

New minerals discovered in Paleolithic black pigments by Transmission Electron Microscopy and micro-X-ray Absorption Near-Edge Structure

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Paleolithic artists used two main colors: red (iron oxide: hematite or red ochre) and black (charcoal or manganese oxides). These pigments could be prepared in different ways, by grinding, by mixing with an extender and/or a binder or by heating, in order to enhance the properties of painting matter. Physicochemical analyses attempt to determine the nature of the matter and its preparation mode, and to get an idea of its provenance.

This work deals with black pigments and more particularly with manganese oxides. The different phases of manganese oxides can be distinguished using their elemental composition, their structure and the oxidation state of the Mn ion (II, III, IV). The present study is limited to two main families: simple (MnO_2 type) and composite ($\text{Ba}_x\text{Mn}_y\text{O}_z$ type) manganese oxides.

Transmission electron microscopy (TEM) was performed to identify the specific phase of manganese oxide and to study structural transformation during heat-treatment. As a complementary technique, Mn K-edge μ -XANES (X ray absorption near-edge structure) spectroscopy was used, for its element specific sensitivity to redox and local structures. The spectra were collected on ID21, using Si(111) double crystal monochromator and a Fresnel focusing device.

Using this combined approach of TEM and μ -XANES, archaeological samples of black painting matter were analyzed. The complex mixtures of manganese oxides studied here belong to the caves of Ekain (Basque country, Spain), Labastide and Gargas (Hautes-Pyrénées, France) and as well as to black “crayons” from the cave of Combe Saunière (Dordogne, France). From these analyses of painting matters, several conclusions are drawn concerning the technical level of Paleolithic artists:

- for the first time, the distinction between natural phase mixtures and mixtures of anthropogenic origin is possible.
- new minerals, never identified before in archaeological context, have been discovered in these painting samples.
- however, black heated pigments have never been found in the studied rock painting samples, in contrast to heated red hematite, that was evidenced mainly in prehistoric funeral context.

Consequently, the sometimes-unusual mineralogy found in these pigments suggests that some of the manganese ores are coming from geological settings that are sometimes relatively far away from the Dordogne and Basque region such as in Ariège.