A PALE BLUE FRITTED CERAMIC GOBLET

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This study was performed using a stereoscopic microscope, an inverted optical microscope (petrographic microscope), a scanning electron microscope (SEM) with back-scattered electron (BSE, composition contrast) and secondary electron (SE, topographic contrast) imaging, coupled with energy-dispersive X-ray element analysis (EDX).
Some samples were observed directly and some were embedded in resin, and a microsection perpendicular to their surface was performed. The microsection surfaces and the microsamples were coated with carbon for the SEM examination. This operation was partly responsible for the carbon peak (C) observed on the elementary X-ray spectra.

Samples of the material used to make the object were analyzed, as well as the surface deposits: P1 consists of fragments of the pale blue coating and purple material, P1A is a contact with the ceramic body, P1B is a massive fragment of the pale blue coating, P1C is a fragment of the purple pupil pattern; P2 are microsamples from the white eye (P2A) and the purple pupil pattern (P2B);
P3 is a green crystallized product, on the pale blue coating inside the goblet; P4 are brown to black deposits on the base surface.

Fig 1 - (H.:7.8 cm, rim Ø: 5.6 cm, neck Ø: 3 cm). China, late Warring States period (481 - 221 BC) to early Han period (206 BC - AD 220).

The goblet (Fig. 1) has an orange-red **ceramic body (Fig. 2a, C)** completely covered with a thick coating of a pale blue, soft micro-granular material. The ceramic body is observed only in some small chips, on the rim and the body of the goblet where it shows a sharp contact with the pale blue coating.

The coating surface has a glossy appearance with a faint yellowish hue (**Fig. 2b, Y**). Under this shiny surface, the material is matte and rather friable.

The cracks spread across the coating, to the ceramic body and are observed on the whole surface of the object.
(**Fig. 2, arrows**). They reach the ceramic body and can be observed on the whole surface of the object.
Numerous blisters develop on the coating, mostly in association with the "eye" designs, but they also occur in plain coated areas (**Fig. 2b and 2c**).

The inner surface (**Fig. 2c**) shows some coating defects, with rounded lacunas that reveal the ceramic body and some detachment of the coating from the ceramic wall.

The rounded surface morphology and the variable thickness of the coating suggest its application as a pasty material on the ceramic body.

The "eye" design consists of a circular white inlay with a purple "pupil".

The inlay process can be reconstructed by studying the surface wear of the goblet: the white droplet is laid first upon the pale blue coating, followed by the purple 'pupil'.

During the final processing of the coating (heating and cooling phase?), some inlays began to melt (**Fig. 3b, arrows**) and important blisters developed under the white material (**Fig. 3c, arrows**) very probably amplifying the rise of the "eye" design.

The yellowish hue and glossy surface (**Fig. 3a, Y**) characterising the pale blue coating can be observed on the best preserved "eye" inlays.

Fig 2 - Detail views of the goblet surface (stereoscopic microscope, x 5, **2a** - rim of the goblet, **2b** - outside, bottom of the "eye" area, localization of sample P1, **2c** - inside).

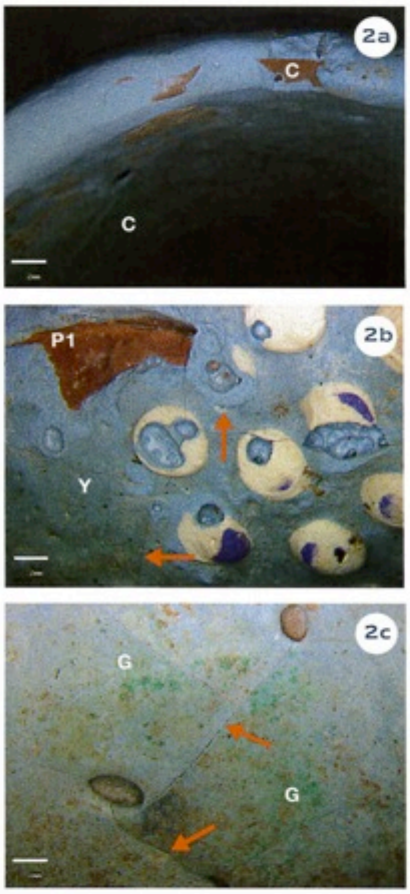


Fig 3 - Detail views of the "eye" design (stereoscopic microscope, **3a** - x 10, , **3b** - x 10, **3c** - x 7)

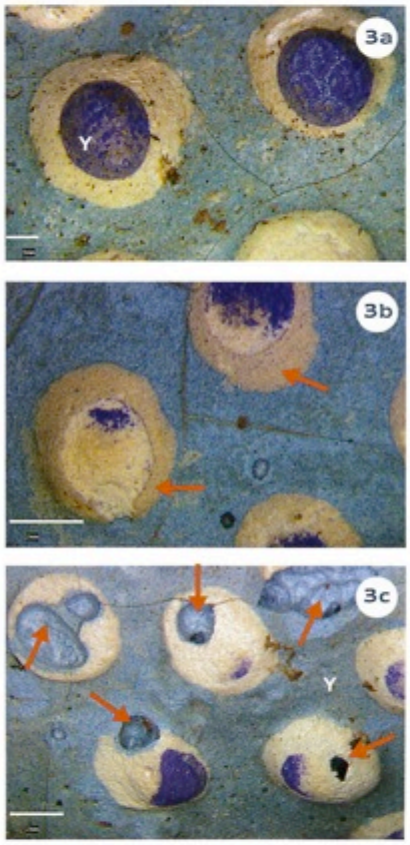


Fig 4 - Detail view of sample P1A (**4a** - inverted optical microscope, x 200, polarized light, **4b** - SEM, BSE, x 500). The square locates **Fig. 6a**.

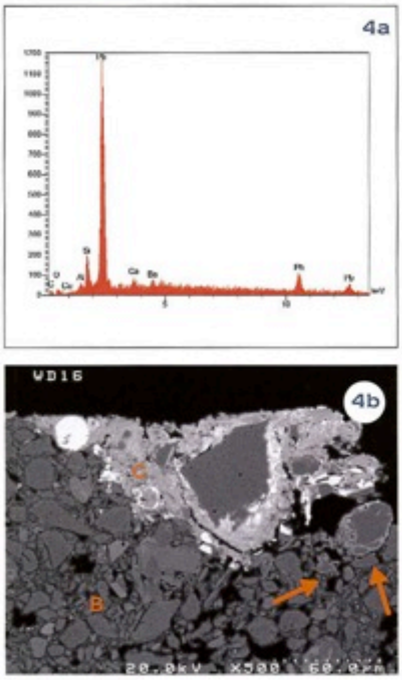
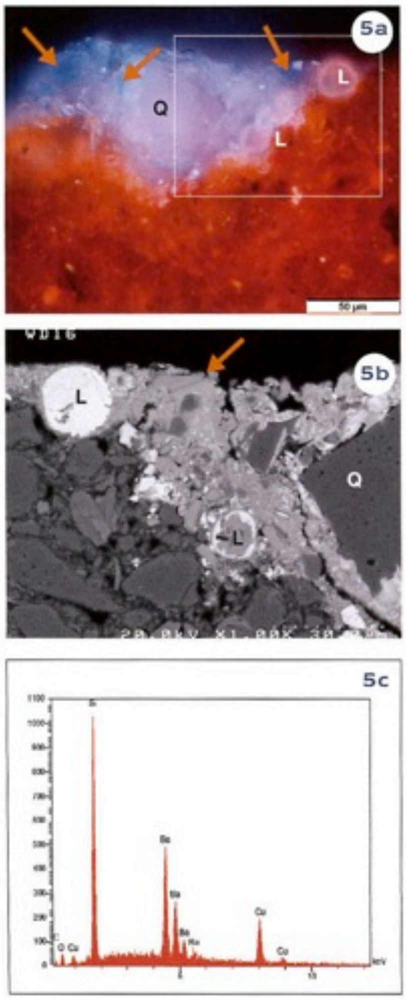


Fig 5 - Detail views (**5a** -, inverted optical microscope, x 500, polarized light, **5b** - SEM, BSE, x 1000) of the pale blue coating, and EDX analysis (**5c** -) of a blue crystal. Microsample P1A.
The square locates **Fig. 5b.**



THE CONSTITUENT MATERIALS

The ceramic body - Sampling (P1-A) from the ceramic body (**Fig. 4, B**), with some adherent pale blue coating material (C) was performed in a chipped off area (**Fig. 2b**).

The ceramic body (**Fig. 5, B**) is a silicate iron-rich material (**Fig. 4a**), a mixture of clay and fine-grained (up to 50 micrometers) mineral particles (mainly quartz and some feldspars). There appears to be very little interaction (**Fig. 4b, arrows**) between the coating and the ceramic body.

The pale blue coating - Observation of the coating shows a heterogeneous translucent material, associating lead-rich translucent spherical structures (**Fig. 5, L**), crushed quartz (Q), and blue particles (**Fig.5, arrows**).

EDX analysis of the blue particles (**Fig. 5c**) -shows a composition typical of Han blue: Si, Ba, Cu as main elements.

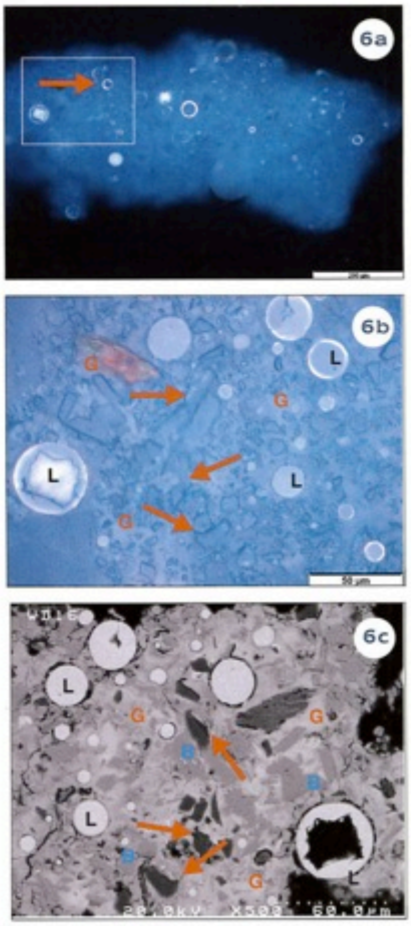
Han blue, a barium copper silicate ($BaCuSi_4O_{10}$) is a pigment which is known to have been synthesized during the Warring States and Han period (1).

The study of sample P1B (**Fig. 6**) allows a better understanding of the nature of the pale blue material.

Observation of the microsection shows a heterogeneous fritted material, whose microstructure has certain similarities to **Egyptian blue frit** (2) obtained by firing.

As observed previously, the bulk blue pale material consists of clusters of crystals, with variable shapes and dimensions, including numerous automorphic Han blue crystals (**Fig. 6** and **7, B**) and unmelted ground quartz particles (**Fig. 5b** and **7a, Q, Fig. 6c, arrows**). The global cohesion is due to abundant low crystalline to glassy connecting phases (**Fig. 6c** and **7a, G**).
The connecting phases (**Fig. 7b**) whose morphology and composition are evidence of a low crystallinity level, show lead saturation and contain translucent lead-rich spherical structures (**Fig. 6b** and **c, Fig. 7a, L**). The silicon level of this connecting phase is usually very low and different from usual silicate glassy materials.

Fig 6 - Detail views of the pale blue material (inverted optical microscope, **6a** - x 100, polarized light, **6b** - x 500, reflected light) and SEM, BSE, x 500 (**6c** - same field as **b** -). Microsample P1B.
The square locates **Fig.8b**.



These observations allow characterising the pale blue material as a frit, and to describe this goblet as a fritted ceramic.

Some studies on ancient Chinese glazes (3) (4) show polychrome ceramic objects with blue patterns of similar appearance and colour. These Han blue coloured objects dating from the Warring States period are described as "early Chinese high-lead glazes".

The table below shows the results of EDX semi quantitative elementary analysis performed on the pale blue frit and the connecting phases, and comparison with materials from the Warring states and Han period.

Table 1 - Elementary compositions (weight %)
Semi-quantitative elementary analysis for the pale blue coating (column 1) is an average value from three global analyses. The second column shows average value of the low crystalline to glassy connecting phases.
The stoechiometric values for Han blue given in the third column can be compared with the pale blue coating (column 1). The "Chinese glasses" values (column 4) are average values for 30 high-lead glass objects from burials dating from the Warring States and Han periods (5) (6). The "Chinese high-lead glaze" (column 5) is obtained from a lead and barium-rich glaze from the same periods (3). The sixth column concerns an octagonal Han purple colour stick (7) described as a "Han purple frit" and containing Han purple crystals (BaCuSi2O6), whose synthesis process is similar to Han blue pigment manufacturing (1) (8). The last column gives the stoechiometric composition of Han purple.
Nd= undetected

	1 Pale blue coating	2 Glassy connecting phases	3 Han blue, Stoechio	4 Chinese glasses	5 Chinese high-lead glazes	6 Han purple frit	7 Han purple Stoechio
SiO_2	30.3	4.4	50.8	49.3	33.4	32.3	34.0
BaO	13.5	0.1	32.4	13.8	7.7	20.7	43.4
CuO	2.5	nd	16.8		3	14.6	22.5
PbO	50.6	91.4		26.1	43.5	14.7	
Al_2O_3	1.2	1.1			3.9	1.0	
K_2O	0.4	nd			0.5	0.2	
CaO	1.3	2.8			2	0.6	
Fe_2O_3	0.1	0.3			2	0.6	
Na_2O	nd	nd		nd	0.4	2.3	
Total :	100,0	100.1	100	89.2	96.4	87.0	100
SiO_2/BaO	2.2	44	1.6	3.6	4.3	1.5	0.8
BaO/CuO	5.4		1.9		2.6	1.4	1.9
SiO_2/PbO	0.6	0.05		1.9	0.8	2.2	

These results show that the pale blue coating has a characteristically very high lead level. Its global elementary composition shows a similarity with a dark-green glaze from the Han dynasty (**Table 1**, column 5), apart from the colour and the material microstructures for which we have no reference (except for the Han purple stick).

If the SiO2/PbO ratio is quite similar, (0.6 and 0.8) the barium level is twice as high (SIO2/BaO = 2.2 and 4.3). In the pale blue coating, the absence of copper in the low crystalline to glassy connecting phases (at least under the detection threshold of the system used) allow us to assume that the copper content (CuO: 2.5%) comes only from the Han blue crystals.

Fig 7 - Detail view (**7a** -, SEM, BSE, x 1500) and EDX analysis spectrum (**7b** - orange spot) of a connecting phase in the pale blue material. Microsample P1B.

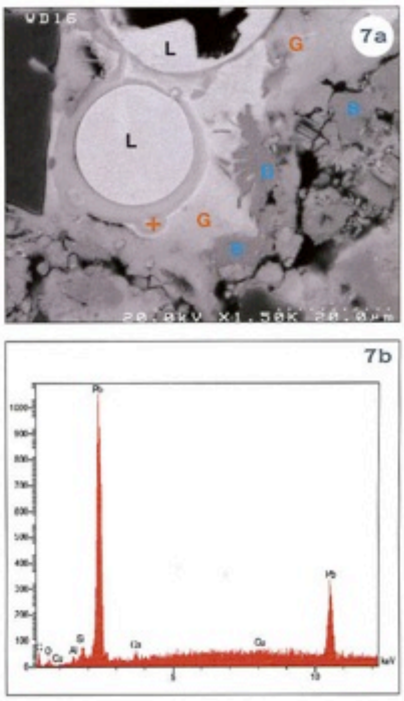


Fig 8 - Detail view of a purple "pupil" (stereoscopic microscope, x 15).

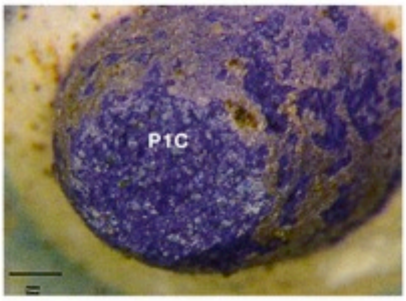
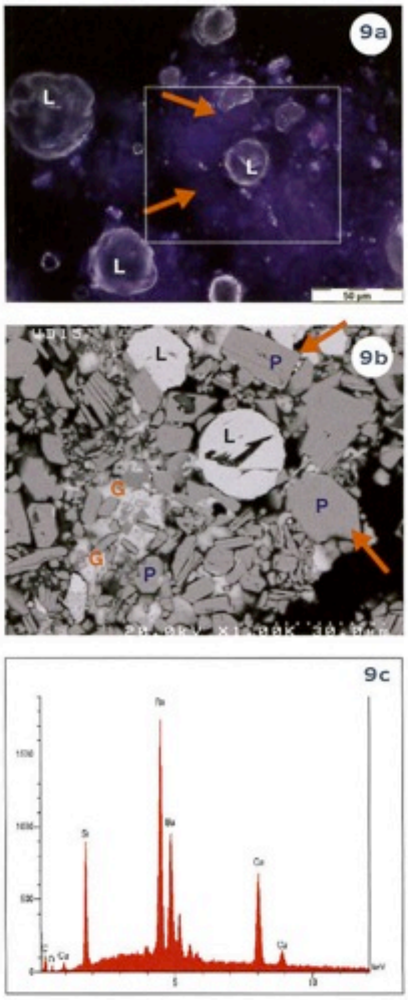


Fig 9 - Detail views of the purple material microsection (**9a** - inverted optical microscope, polarized light, x 100, **9b** - SEM, BSE, x 1000) and EDX analysis of a purple crystal (**9c** -). Sample P1C. The square locates **Fig.8b**.



The very high level of lead in the pale blue frit compared to Han purple frit and the presence of lead-rich droplets (spherical phases) inside the glassy connecting material are evidence that a large proportion of the lead was added to the material as metallic lead during the manufacturing process. Excess lead generated the spherical structures (globules) during the cooling phase.

This high lead level, which acts here as a flux, the nature and relative amounts of the different components, as well as the conservation of numerous unreacted quartz and Han blue automorphic crystals, are evidence of a low firing temperature (between 650 and 800°C).

The purple material is microgranular and consists of a mixture of coarse white or colourless particles with fine-grained purple to bluish purple particles (**Fig. 8**).

This material seems to be more friable than its white support (see **Fig. 3b**).

The microsection of the **purple** material shows, as in the blue pale coating, a heterogeneous **fritted material**, sometimes associating automorphic purple crystals of variable shape and dimensions, (**Fig; 9, P**), translucent lead-rich globules (**Fig. 9, L**) and a glassy connecting phase (**Fig. 9b, G**).

SEM- EDX analysis of the purple crystals (**Fig. 9**, arrows) show an elementary composition (**Fig. 11b**) typical of **Han purple**: Si, Ba Cu as main elements with a high level of barium, in accordance with (7) (**Table1**, column 6).

Han purple, a barium copper silicate (BaCuSi2O6) is a pigment which, as the Han blue, is known to have been synthesized during the Warring States and Han period (1)(8).

The white material is heterogeneous, with coarse grained translucent particles in a fine grained white matrix (**Fig. 10a**).

EDX analysis (**Fig. 10b**) suggests a similarity with the glassy connecting phases (**Fig. 7b** and **table 1**): lead is the main component, with only trace amounts of silicon, aluminium, calcium and barium.

The material consists of lead-rich spherical phases (**Fig. 11**, arrows) with sometimes hollow, massive lead-rich fragments (translucent coarse particles? **Fig. 11, C**) in a lead-rich matrix with a very complex (weathered?) microstructure (**Fig. 11, M**).

This is very probably the base material of the frit (glassy lead-rich matrix, lead-rich globules), without the blue and purple pigments.

Fig 10 - Detail view (**10a** -, stereoscopic microscope, x 40) and global EDX analysis spectrum (**10b** -) of the white material. Localization of microsample P2A.

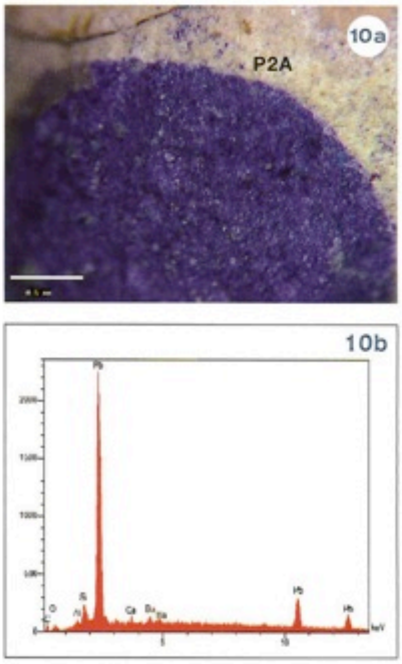
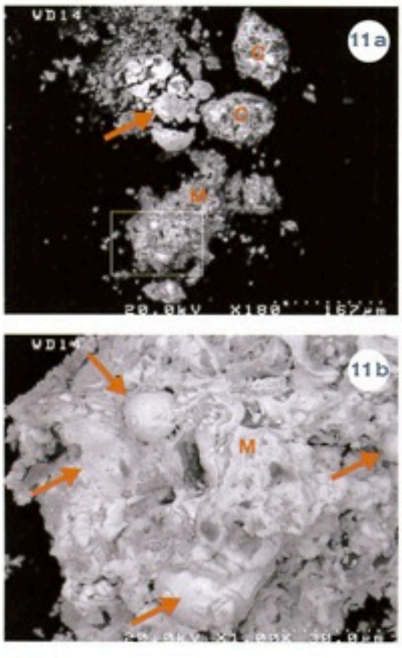


Fig 11 - Detail views (SEM, BSE, **11a** - x180, **11b** - x 1000) of the white material. Microsample P2A. The square locates **Fig. 11b**.



THE WEATHERING PROCESS

The « lead globules »

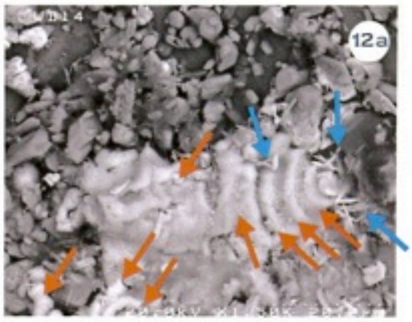
TThe presence of lead-rich spherical phases of various dimensions characterizes the material that constitutes the coating and the "eye" inlays. We have made the assumption that these spherical phases were in fact metallic lead globules, formed during the cooling of the frit due to an excess of lead (saturation).

Optical microscopy observations of the pale blue frit in a micro section (**Fig. 6** and **9**) shows that these lead globules are no more in a metallic state, as they are translucent when observed under polarized or reflected light. This suggests that the lead has undergone complete alteration and turned from a metallic state into a mineral lead compound. Furthermore, observation of lead-rich fragments of glassy component material sometimes shows an important surface microcrystalline coating, revealing concentric patterns (**Fig. 12a**, orange arrows), and some acicular crystals (blue arrows) which could be related to an alteration process.

EDX analysis of these microcrystalline products does not show important modifications in comparison to the chemical composition of the original glassy connecting phase (**Fig. 7b**).

The lead compound, replacing metallic lead in the globule and the microcrystalline coating, could be lead carbonate precipitate, which seems to occur quite easily in lead-rich slags weathering (9) caused by a standard water leaching process.

Fig 12 - Detail view (**12a** - SEM, BSE, x 1500) and EDX analysis spectrum (**12b** -) of the lead-rich connecting phase surface coating.



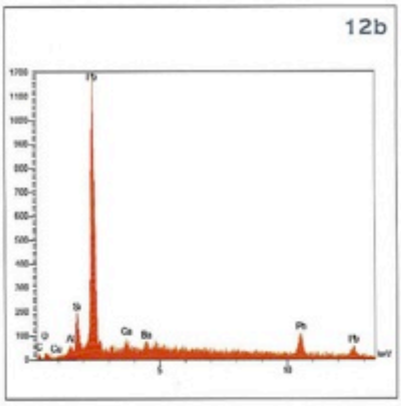


Fig 13 - Detail view (stereoscopic microscope x 12) of the green coloured areas inside the goblet.

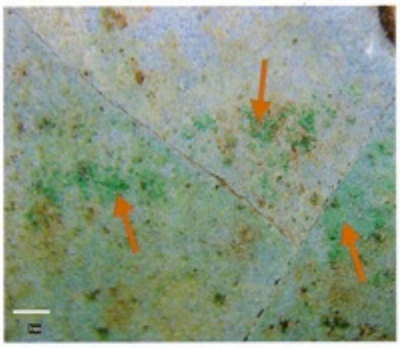
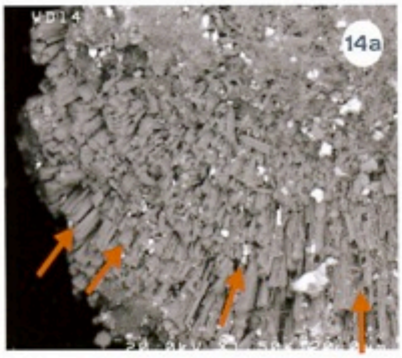
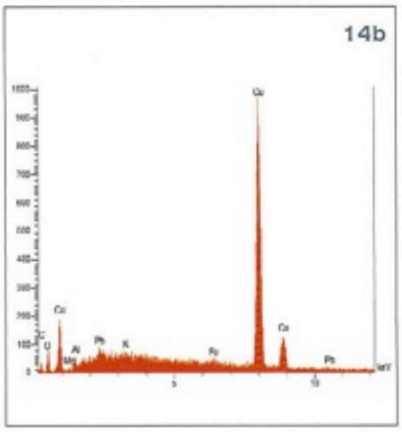


Fig 14 - Detail view (**14a** - SEM, BSE, x 1500) and EDX analysis spectrum (**14b** -) of the green products.





The green coloured products

Some green coloured areas observed inside the goblet originate from finely crystallized green products (**Fig. 13**, arrows) which appear on the coating surface.

SEM-EDX observation of this crystalline product shows radiating acicular crystals (**Fig.14**, arrows) with copper as the main elements and traces of lead and aluminium (**Fig. 14b**).

These morphology and composition suggest the identification of the green products as copper carbonate (malachite). This could be the result of copper leaching from the Han blue pigments inside the coating. It is noteworthy that these green products appear in an area where the coating has detached itself from the ceramic body during the firing, and has thus become more prone to weathering on both sides of the coating layer.

THE SURFACE DEPOSITS

The brown to dark brown deposit

This deposit consists of a brown terrigenous material, probably from a burial environment, mixed with a fine granular dark brown product; it forms irregular crusting (**Fig. 15a**, arrows).

The deposit has sometimes a dendritic appearance and follows flexuous lines (**Fig.15b**, arrows) suggesting a contact with tiny vegetal elements such as rootlets.

This deposit consists of a microcrystalline material with a complex composition. Lead, silicon, manganese and iron are the major elements, with potassium, calcium and aluminum as minor ones.

The layered, sometime humpy structure of the deposit is indicative of a long-term formation. It could be the result of a mixture of manganese and iron-rich minerals (oxide, hydroxide) originating from the environment of the object and weathering products from the object surface.

Manganese and iron oxide deposits are usually related to a biological origin (bacteria), in areas with fluctuating underground water levels. Such an environment can be responsible for the surface deposit but also for the extensive weathering (lead globules carbonation, copper carbonate crystallization...) of the coating.

CONCLUSIONS

In this study, we considered the following elements in succession: the technique and the materials used to make the object, the type of weathering, and the surface deposits.
Examination and analysis revealed that:

- The goblet is a fritted ceramic.

- The use of Han blue pigment, a barium copper silicate ($BaCuSi_4O_{10}$), is responsible for the colour of the pale blue frit coating over the ceramic body. The frit has a very high lead level.
- The "eye" pattern was formed by application of the same type of material, with high lead content. The colouring agent in the purple "pupils" is Han purple, a barium copper silicate ($BaCuSi_2O_6$).
- Han blue and Han purple are known to have been synthesized during the Warring States and Han period.
- The fritted material shows evidences of weathering, which affects mainly the lead components and more locally the Han blue pigment.
- These weathering processes could have occurred during burial in a sedimentary environment with fluctuating water levels.

Fig 15 - Detail views (stereoscopic microscope, **15a** - x 17, **15b** - x 9) of the brown deposits.

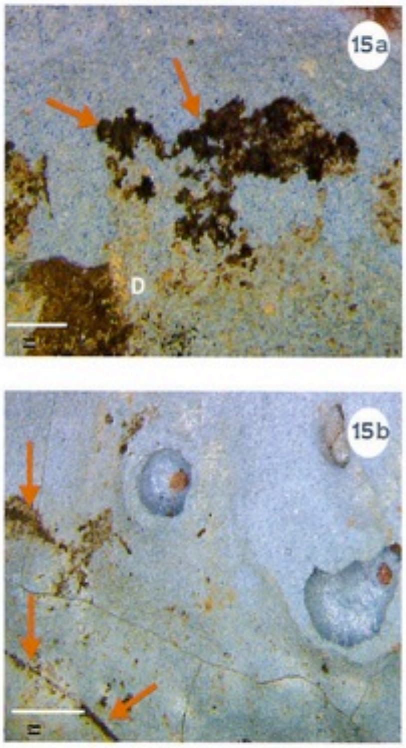
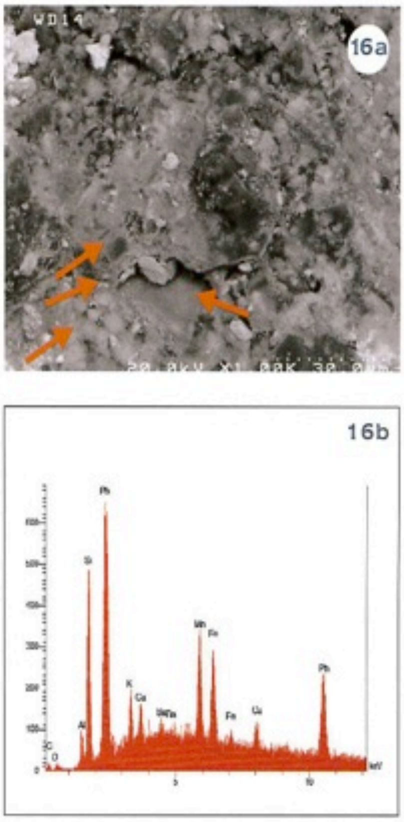


Fig 16 - Detail view (**16a** - SEM, BSE, x 1000) and EDX analysis spectrum (**16b** -) of the dark brown product. Microsample P2.



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