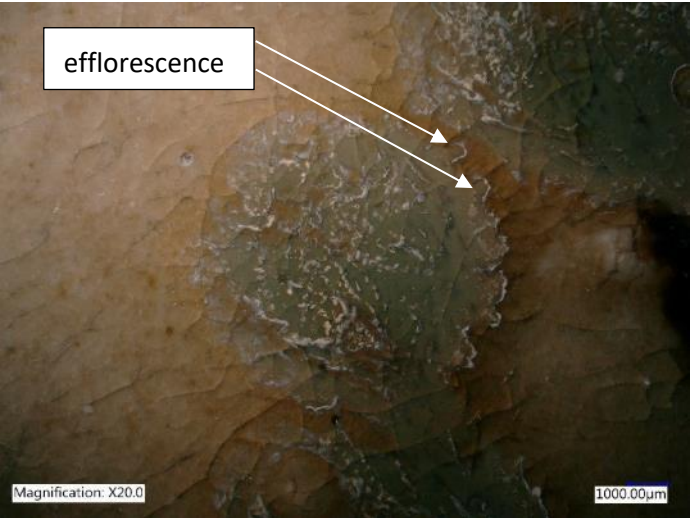
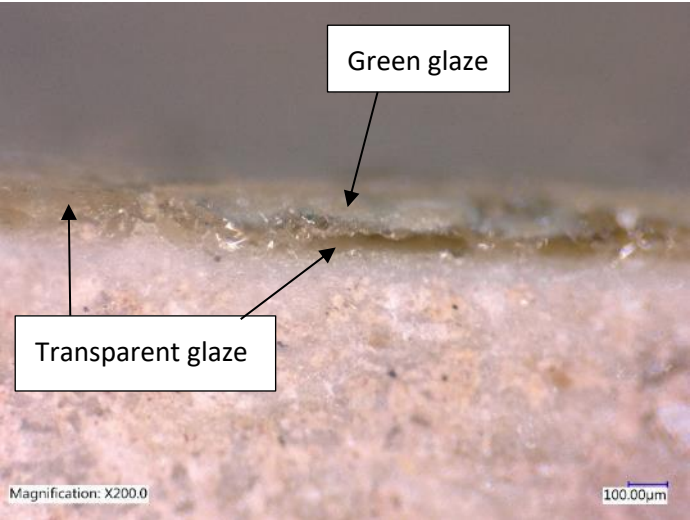
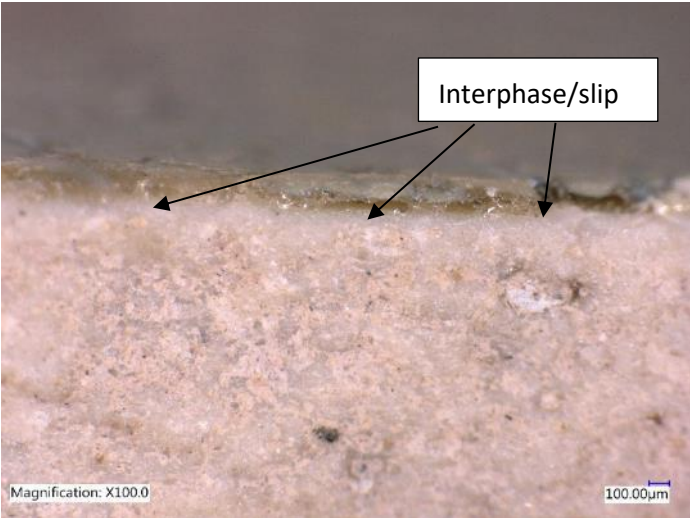
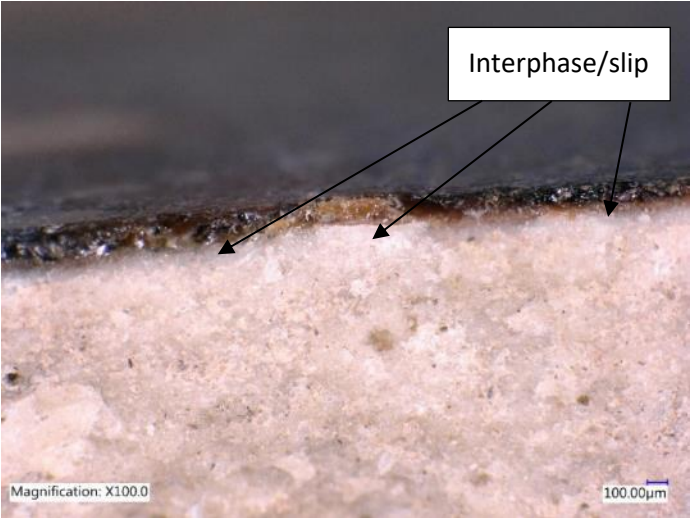
Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
T2	Provenance: Gongxian kiln, Henan city site General description: shard of 5.8 x 4.5 x0.5 cm, slipped and glazed on convex side (exterior) and just glazed on concave side (interior). Glaze: dark brown translucent glossy glaze on the exterior, not covering the whole shard and applied by immersion or splashed; light greenish glossy glaze in the interior, covering the whole shard and applied by immersion. Slip: white slip applied on the exterior, covering the whole shard and applied evenly. No slip in the interior. Clay: pinkish stoneware clay of changing thickness (3-6mm).	<u>Dark brown glaze (exterior):</u> Good adhesion to the slip. Very thin crazing and bubbles at different levels.   <u>Light greenish glaze (interior):</u> Very irregular and with lots of bumps	<u>White slip (exterior):</u> Strong and good adhesion to clay and glaze. 	<u>Pinkish stoneware:</u> Good condition and good adhesion to slip. No visible cracks or air pockets.  

Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
T3	Provenance: Gongxian kiln, Kiln site General description: small artefact of 5.5 x 7 x 3.3 cm, fully slipped and partially glazed. Clay was moulded in the shape of an animal. Glaze: mixture of light brown and green translucent glossy glazes, applied side-by-side, with large areas of white-silvery layers. Slip: white-creamy colour slip covering all artefact, including base. Clay: pinkish stoneware clay moulded in two halves and put together; the interior is hollow.	<u>Brown and green glazes (exterior):</u> Many areas of lost glazes. Well attached to white slip. Very fine, almost not visible crazing. No visible air bubbles Many dark spots on brown glaze Remains of mud on surface from the site.	<u>White slip:</u> Areas of lost slip. Remains are well attached to the clay body and glazes.	<u>Pinkish stoneware claybody:</u> Many small missing sections of clay and small fine cracks. Clay is well attached to slip
		 <u>White-silvery layer:</u> Possibly due to corrosion 	 	 

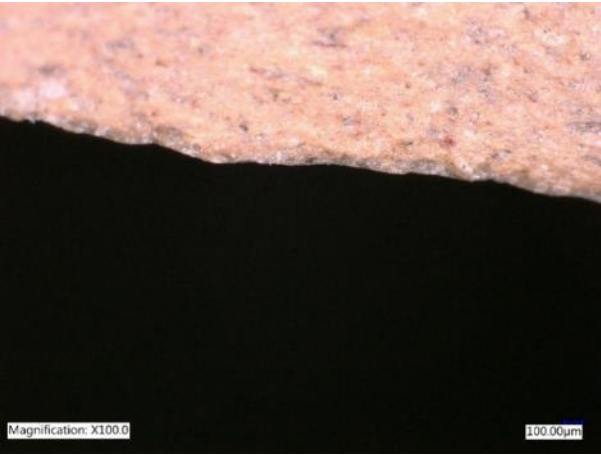
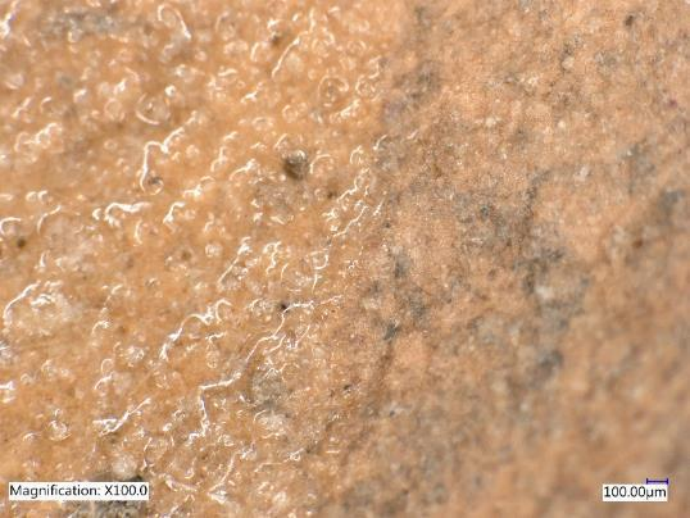
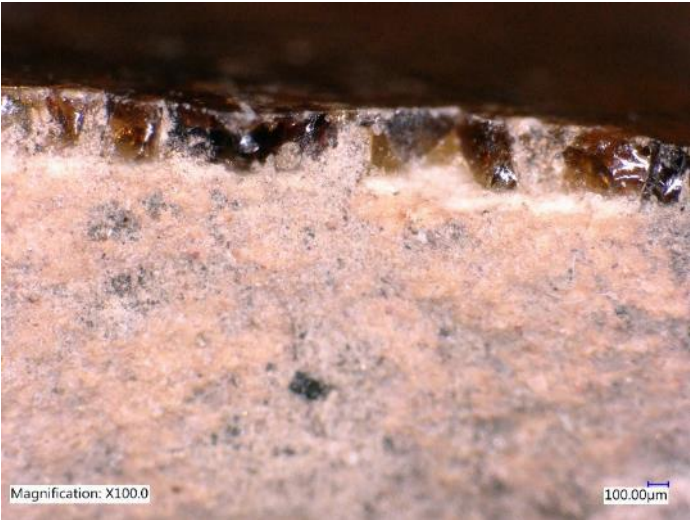
Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
T4	Provenance: Gongxian kiln, Henan city site General description: shard of 5.6 x 3.9 x 0.5 cm; glazed on the convex (exterior) and not glazed in the concave (interior) Glaze: transparent and dark green translucent glossy glazes; the transparent applied by immersion and dark green applied on top of transparent. Slip: no slip found on any side. Clay: light pinkish stoneware clay of 0.5cm in htinckness.	<u>Transparent and dark green glazes (exterior):</u> Extremely fine crazing of glaze. Many bubbles in both glazes.  Magnification: X200.0 500.00µm crazing Well attachment of both glazes to clay body  transparent glaze clay body Magnification: X100.0 500.00µm  dark green glaze clay body Magnification: X200.0 500.00µm	Not applicable.	<u>Light pinkish stoneware:</u> Very well attachment of clay to glaze. No visible cracks and some very small air pockets.  Magnification: X30.0 100.00µm  Air pockets Magnification: X100.0 100.00µm

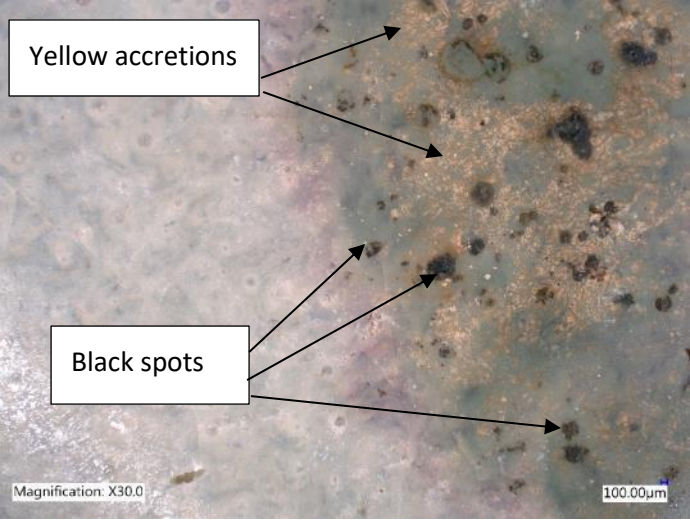
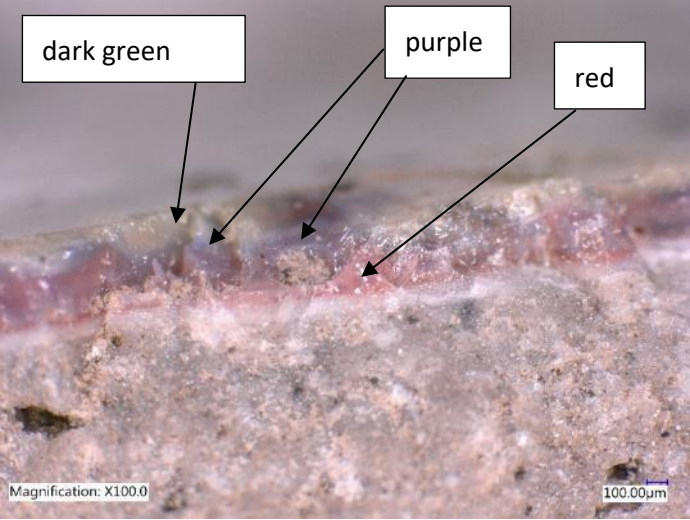
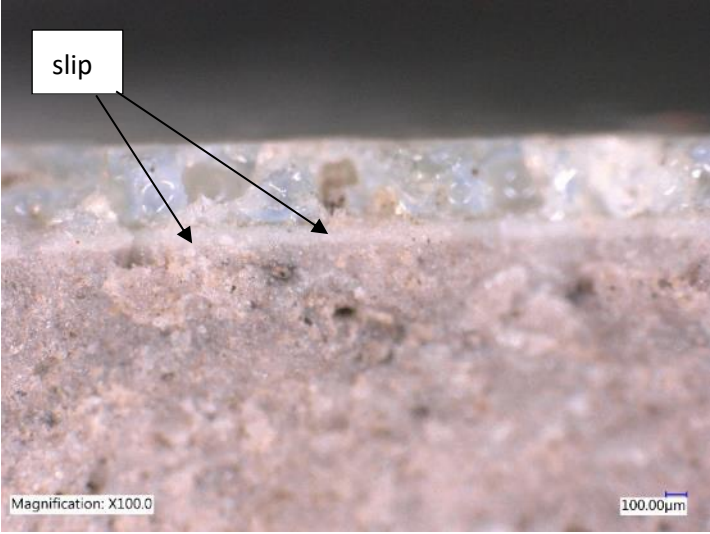
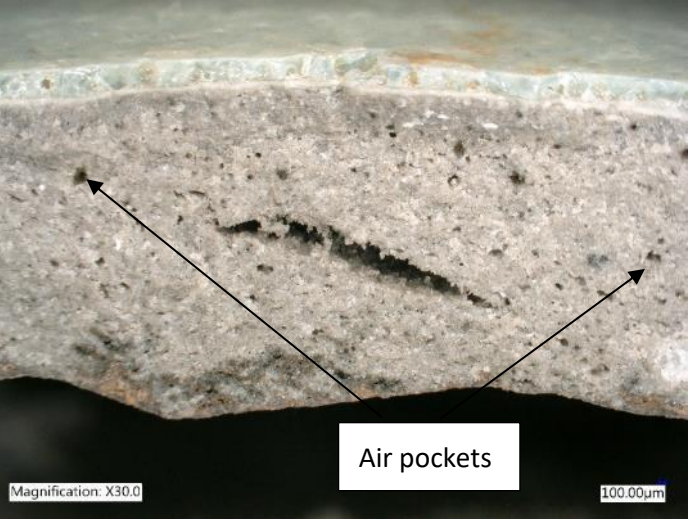
Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
T5	Provenance: Xing kiln, Shandong city site General description: shard of 8.4 x 4.7 x 0.4cm; partially slipped on concave side (interior) and fully slipped and glazed on convex side (exterior). Many accretions on surface from site. Glaze: transparent and dark green glossy glazes; the glazes were applied side by side or firstly transparent glaze was applied and green glaze on top of it Slip: thin and homogeneous white slip on the exterior and same slip partially applied in the interior. Clay: pinkish stoneware clay	<u>Transparent and dark green glazes:</u> Very good attachment to slip. Very fine crazing and no visible bubbles. Magnification: X100.0 500.00µm dark green glaze Magnification: X100.0 500.00µm Transition from transparent to green glaze Magnification: X200.0 500.00µm	<u>White slip (interior and exterior):</u> Fine and in good condition slip conferring the white colour under the transparent glaze. Good adhesion to glaze and clay. slip clay Magnification: X20.0 1000.00µm slip Magnification: X150.0 100.00µm	<u>Pinkish stoneware clay:</u> Good attachment to slip Some accretions on surface of clay form burial. Many small air pockets and no cracks. Magnification: X50.0 100.00µm Magnification: X150.0 100.00µm

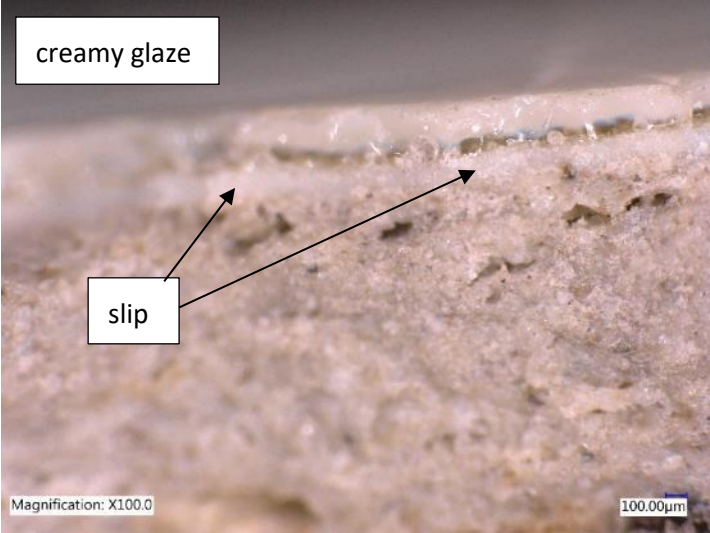
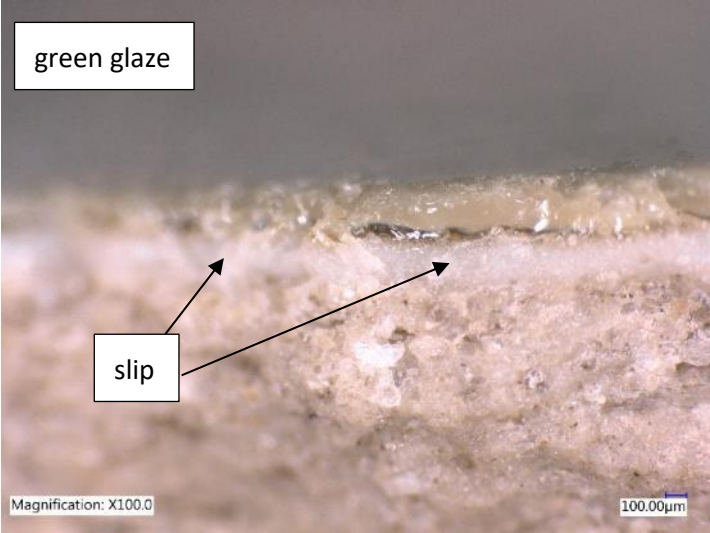
Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
T6	Blue and Yellow patches on white base Provenance: Unknown kiln, Yangzhou city site General description: shard of 10.5 x 4.5 x 0.7 cm, glazed in the exterior and partially slipped in the interior. Glaze: mixture of dark blue, brown and transparent glossy glazes applied side by side. In the conjunction of brown and blue, a green glaze is produced. Only exterior side (concave) is glazed. Slip: no visible slip on exterior and partially slipped in the interior with salmon coloured slip. Clay: white stoneware clay  	<u>Dark blue, brown and transparent glazes:</u>  Very fine crazing and few air bubbles.  Good attachment to clay body 	Not applicable	<u>White stoneware clay:</u> The clay is very homogeneous, fine and hard. Some dirt and accretions from site.  

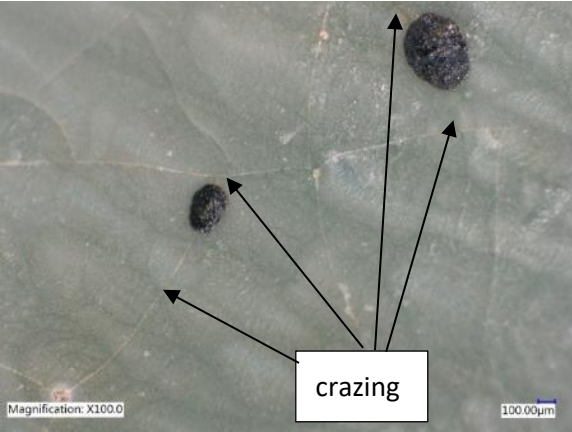
Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
C1	Brown and light green-blue dots on light yellow base Provenance: Changsha kiln, Changsha city site General description: shard of 7.4 x 5.9 x 0.4 cm, totally glazed in the outside (concave) and not glaze in the inside (convex). Glaze: transparent/yellowish base decorated with dark brown and green large dots. First coat with transparent glaze and brown and green dots applied on top. Slip: slip or interphase Clay: light grey stoneware clay	<u>Light yellow, dark brown and green-blueish glazes:</u> The glaze is finely crazed. White salt efflorescences on green glaze, mainly on the edges. Brown glaze is not as glossy as green and translucent glaze.	<u>Interphase or slip:</u> Very thin interphase or slip (possible same type of clay and clay body) between clay and glaze. Very good adhesion between all layers.	<u>Light grey stoneware clay:</u> The clay is light grey in colour, very compact, no air pockets or visible cracks. Made of thin particles. Accretions on surface from burial.
	 	 	 	 

Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
C2	Yellow and purple-read on light green base Provenance: Changsha kiln, Yangzhou city site General description: shard of 9.2 x 6.1 x 1.7 cm, partially glaze in the exterior (convex) and totally glazed in the interior (concave) Glaze: transparent-light green glaze with decorations in brown and purple red. First coat of transparent glaze; second coat of brown glaze at the rim and decorations applied by brush in brown and red purple Slip: no visible slip Clay: Grey and pinkish stoneware clay  	<u>Transparent-light green, brown and purple red glazes:</u> Very fine crazing. Many bubbles at different levels of glaze. Good attachment to clay.  	Not applicable	<u>Grey and pinkish stoneware clay:</u> Same clay but two different colours due to different localized reached temperatures during firing; related to presecnce or not of glaze on the surface.  Good adhesion between glaze and clay.  Some localized air pockets (one very large) horizontally distributed in relation to surface.. 

Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
C3	Brown Provenance: Changsha kiln, Changsha city site General description: shard of 9.1 x 8.1 x 3 cm totally glazed and slipped in the exterior (convex) and partially glazed in the interior (concave). Glaze: dark brown glaze (exterior) and transparent glaze (interior). Slip: very fine white slip under brown glaze (exterior). No slip in the interior Clay: salmon and dark grey stoneware clay 	<u>Brown glaze (exterior):</u> Fine crazing, bubbles, scratches and some light brown accretions.  <u>Transparent glaze (interior):</u> Very fine glaze with good adhesion to clay body.  	<u>White slip (exterior):</u> Good adhesion between slip, glaze and clay. Accretions on slip from burrial site. 	<u>Salmon and dark grey stoneware clay:</u> Same clay but two different colours due to different localized reached temperatures during firing. Some short horizontal fine cracks Depositions on clay from site.  

Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
C4	Green-purple-red patches on light opaque blue base Provenance: Changsha kiln, Unknown site General description: shard of 6.4 x 3.6 x 1.4cm; totally slipped and glaze on the outside (convex) Glaze: dark and light green. First layer of light green covering all surface. Decorative Slip: white slip Clay: grey stoneware clay	<u>Dark and light green glazes:</u> Yellow depositions on localized areas. Black spots on localized area  Croos section of dark green with red-purplish colour at base. The red-purplish colour is visible in the insersection between light and dark green. 	<u>White slip:</u> Fine and hoogeneous white slip. Good adhesion between slip, clay and glaze. 	<u>Grey stoneware clay:</u> Some small and large air pockets. Large pockets are horizontal in relation to surface 

Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
C5	Green patches on opaque white base Provenance: Changsha kiln, Unknown site General description: shard of 6.8 x 6.8 x 1.7 cm fully slipped and glazed on the exterior (convex). Glaze: green glaze applied on top of creamy opaque glaze; both glossy (exterior) Slip: white slip Clay: light brown stoneware clay 	<u>Creamy and green glazes (exterior):</u> Light brown accretions on surface Fine crazing Bursts in circular shape, possibly due to many air pockets in the clay body and produced during firing.  	<u>White slip:</u> Fine and homogeneous white slip. Good adhesion to clay. Some areas may appeared to be detached to glaze, but they are transparent glaze, not voids.  	<u>Light brown stoneware clay:</u> Many and large air pockets in the body clay extending horizontally in relation to glaze surface.  

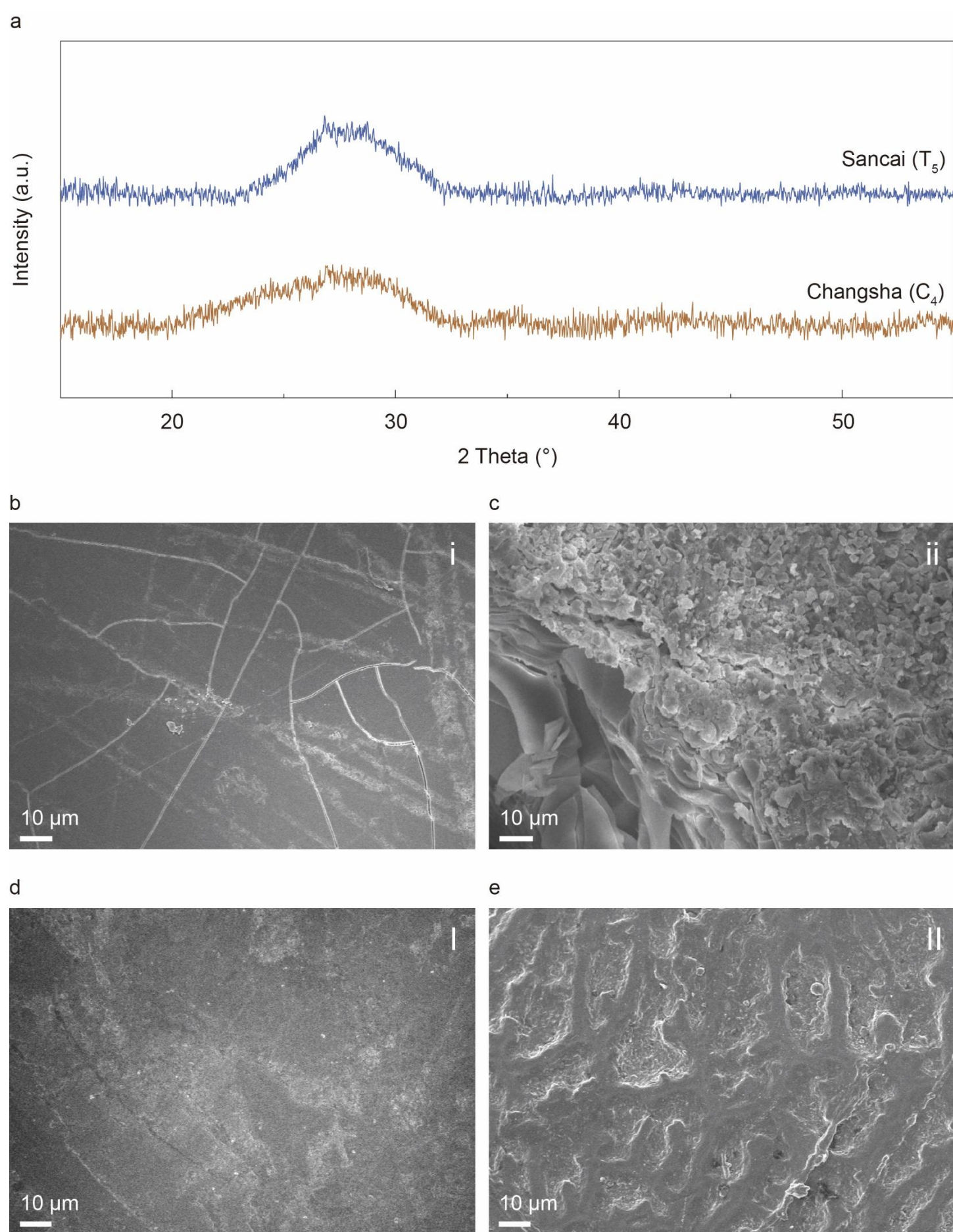
Sample	Sample provenance and description	Glaze condition	Slip condition	Clay condition
C6	Opaque green Provenance: Changsha kiln, Changsha city site General description: shard of 5 x 4.5 x 1cm, fully glazed on the exterior (convex) and partially glazed in the interior (concave) Glaze: dark green opaque glossy and transparent glazes. Fine layer of transparent glaze applied first and covered with thicker layer of opaque green glaze Slip: none Clay: grey stoneware clay 	<u>Green glaze:</u> Fine crazing. Black spots on surface. Could be clay body components or corrosion material migrated from clay body to glaze surface though crazing. All black spots are located on top of crazing lines.  <u>Transparent glaze:</u> Good adhesion between glaze and clay body 	Not applicable	<u>Grey stoneware clay:</u> Good adhesion between clay and glaze Fine and compact clay with some very small air pockets  

Supplementary Table S2. Chemical compositions (wt%) of Tang Sancai glazes.

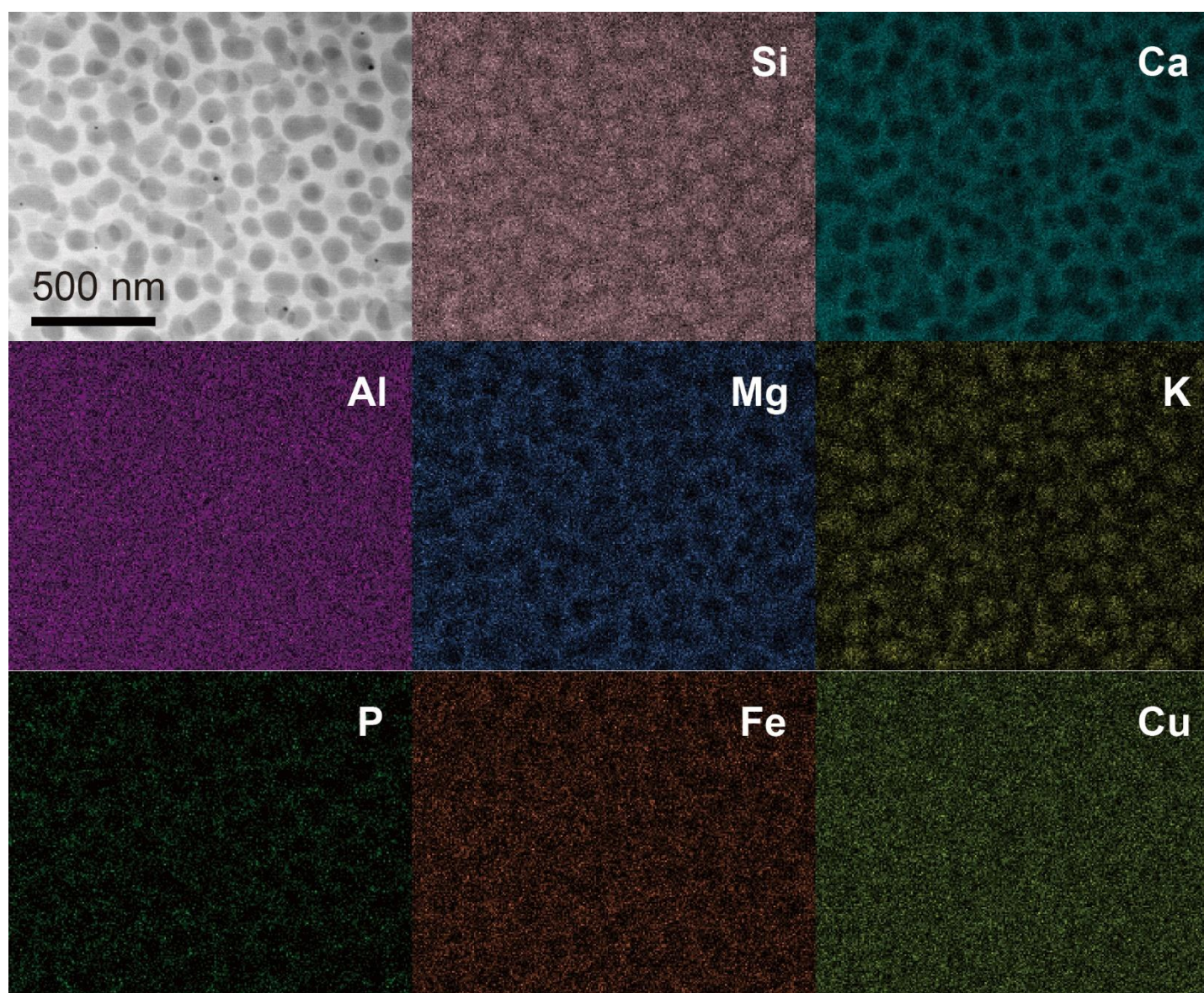
Specimen Colour	SiO ₂	PbO	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	CuO	CoO	TiO ₂	K ₂ O	Na ₂ O	P ₂ O ₅	Ref.
Yellow-Orange	30.5	50.5	6.9	1.2	2.1	4.9	--	--	nt	0.2	--	nt	¹
Yellow-Orange	29.3	59.6	5.7	1.6	0.5	2.3	--	--	nt	1.0	0.5	nt	¹
Green	30.6	50.00	6.5	0.9	0.2	0.5	3.8	--	nt	0.3	0.3	nt	¹
Blue	34.4	42.1	nt	2.3	0.5	1.1	--	1.2	nt	0.2	0.1	nt	¹
Blue	nt	45.0	nt	0.8	0.4	1.0	0.4	1.0	nt	0.3	0.2	nt	¹
Light Yellow	25.0	69.0	3.1	0.6	0.3	2.0	--	--	--	--	0.1	nt	²
Yellow-Orange	34.8	55.7	5.8	0.5	0.2	2.8	--	--	0.2	--	--	nt	²
Green	26.1	68.5	3.6	0.4	0.3	0.4	1.0	--	--	--	--	nt	²
White	31.9	52.6	5.8	2.2	1.3	2.1	--	--	nt	0.5	0.1	nt	²
Green	35.8	44.2	11.0	1.3	0.4	2.3	2.8	--	--	1.2	0.6		³
Yellow	28.7	54.6	8.1	1.7	0.4	4.1	--	--	nt	0.8	0.5	nt	⁴
Green	30.7	49.8	6.6	0.9	0.3	0.6	3.8	nt	nt	0.8	0.4	nt	⁴
Light Yellow, T ₁	29.1	58.6	8.3	0.5	0.8	0.9	--	--	0.8	0.7	0.2	--	This work
Yellow-Orange, T ₂	27.2	57.4	7.7	1.3	0.4	5.3	nt	--	--	0.4	0.1	--	This work
Yellow, T ₃	52.8	30.3	6.8	3.4	1.0	4.6	0.2	--	0.6	--	0.2	--	This work
Yellow, T ₆	25.6	60.6	7.1	0.9	0.6	4.2	0.1	--	--	0.3	0.7	--	This work
Green, T ₃	48.7	37.8	6.9	2.4	1.1	1.4	0.9	--	0.1	0.1	0.6	nt	This work
Olive green, T ₄	35.4	42.3	7.1	0.5	0.8	0.5	11.5	--	--	0.5	0.4	--	This work
Green, T ₅	31.5	56.3	6.8	1.5	0.8	nt	1.6	--	1.0	0.6	--	--	This work
Blue, T ₆	36.2	51.0	5.8	0.7	0.9	1.8	1.0	1.2	--	0.8	0.4	nt	This work
Silver (corroded), T ₃	17.1	56.4	2.5	17.2	0.3	2.8	0.5	--	0.1	--	--	3.0	This work

Supplementary Table S3. Chemical compositions (wt%) of Tang Changsha glazes.

Specimen Colour	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	CuO	TiO ₂	MnO	K ₂ O	Na ₂ O	P ₂ O ₅	Ref.
Yellow-Green	61.67	14.28	15.29	1.79	1.48	--	0.86	0.47	2.04	0.19	1.16	⁵
Grey-White	58.99	9.67	20.65	2.87	1.00	--	0.79	0.59	2.19	0.33	2.14	⁵
Dark-Green	54.85	8.73	19.44	2.82	1.56	3.78	0.87	0.52	1.93	0.20	1.98	⁵
Black-Brown	53.19	12.65	14.98	2.87	8.00	--	0.98	0.62	1.95	0.11	2.02	⁵
Bea-Green	57.38	8.09	18.03	3.09	1.19	3.13	0.56	0.66	2.07	0.34	2.19	⁵
Yellow-Grey	62.99	12.32	15.39	2.46	1.72	--	0.76	0.54	2.26	0.77	1.78	⁵
Brown	56.48	11.27	19.33	2.42	4.35	--	0.89	1.97	1.82	9.22	1.05	⁵
Yellowish glaze	62.08	12.29	14.91	2.25	1.40	--	0.88	0.47	1.98	0.11	1.32	⁶
Opaque yellowish glaze	59.88	9.24	16.95	3.37	0.85	--	0.78	0.76	2.10	0.22	3.04	⁶
Painted opaque green	57.44	8.73	18.54	2.59	0.88	2.98	0.65	0.66	1.77	0.25	2.28	⁶
Painted brown	57.04	12.06	15.71	2.39	5.15	--	0.87	3.31	1.67	0.23	1.05	⁶
Painted red	66.15	8.15	20.37	n.t	1.56	0.30	0.55	0.32	1.98	n.t.	0.59	⁷
Opaque green glaze	65.09	7.24	23.14	n.t.	1.30	0.03	0.55	0.34	1.78	n.t.	0.52	⁷
Glaze	64.92	11.08	13.30	2.01	2.49	0.03	0.51	0.51	2.46	0.66	1.59	⁸
Brown	56.54	10.81	12.89	2.01	10.88	0.06	0.83	0.83	2.55	0.65	1.64	⁸
Green	53.70	8.13	23.27	2.01	1.74	3.81	0.86	0.86	1.80	0.67	2.19	⁸
Brown, C ₁	64.3	6.9	11.9	2.1	6.0	--	0.5	3.0	4.9	0.2	0.3	This work
Green, C ₁	55.1	8.0	19.1	4.3	2.7	4.9	1.1	1.5	1.0	0.3	1.9	This work
Red, C ₂	60.2	13.9	16.3	1.9	1.8	2.1	0.6	0.2	1.8	0.2	0.9	This work
Brown, C ₂	63.2	14.9	9.8	2.4	4.4	0.2	1.6	2.7	6.6	1.0	--	This work
Celadon glaze, C ₂	64.0	14.4	14.5	2.1	1.0	0.2	0.6	0.2	1.8	0.2	0.9	This work
Brown, C ₃	55.8	9.1	15.5	2.1	8.1	--	0.4	3.3	3.5	0.5	1.8	This work
Green Blue, C ₄	60.8	9.5	15.4	3.0	1.5	5.3	0.8	0.4	2.2	--	1.1	This work
Green, C ₅	63.7	7.7	18.7	3.5	2.0	1.2	0.5	0.9	1.6	0.2	--	This work
Opaque white glaze, C ₅	65.4	7.8	18.8	3.6	2.3	--	0.3	0.3	1.5	0.4	--	This work
Green blue, C ₆	69.7	10.4	12.9	2.8	0.8	0.6	0.5	--	0.9	0.1	1.3	This work



Supplementary Fig. S1 Characterization of Tang Sancai and Changsha samples. (a) XRD patterns of Sancai (T₅) and Changsha (C₄) glazes, (b) SEM images of (b) yellow area (i) and (c) green area (ii) of Sancai sample T₃ and (d) brown area (I) and (e) blueish green area (II) of Changsha sample C₁.



Supplementary Fig. S2 TEM image and EDX elemental mappings of Changsha sample C4 glaze.

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