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Analytical Study of an Organic Binder in a Rock Art Motif from Putli Karar, Raisen District, Madhya Pradesh

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Abstract

This paper highlights the results of investigations using micro-Raman spectroscopy and ATR-FT-IR techniques on a rock art pigment from Putli Karar, Raisen District, Madhya Pradesh. It scientifically demonstrates that haematite was the raw material used to prepare the pigment. This study establishes the presence of an unidentified proteinaceous material used as an adhesive agent in its preparation. The presence of carbon in this rock art pigment was convincingly revealed through this analysis.

Introduction

It was only in the nineteenth century that the study of rock art in India gained interest. This deficiency was partially due to the lack of facilities and interest in the scientific study of the rock paintings. For long, the composition of the pigments, as well as establishing a chronometric sequence to different types of rock paintings, ranging from the Upper Palaeolithic to Historic and Medieval periods, did not gain interest (Shaik 2015, 2017). However, with time and new techniques, limited efforts were made to study the composition of the pigments of the rock paintings, including their dating (Agrawal and Kharakwal 1994; Sharma 1996; Bednarik *et al.* 2005; Tacon *et al.* 2013; Banerjee and Chakravarty 2014). The work carried out by Ravindran *et al.* (2012) suggested the possible use of egg yolk that may have been used as a binder. However, its presence was not confirmed entirely. Rock paintings found in different parts of the Indian subcontinent were thought to have been drawn using naturally available red and yellow ochre and calcium carbonate nodules, including those of chert in various colours, which were used to prepare the pigments and mixed with different types of organic and inorganic binders. However, very little was known about the kind of raw materials and binders used in their preparation (Shaik 2015).

Putli Karar Rock Art Site

The Putli Karar rock art site is located on the Raisen-Sagar Road and contains one of the largest concentrations as well as the oldest rock paintings (Fig. 1). Using relative dating methods, these were assigned to the Upper Palaeolithic, Mesolithic, Early Agriculturalists and Cattle Keepers phase (Neolithic period), Chalcolithic, Historic and Medieval periods (Wakankar and Brooks 1976). The rock shelters formed in the Vindhyan hill ranges are found in the quartzitic sandstones environments.

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Materials and Methods

PTLK-10 pigment sample: The *Bos gaurus* figure at Putli Karar was drawn in naturalistic outlines, and the body portion was filled in with dull red colour (Fig. 2). It was superimposed on partially faded deer figures painted in white colour, including a deer and an unidentified bird figure in red colour. A pigment sample was collected from the neck and body portions of the *Bos gaurus* figure. All these animals and the bird figures were relatively assigned to the Mesolithic period based on the study of the rock art attributes/parameters, such as style, superimpositions, theme, and subject matter.

Micro-Raman: A Renishaw Raman Spectrometer equipped with 3 lasers (488/514 nm, 633 nm and 785 nm), a Leica microscope with 5X, 20X, 50X and 100X objectives, high-resolution gratings (1200 lines/mm and 1800 lines/mm for NIR and visible, respectively) and a highly sensitive CCD camera was used in the processing of the pigment samples. A pigment sample was analysed using a micro-Raman

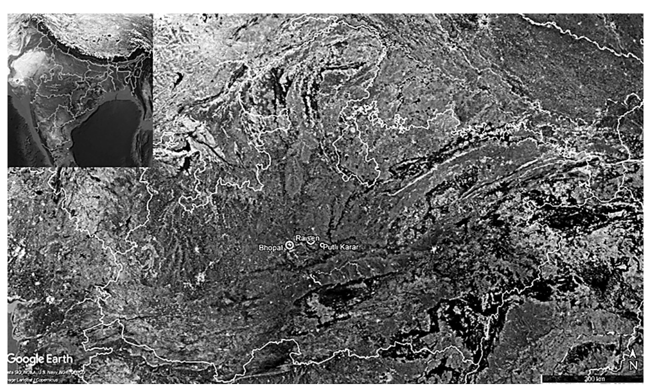

Fig. 1: Location of Putli Karar, Raisen District,Madhya Pradesh

Fig. 2: *Bos gaurus* figure at Putli Karar

spectroscope with a 785 nm laser, a 1200 grating, and an exposure time of 10 seconds. The intensity of the laser was changed according to the sample, scanning over a spectral range of 400-3200 cm^{-1}. Three Raman spectra were collected from three different points of the pigment sample and was averaged out.

ATR-FT-IR: Spectra of the pigment sample was collected using the Thermo Scientific Nicolet Summit LITE ATR-FT-IR Spectrometer, and it is equipped with a $LiTaO_3$ detector in the transmission mode. The spectra of the pigment sample was collected from a single point in the range of 4000-400 cm^{-1} with a spectral resolution of 4 cm^{-1}, averaging 64 scans per spectrum.

Results of micro-Raman Analysis

The characteristic Raman features of haematite were observed at 231 cm^{-1}, 250 cm^{-1}, 299 cm^{-1}, 413 cm^{-1} and 613 cm^{-1}, and the quartz was observed at 202 cm^{-1} and 468 cm^{-1} (Fig. 3) (Smith *et al.* 1999; Marketou *et al.* 2019). Two broad bands at 1584 cm^{-1} (G band) and 1302 cm^{-1} (D band) were observed. Among them, the first represents the planar configuration of sp^2-bonded carbon that constitutes graphene, whereas the second defines the disorder in the graphitic structure. These bands suggest the presence of amorphous carbonic materials like soot and lampblack (Fig. 3). The Raman bands at 725 cm^{-1}, 811 cm^{-1}, and 874 cm^{-1} can be attributed to the deformation mode of aromatic C-H bonds (Tomasini *et al*. 2012; Tascon *et al.* 2016). The presence of these aromatic C-H bonds in the PTLK-10 pigment sample confirms the presence of a proteinaceous binding material that was used in the preparation of the PTLK-10 pigment sample (Kahrovic *et al.* 2020).

Raman peaks at 508 cm^{-1}, 902 cm^{-1}, 1466 cm^{-1}, 1494 cm^{-1}, and 1634 cm^{-1} are attributed to the presence of calcium oxalate. A Raman band observed between 890 and 910 cm^{-1} is assigned to the ν (C-C) stretching mode. Two sharp peaks are identified around 1466 cm^{-1} and 1494 cm^{-1} in the spectra, and this doublet is characteristic of calcium oxalate monohydrate (whewellite). An additional band

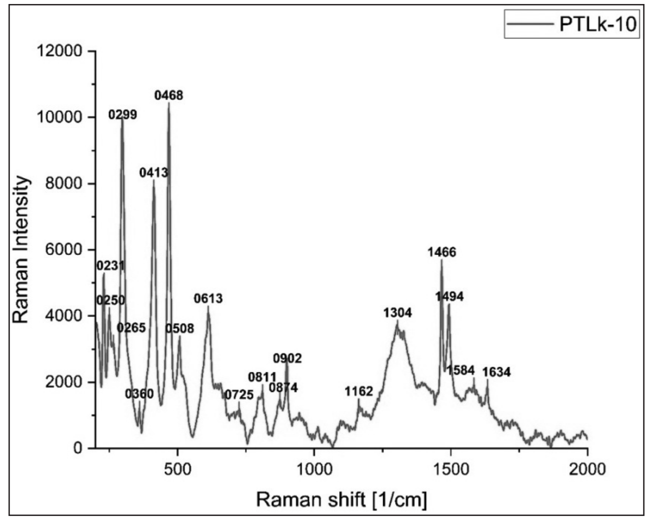

Fig. 3: Raman Spectra of PTLK-10 pigment sample

at 508 cm^{-1} can be attributed to O-C-O bending modes. Its presence indicates the metabolic products of lichen invasion in ancient times, and the small peaks around 1162 cm^{-1} can be attributed to lichen metabolic products such as phenolic acids and depsides (Fig. 3) (Edwards 2000; Edwards *et al.* 2002, 2003; Frost 2004; Frausto-Reyes *et al.* 2014).

Results of ATR-FT-IR

ATR-FT-IR spectra indicate the contemporary presence of calcium oxalates (νsymCOO- at 1375 cm^{-1} and 1313 cm^{-1}), including silicate deposition materials (νSi-O at 1071 cm^{-1}, 1032 cm^{-1}) (Maryse 2009) (Fig. 4). Calcium oxalate bands are visible, and the peak at 1617 cm^{-1} is ascribable to the H_2O bending, and the one at 1313 cm^{-1} is due to the C–O–C stretching along with the other bands at 667 cm^{-1}, and these bands correspond to the OH stretching near

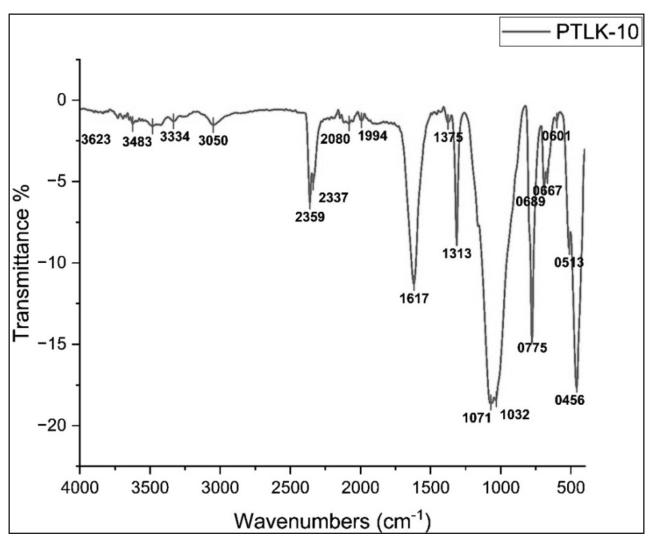

Fig. 4: ATR-FT-IR Spectra of PTLK-10 pigment sample

3400 cm^{-1} (Lofrumento *et al.* 2012) (Fig. 4). However, Amide I, a component part of a proteinaceous material, has also been identified in the same area at 1617 cm^{-1}. This suggests the presence of a proteinaceous material, i.e., an organic binding material (Smith *et al.* 1999; Maryse 2009; Lofrumento *et al.* 2012; Nandiyanto *et al.* 2019; Kahrovic *et al.* 2020; Jozanikohan and Abarghooei 2022; Enache *et al.* 2023) (Fig. 4). However, there are no other peaks, thus suggesting the presence of the proteinaceous binding material. The peak at 601 cm^{-1} is attributed to the CH out-of-plane bending vibrations of the organic material (Nandiyanto *et al.* 2019). The bands at 775 cm^{-1} and 689 cm^{-1} indicated that the sample was quartz-rich (Fig. 4) (Jozanikohan and Abarghooei 2022). The bands present at 2359 cm^{-1} and 2337 cm^{-1} characterise the R branch and P branch of the CO_2 from the atmospheric air (Fig. 4) (Enache *et al.* 2023). Bands at 513 cm^{-1} and 456 cm^{-1} are attributed to the Fe-O functional group. These bands confirm the presence of haematite, i.e., red ochre (Fig. 4) (Khorshidi and Azadmehr 2017).

Discussion and Conclusion

The micro-Raman spectroscopic and ATR-FT-IR investigations of the PTLK-10 pigment sample of the *Bos gaurus* figure (Fig. 2) collected from Putli Karar suggests that haematite, i.e., red ochre, was used to prepare the pigment (Figs. 3-4). This was rich in quartz, and the reason behind it is that a part of the substrate was also collected during the selection of the PTLK-10 pigment sample (Fig. 2).

The micro-Raman analysis of the pigment sample suggests the presence of amorphous carbon (Fig. 3). But, the effort in establishing an AMS date for this rock art motif remained unsuccessful due to the lack of the required amount of carbon (Fig. 2). The peak observed at 1617 cm^{-1} in the micro-Raman spectroscopic investigation of the pigment sample suggests the presence of calcium oxalate monohydrate (whewellite) and indicates the presence of metabolic products caused by lichen invasion in ancient times, which contains the phenolic acids and depsides (Fig. 3). This peak identified at 1617 cm^{-1} in the ATR-FT-IR investigation has also confirmed the presence of calcium oxalates and silicate deposition materials. But the ATR-FT-IR investigation of this pigment sample has identified the presence of Amide I, a component part of a proteinaceous material, at the same peak as at 1617 cm^{-1}. This suggests that the pigment was prepared using a proteinaceous binding material (Fig. 4), and was mixed with the haematite in order to draw the *Bos gaurus* figure (Fig. 2). The Raman bands at 725 cm^{-1}, 811 cm^{-1}, and 874 cm^{-1} can be attributed to the deformation mode of aromatic C-H bonds, and they are the component parts of the proteinaceous material (Fig. 4) (Kahrovic *et al.* 2012; Tomasini *et al.* 2012; Tascon *et al.* 2016). Nevertheless, the nature of this proteinaceous binding material needs further investigation. The possibility of using egg white in the preparation of the PTLK-10 pigment sample cannot be ruled out.

The present study is significant, as little is known about the binders and the different types of raw materials and binders used in the preparation of the pigments of the rock art motifs found in the rock art sites in the Indian subcontinent (Shaik 2015). This research study lays the basis for future focussed efforts on the study of rock paintings on a proper scientific basis. This is the need of the hour, as a large number of rock paintings found at the Indian rock art sites are slowly fading beyond recognition due to various taphonomical factors (Shaik and Chauhan 2019). Employing such scientific studies, precautionary measures can be suggested to preserve the Indian rock art heritage.

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