Palaeolithic paint palette used at La Garma cave (Cantabria, Spain) investigated by means of high-resolution micro-XRF and XANES at the Fe K-edge

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Understanding of graphic expression is one of the key issues of prehistoric research. It provides significant sources of information for the study of the symbolic and ideological realm of past societies. Two main colours stand out in the prehistoric paint palette, red and black, composed by respectively iron oxides and manganese oxides, and more rarely charcoal. A precise distinction of the mineral phase of the pictorial matter used for a colour is crucial in order to understand the organisation of the rock art in a cave, to explain its singularities, discriminate between different hands that potentially performed the decorations of distinct figures in different rooms.

This is also the aim of the study of paint micro-samples taken from La Garma cave (Cantabria, Spain). The cave is part of a range of exceptional sites discovered at the end of the 20th century, which might provide new insight in the Upper Palaeolithic in the North of Spain. Listed as World Heritage by the UNESCO in 2008, the La Garma cave features more than 500 graphic units covering a wide chronological range, dating from the Aurignacian (approximately between 27 000 and 21 000 years) to the Magdalenian period (approximately between 16 500 and 11 500 years), which are connected with large surfaces rich in occupational remains, as illustrated in Fig.1 [1, 2].

Forty-six samples taken from the medium and lower gallery of the cave, covering at the same time red, yellow, purple and black colours, have been preliminary analysed by energy dispersive X-ray spectrometry in a scanning electron microscope (SEM-EDS). It allowed distinguishing different types of hematite (Fe₂O₃) and goethite (FeOOH), revealing the use of different paint mixtures ("paint pots") by prehistoric artists. A Fe speciation analysis of a part of these samples was performed at the beamline P06 of PETRA III by micro X-ray absorption near edge structure (XANES) imaging at the Fe K-edge, employing a Maia detector [3]. These experiments aimed at giving a more detailed insight into the oxidation state and the coordination environment of Fe, similar to the work of M. Wilke and co-workers [4].

While data processing is still ongoing, it is expected that the results will provide new information about the composition of the “paint pots”, yielding a more complete picture of the decorative steps of this cave. Complementary, to have a global comprehension of the rock art repartition inside the cave, an on-site systematically study of the prehistoric representations has been initiated by the implementation of a self-built X-ray fluorescence (XRF) portable and non-invasive spectrometer. In a wider perspective, the combination of such complementary analytical methods might support a better understanding of the symbolic practices of past societies and the cultural relationships within the Cantabrian region at the Upper Paleolithic.
Figure 1: a) Map of the Lower Gallery with the localisation of the surface deposit areas (brown), the major decorated walls (red) and the samples [1], b) Picture of the XRF portable spectrometer in front of the paintings and c) XANES profiles extracted from selected samples. The colours of the labels represent the coloration of the paint samples.

References