# A highly unusual constituent in Roman polychromy

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KEYWORDS

*Vanadium*

*Egyptian blue*

*Ancient polychromy*

*Elemental and mineralogical analyses*

**Fig. 1**
The studied mould-made, polychrome terracotta relief (H 32 cm, W 35 cm) from the NCG (Inv.no. IN 1708). The red dot marks the sampling area for the cross-section in Figs. 4–7.

**Fig. 2**
VIL image of the Campana relief showing the distribution of Egyptian blue.

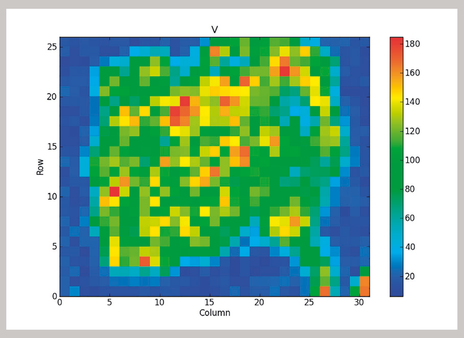


**Fig. 3** EDXRF mapping of one of the leaves showing the distribution of V.


**Fig. 4** Micrograph (DIC) of a cross-section representing the pale, greenish yellow paint on one of the leaves. The white circle marks a characteristic vanadinite crystal formation.

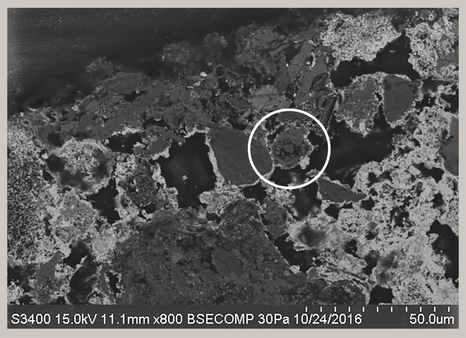


**Fig. 5** SEM image of the cross-section in Fig. 4. The white circle marks a characteristic vanadinite crystal formation.

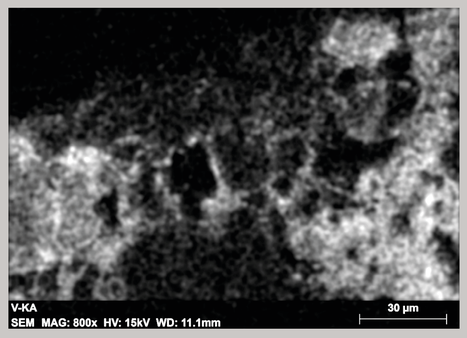


**Fig. 6** SEM-EDS image showing the distribution of V in the cross-section depicted in Fig. 4.

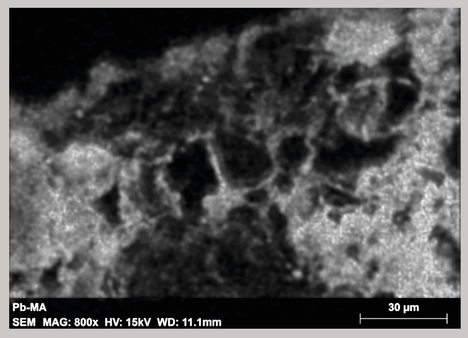


**Fig. 7** SEM-EDS image showing the distribution of Pb in the cross-section depicted in Fig. 4.

## INTRODUCTION

During a demonstration of handheld energy dispersive X-ray fluorescence (HH-EDXRF) equipment, vanadium (V) was unexpectedly detected in pale, greenish yellow and greenish blue paint layers on a so-called Campana relief from the antique collection of the Ny Carlsberg Glyptotek (NCG), Copenhagen (Fig. 1). Campana reliefs are Roman terracotta reliefs produced between the 1st c. BC and the 2nd c. AD, primarily in the area of Latium around the city of Rome. They were used as exterior and interior wall decorations for temples, public and private buildings. The exact provenance of the examined relief is unknown. It was acquired by the NCG at an auction in Rome in 1899. According to the museum records, no mounting, restauration or conservation has been carried out on the relief since its acquisition.

The chance discovery of V prompted further analyses. The investigation is aimed at characterising the V compound addressing questions of originality and intentionality.

## CONCLUSION AND AVENUES OF FURTHER RESEARCH

- By means of ICP-SFMS, PLM, and SEM-EDS, the investigated V compound has been identified as vanadinite ($Pb_5(VO_4)_3Cl$).
- The presence of the synthetic pigment Egyptian blue ($CaCuSi_4O_{10}$) in the vanadinite-containing paint layers attests to their ancient origin.
- The concentration of vanadinite is high indicating intentional use.

In our further research we will investigate the polychromy of ancient artefacts, such as other Campana reliefs, for the occurrence of vanadinite and related minerals e.g. mimetite ($Pb_5(AsO_4)_3Cl$) and pyromorphite ($Pb_5(PO_4)_3Cl$).

## METHODS AND MATERIALS

The relief was first examined using different photographic techniques incl. visible-induced luminescence (VIL) imaging to identify any traces of Egyptian blue. Preliminary elemental analyses were performed with handheld and portable EDXRF (Bruker Tracer III-SD Bruker and XGLab ELIO, respectively). Informed by this preliminary investigation, pigment layers were sampled for major and trace element analyses (ICP-SFMS, Thermo Scientific ELEMENT XR), and for cross-sections used for the characterisation of the microstratigraphy of the painted decoration (PLM, Zeiss Axioplan 2, 10×–100×; SEM-EDS, Hitachi S-3400N with Quantax 200 with XFlash 6|30 from Bruker), respectively.

## RESULTS

The VIL image strongly indicates the presence of Egyptian blue in the polychrome decoration. The blue background and the bluish rim at the bottom of the scene appear to contain very high concentrations of the pigment, whereas areas painted black, brownish yellow, and pale, greenish yellow seem to contain lower concentrations indicating pigment mixtures (Fig. 2).

The XRF analyses showed elevated V counts in the greenish paint layers on the leaves (Fig. 3) and stem as well as in the bluish paint on the rim. Also, the polychromy in the said areas has a high Pb content. These preliminary XRF results were confirmed by major and trace element analyses.

Consulting the cross-sections, it is apparent that the paint layer is applied directly onto the terracotta substrate. The paint consists of a pale yellow matrix with red and angular, light blue inclusions. It is a classic example of a mixed green colour. Ruby-red, stubby, hexagonal crystals characteristic of lead vanadate or vanadinite ($Pb_5(VO_4)_3Cl$) have been identified in the matrix (Fig. 4). The SEM-EDS mapping and point analysis confirm that the primary constituents in the yellow matrix are Pb, V, Cl, and O which is in agreement with vanadinite (Figs. 5–7). The blue grains in the paint layer contain Si, Ca, and Cu in accordance with Egyptian blue.

## DISCUSSION

According to the instrumental and microscopic analyses, vanadinite forms a substantial part of the greenish hues of the polychromy. Vanadinite is a comparatively rare, secondary lead mineral occurring in the oxidised zone. Vanadinite is a highly unusual constituent in Roman polychromy which could suggest modern intervention. However, the presence of Egyptian blue in the vanadinite-containing paint layers testifies to their ancient origin: knowledge of the production of Egyptian blue was lost sometime after the Roman era. It was first synthesised again in 1959, and it was therefore not available at the turn of the 20th century.

Although vanadinite is a rare find, its occurrence in ancient polychromy has been documented before. Three cases are studies of polychrome sculpture in the Mediterranean area.[1–2] Vanadinite has also been identified in yellow ochre used for a polychrome, preparatory drawing (sinopia) underneath the Roman mosaic of Lod, Israel.[3] The mineral has also been identified in association with wulfenite on Early Islamic painted fragments from Nishapur, NE Iran[4] and on Late Sasanian painted stucco in Ramavand, W Iran.[5] In the two latter cases the exploitation of nearby mineral resources is indicated as the most likely provenance and the presence of vanadinite is generally used as indicator of provenance.

Judging from the few examples available for comparison, it would seem that vanadinite often constitutes a contaminant rather than a main component. In the case of the studied Campana relief, however, the concentration of vanadinite is higher than background levels indicating intentional use.

## ACKNOWLEDGEMENTS

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