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POSTER

A Multi-Analytical Investigation of the Materials and Painting Techniques of Wall Paintings in the Eighth to Tenth-Century CE Jain Caves at Ellora, India

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Introduction

The numerous decorative wall paintings in the eighth to tenth-century CE Jain caves at Ellora provide an excellent opportunity to analyze their composition and to explore technological similarities that illustrate different levels of technological transfer, change and innovation. Although similar to other Hindu and Buddhist caves in Ellora, the Jain caves have the largest range of paintings on the sidewalls and ceiling. The five Jain shrines at the north end of Ellora are the Chhota Kailash (Cave 30), Indra Sabha (Cave 32), Jagannath Sabha (Cave 33), an unfinished four-pillared hall (Cave 31), and a small cave (Cave 34). These Jain caves belong to the Digambara sect, which was active in the ninth and early tenth centuries. Although other parts of the caves were painted the most varied works of art survive on the ceiling, with some traces remaining on side walls and pillars (Kamiya 1993). In the Indra Sabha, paintings are found on the ceiling and parts of the wall in the chamber attached to the east hall; the main hall ceiling was once adorned with paintings that have flaked off. A sizeable area on the first floor of the cave's front verandah has two layers of paintings, the lower seen where patches of the upper layer have fallen. The clouds, flying figures and other motifs in these paintings are similar to those in the western porch of Hindu caves but are considered to be of a later date (Shah 2008).

Materials and methods

Sampling

In this paper, five fragments – from red, orange, green, black and brown zones – containing representative examples of the pigments used for mural decoration were studied. All the specimens had a pigment layer of 0.9–2.1µm thick supported by a combination of mud and lime plaster ground on the rock surface. In addition, a sixth sample, taken from the ground, was studied (Figure 1).

Analytical methods

The multi-analytical study reported here used: micro X-ray fluorescence (micro-XRF: Artax 200) for elemental analysis; X-ray diffraction (XRD: Rigaku SmartLab) to identify the phases of pigments; Fourier transform infrared spectroscopy (FTIR: VERTEX 70v vacuum FTIR spectrometer with a diamond single bounce ATR accessory); and Raman spectroscopy (Renishaw inVia with a Leica microscope attachment and lasers operating at 514.5 and 785 nm).

Results and discussion

From the XRF data (Table 1), calcium, iron and manganese are present in most of the samples, perhaps reflecting the use of slag from the surrounding mining area (Papadimitriou and Kordatos 1995). The presence of calcium may have its origin in the mud plaster ground layer or in a white material blended with the pigment to accomplish a specific hue and tone. Iron-containing compounds are found in many minerals and are strong coloring agents (Singh and Arbad 2013).

Sample E.G

XRF and XRD analysis (Figure 2a) revealed that the sample E.G is composed of silicates with significant concentrations of calcium, iron, and potassium. An absence of copper excludes the presence of malachite or atacamite. The higher amounts of calcium, iron and potassium suggested that the predominant pigment in the decoration is green earth. The Raman spectrum of sample E.G showed no characteristic peaks.

Sample E.R

The combined results of XRF and XRD (Figure 2b) confirmed the presence of mercury sulfide (cinnabar) as the primary component, and magnetite, calcite,

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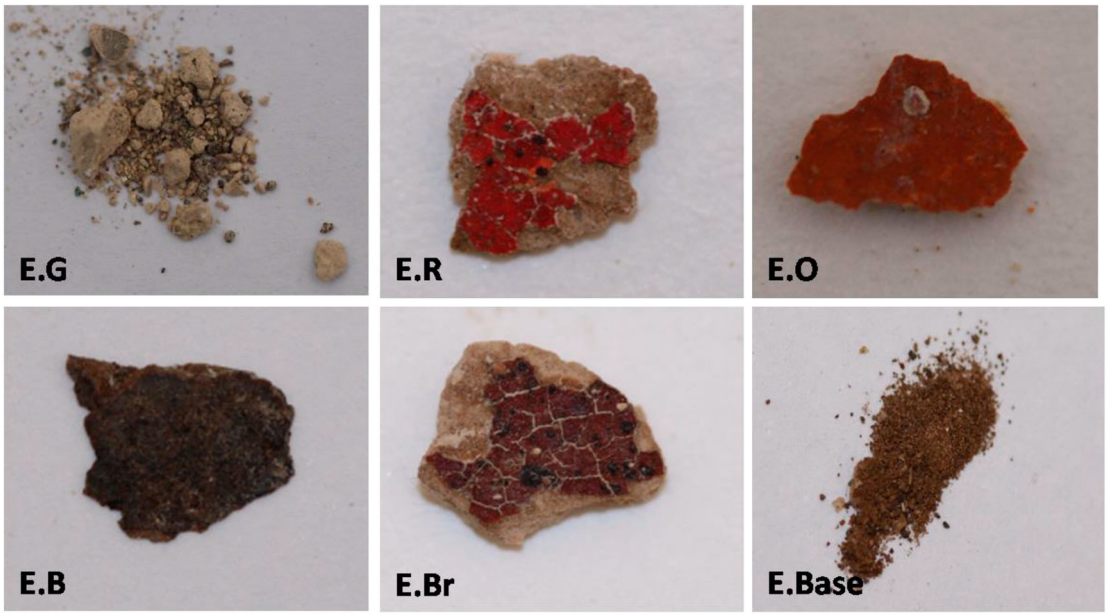

Figure 1. Decorative plaster fragments of the Jain cave, Ellora, India, from which samples were taken from green (E.G), red (E.R), orange (E.O), black (E.B) and brown (E.Br) areas, and from the ground (E.Base).

iron oxide hydroxide and iron sulfate as secondary components. By Raman analysis (Figure 3a), hematite was detected from its characteristic peak at 482 cm^{-1}, and strong bands were identified for calcite and gypsum at 1086 and 1006 cm^{-1} respectively (Mateos et al. 2015).

Sample E.O

The XRF analysis of E.O showed arsenic in higher concentrations (85 wt%) with lesser amounts of mercury, iron and calcium (<7 wt%). Iron arsenide, calcium carbonate, magnetite and gypsum were detected by XRD (Figure 2c). These findings lead to the conclusion that the orange color of the pigment comes from mixing yellow arsenic sulfide (also known as orpiment) with red hematite and cinnabar. Generally, pigments were blended to accomplish a specific hue and the craftsmen varied the particle size, pigment ratio and pigment to binder ratio to accomplish tonal variation and other surface features. There were, however, no phases of either arsenic sulfide or cinnabar detectable in the XRD results (Figure 2c), probably because the sulfur has combined with other elements to form new compounds.

Sample E.B

Peaks in the FTIR spectrum (Figure 4b) at 598, 672 and 1008 cm^{-1} are characteristic of gypsum, while in the Raman spectrum (Figure 3c) bands at 1086 and 548 cm^{-1} indicate the presence of calcite, while those at 225 and 488 cm^{-1} are for hematite, a single peak at 352 cm^{-1} is for cinnabar, and there are other signals for quartz and clay minerals. Peaks at 689 cm^{-1} (C–S stretch) and 488 cm^{-1} (S-S stretch) were associated with a carbon disulfide group that usually indicates the material derives from an anthropogenic source. Calcite, cinnabar, arsenic sulfide, mercury sulfate and hematite were identified in the XRD diffraction pattern (Figure 1d), which suggests that the pigment contains red or yellow components.

Table 1. List of samples, analyses performed, and pigments identified.

Sample Code	Observed Color	Chemical composition (wt. %) of elements by XRF	Pigments identified by XRD, XRF, FTIR and Raman
E.G	Green	**Major:** Ca(30.23), K(3.25), Pb(6.12), Fe(57.38) **Minor:** S(0.62), Cl(0.25), Ti(0.86), Mn(1.25)	Green ochre
E.R	Red	**Major:** Ca(15.94), Hg(75.06), Fe(7.06) **Minor:** S(1.00), Mn(0.91)	Cinnabar Hematite Calcite
E.O	Orange	**Major:** Ca(4.28), As(85.74), Hg(6.28), Fe(3.14) **Minor:** Mn(0.54)	Orpiment Cinnabar hematite
E.B	Black	**Major:** Ca(49.55), As(7.69), Hg(5.73), Fe(32.58) **Minor:** K(1.42), Ti(1.44), Mn(1.54)	Cinnabar Hematite
E.Br	Brown	**Major:** Ca(17.67), Hg(70.23), Fe(9.05) **Minor:** S(0.91), Ti(0.64), Mn(0.91)	Cinnabar
E.Base	Brownish white	**Major:** Ca(5.56), Ti(4.75), Mn(2.00), Fe(84.75), K(0.56)	Quartz Calcite

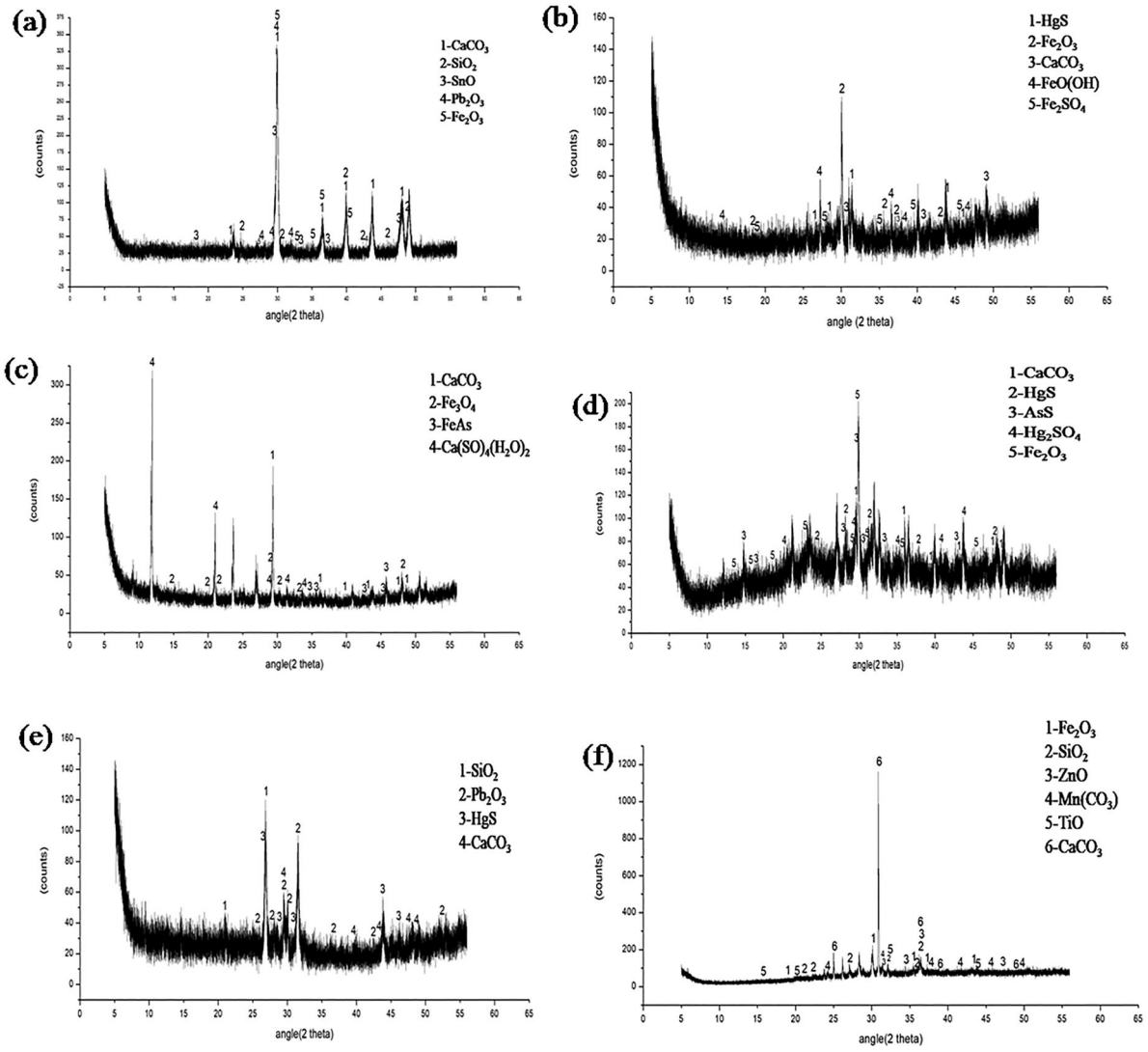

Figure 2. X-ray diffractograms for samples: E.G (a); E.R (b); E.O (c); E.B (d); E.Br (e); and E.Base (f).

Sample E.Br

XRD analysis of this sample (Figure 2e) included a peak for mercury sulfate, which may derive from the oxidation of mercury sulfide, akin to the production of calcium sulfate (gypsum) from calcite under certain conditions (Radepont 2013).

Sample E.Base

From the XRF and XRD (Figure 2f) analyses, calcite, quartz and hematite are the main components of the ground sample, along with carbonates and oxides of zinc and titanium. The finding that the amount of calcium in the ground is lower than that of iron suggests that calcite was not the primary component.

The FTIR results (Figure 4) generally show a diagnostic peak in a range of 1420–1460 cm^{-1}, which is characteristic of calcite and suggests it was present in all the samples. The various bands in the region 3000–3800 cm^{-1} are due to OH bending modes of water or hydroxyl groups. The bands at 2870–2990 cm^{-1}(ν_{asym}-ν_{sym} CH_2) are probably due to the presence of hydrocarbons, while those at 1640–1801 cm^{-1} imply that fatty acids are present. The presence of fatty acids and hydrocarbons suggests the possibility that vegetable compounds or wax may be present as organic binders. It might be, therefore, that pigments were mixed with a binder – perhaps an egg emulsion, animal fats or plant oils – and then applied to the dry plaster (the *secco* technique).

Conclusion

The analytical investigation of the wall painting fragments from the eighth- to tenth-century CE Jain caves gave an insight into the materials used on the painted surfaces. The red pigment was identified as a combination of hematite and cinnabar along with the presence of calcite. The green pigment was identified as green ochre and the yellow as orpiment. A combination of pigments was used to produce brown and orange tones. FTIR and Raman analyses were not helpful in identifying the black pigment, although the XRF and XRD studies show that it contains mainly hematite and cinnabar. The ground (support) plaster

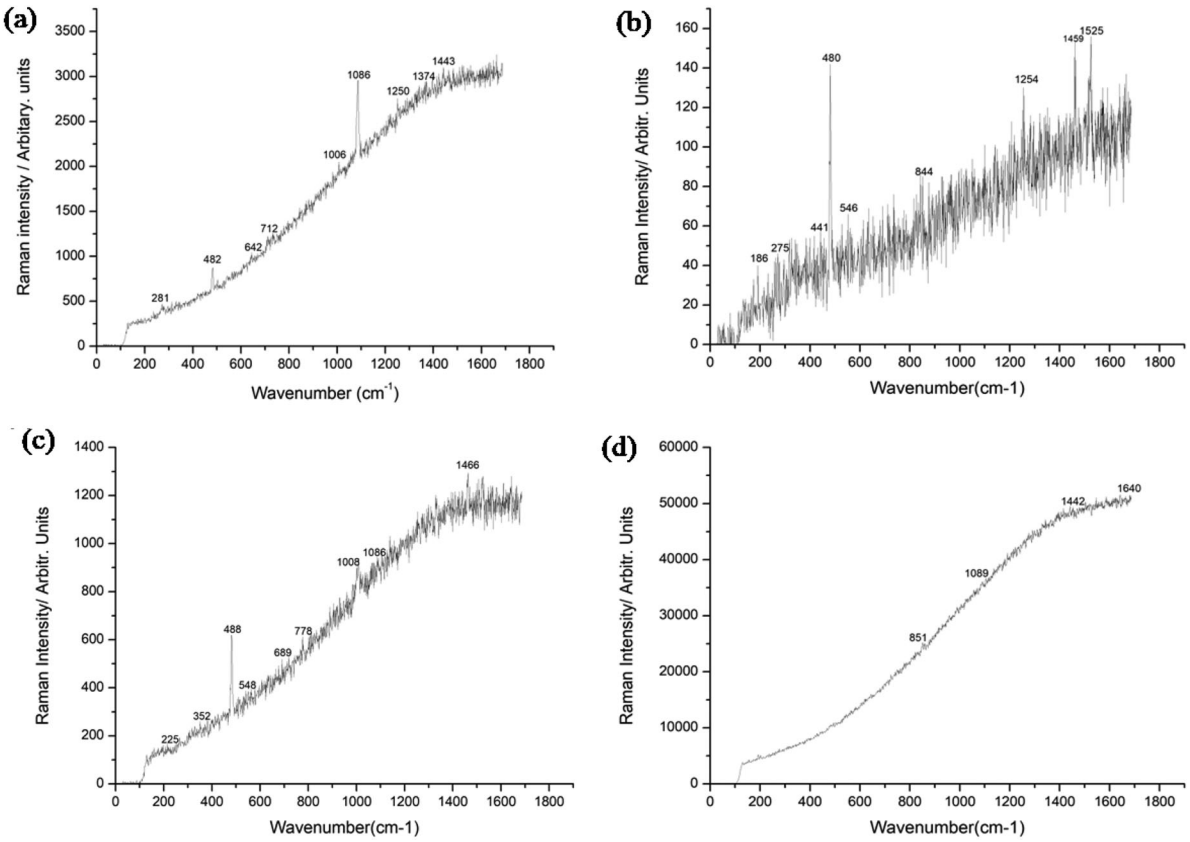

Figure 3. Raman spectra for samples: E.R (a); E.O (b); E.B (c); and E.Br (d).

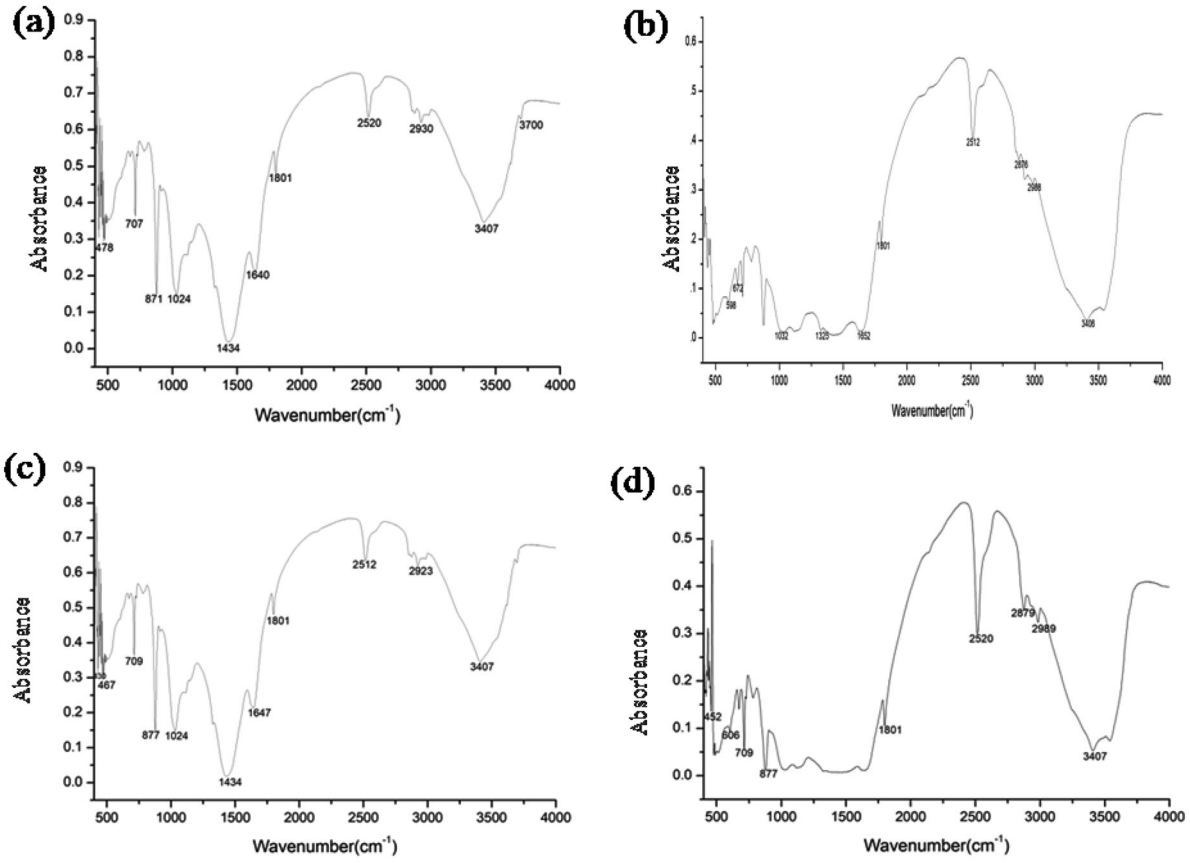

Figure 4. FTIR spectra for samples: E.Base (a); E.B (b); E.R (c); and E.O (d).

layer of the decorative fragments was identified as calcium carbonate and iron oxide along with other manganese- and iron-containing minerals. The ground layer has detached from the underlying basaltic rock support in isolated areas due to a loss of cohesion. The current condition of paintings in the Jain caves will necessitate a great deal of effort if they are to be conserved, but the information obtained from this research will be crucial in improving the understanding of their materials and preparation techniques, and informing the conservation of these wall paintings.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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