# Tracking the composition of carbon-black samples from Pompeii

A better knowledge of past societies and of their degree of technological development can come from scientific analysis of archaeological remains. However, the study of residues from archaeological finds poses a series of challenges for materials science. Carbon-based materials, easy to make by burning diverse organic matter, have been used since prehistoric times as pigments for drawings and paintings and also as dyes, inks and cosmetics. These materials are often ill-ordered and it has not been easy to characterize their specificities and their differences by traditional crystallography. Now, the identification, quantification and mapping of the different phases in such heterogeneous samples can be accomplished using synchrotron based techniques.

The excellent preservation state of the Pompeii ruins and of many everyday objects, since the eruption of Mount Vesuvius in AD 79, represents an extraordinary opportunity for studying Roman society. In our work, black powders found in Pompeii houses in different types of closed containers were characterized in order to assess a correspondence between the composition and the type of container and to specify the use of these compounds as ink and/or cosmetics.

We have investigated five micro samples from the Roman carbon black found in Pompeii and preserved in their original containers made of glass or bronze (Fig. 1). Preliminary studies of these precious materials in the laboratory revealed their complexity: they contain both amorphous and crystalline constituents. For a precise analysis of these heterogeneous samples, we proposed a new methodology employing synchrotron radiation. The measurements were done at the French Collaborative Research Group's beamline (BM2-D2AM) at the European Synchrotron Radiation Facility, Grenoble.

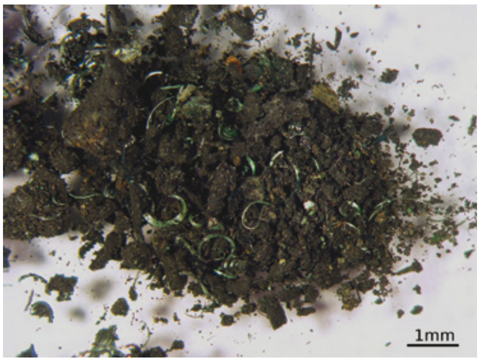


*Fig. 1: **At left**, containers for ink and cosmetics from the excavations at Pompeii. **At right**, optical microscope image of an archaeological sample, showing the heterogeneous nature and the complexity of the powder, which consists of particles having widely varying shapes, sizes and compositions.*

We first identified and quantified the crystalline phases present by using a combination of X-ray powder diffraction and elemental microanalysis, assisted by Computed Tomography. This technique allows us to localize in 3D the different constituent phases in a sample and to extract their individual diffraction diagrams. Secondly, we used analysis of the Pair Distribution Function (*i.e.* the distribution of the inter-atomic distances), utilizing the entire Bragg diffraction and diffuse scattering signal from a sample, to obtain information about the non-crystalline (amorphous) phase. This was identified as non-graphitic carbon: planes of carbon with nearest and next-nearest carbon-carbon bond distances of 1.4 and 2.4 Angstroms respectively, as in a graphite-layer plane, but without ordering perpendicular to these planes. Data sets for reference samples were used as models for the amorphous phase to determine its content in each sample. In the last step, the pair distribution functions were modelled in order to determine the fractions of amorphous and crystalline phases.

Thanks to this procedure, a description of the entire content of this kind of archaeological sample could be achieved for the first time. It allowed us to clarify the composition of the mixtures contained in three different types of containers. The origin of the carbon black pigments was obtained: We were able to demonstrate the use of charred vegetable materials, independently of the shape and the nature of the container. This means that in Pompeii, at AD 79, carbon-based inks were still in use for writing, and metallic inks had not yet been introduced.

As concerns the crystalline fractions, three of the samples contain well-known mineral phases or metallic compounds resulting from degradation of the bronze container. The two other samples reveal unexpected mineral phases of calcium phosphate, namely whitlockite $Ca_9(Fe,Mg)(PO_3OH)(PO_4)_6$ and phosphohedyphane $Ca_2Pb_3(PO_4)_3Cl$. We now have to extend the archaeological corpus in order to study the occurrence of these two exotic minerals in other similar samples and to understand the conditions of their formation.

Very recently (P. Tack *et al.*, 2016), the presence of lead atoms was reported in the ink of two papyrus fragments from the nearby site of Herculaneum, contemporaries of our Pompeian containers. Although the precise state of this lead was not determined, the elemental composition of the unknown lead-containing ingredient appears compatible with that of the phosphohedyphane phase of the Pompeii pigments. Further investigations are underway to determine if this rare mineral phosphohedyphane can be used as a tracer of the origin of ancient Roman inks.

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## FURTHER READING...

**"Identifying and quantifying amorphous and crystalline content in complex powdered samples: application to archaeological carbon blacks"**
S. Cersoy, P. Martinetto, P. Bordet, J. L. Hodeau, E. Van Elslande and P. Walter
***J. Appl. Cryst* 49**, 585-593 (2016).