9th International Conference on NDT of Art, Jerusalem Israel, 25-30 May 2008
For more papers of this publication click: www.ndt.net/search/docs.php3?MainSource=65

MURAL PAINTINGS OF AJANTA CAVES, PART II: NON DESTRUCTIVE INVESTIGATIONS AND MICROANALYSIS ON EXECUTION TECHNIQUE AND STATE OF CONSERVATION

D. Artioli[1], F. Capanna[1], A. Giovagnoli[1], M. Ioele[1], A. Marcone[1],
M. Mariottini[1], E. Ozino-Caligaris[1], L. Rissotto[1], M. Singh[2]
[1] Istituto Centrale per il Restauro - Piazza S. Francesco di Paola 9 - 00184 Rome, Italy
[2] Archaeological Survey of India Science Branch Ajanta Caves,
Fardapur, 431118, Maharashtra, India

ABSTRACT

The Ajanta mural paintings represent the remarkable Buddhist renaissance in India. The support of the mural paintings is constituted by the walls of the caves, directly excavated in the rock of the cliffs. Most of the caves, in particular cave 17th and its porch dated V A.C., are completely decorated with mural paintings illustrating the Jataka of Buddha. During the cooperation project between Italian and Indian government aimed at the study and conservation of the pictorial cycle at Ajanta site on cave 17, an extensive campaign of scientific analyses has been carried out. In the preliminary documentation step, to better understand the execution technique and conservation state, scientific investigations were carried out using non destructive techniques such as portable ED-XRF, portable microscope (microwatch), UV light observation and spectrocolorimetry. In the case of the paintings under study, the points of investigation were chosen with the collaboration between the Italian team of scientist and restorers and Indian personnel in such a way to include all the original colour zones and areas with different conservation problems. Results obtained with non destructive tests enabled the team to optimize the choice of the points for micro sampling. Samples were submitted to microscopic and micro-chemical analyses conducted with mineralogical microscope, SEM-EDS, micro-FTIR, XRD, micro-Raman. The combination of the observation coming from the accurate visual examination, the results obtained by non destructive scientific analyses completed by the destructive analyses, have enabled us to acquire information on the pigments and binding materials used, on the succession of layers and their state of conservation.

CHARACTERIZATION OF CONSTITUTIVE MATERIALS BY NON DESTRUCTIVE TESTS

In order to have preliminary information about constitutive materials of pigments and preparatory layers, more than 350 XRF analyses have been carried out in cave 17 including all walls, inside and outside the cave. Points investigated represent all different colour areas as well as preparatory layers. XRF measurements were carried out with a EIS instrument (tungsten anode, operative conditions 30 KeV, 0.12mA, acquisition time 100 sec). With the experimental acquisition conditions employed XRF analysis does not allow to detect element lighter than potassium. It is therefore not possible to detect organic colorants as well as mineral such as lapis lazuli which only contain light elements. The hypothesis of the presence of a not visible compound can however be formulated when a particular colour is observed in the absence an element associated with a visible mineral. For example when on a red area an element indicating a red mineral (Fe, Hg, Pb, As) is not present, the presence of a red colorant such as a lake it is very likely. It can also happen that even if in a red area a little amount of an element indicating a red mineral is present (for example iron), the colour of the area is too red to be justified by the only presence of that little red ochre. In this case the simultaneous presence of a red colorant can be assumed. For this hypothesis to be plausible however colours must not be affected by the presence of superimposed layers.

Combination of XRF and Colour Measurement Results:
The Case of the External Porch

The combination of X-ray fluorescence and spectrocolorimetric analyses represents an interesting approach for the characterization of pigments constitutive of a paint layer. On the basis of a careful reading of the combination of results it is in fact possible, without sampling to formulate an hypothesis about the nature of pigments. The area chosen for this double control is a portion of the external porch (figure 1). In this area, differently than inside the cave where colours of the painted surface are strongly affected by the presence of dirt, smoke, bat excretion and altered conservation materials, colours appear bright and presumably more similar to their original appearance. On the porch 25 points, representing different colour zones, have been analysed with these two techniques and elements found with XRF measure have been associated with the chromatic coordinates. The results obtained are shown in Table1. Colour measurements have been carried out using a Minolta CM2002 spectrocolorimeter, with these instrumental conditions: illuminant D65 10° specular component excluded. Chromatic values are expressed as colour coordinates in the CIE Lab space (1976), where **L** coordinate or brightness indicates the degree of white, **a** coordinate (red-green component) indicates the degree of red (positive values) or green (negative values), **b** coordinate (yellow-blue component) indicates the degree of yellow (positive values) or blue (negative values).

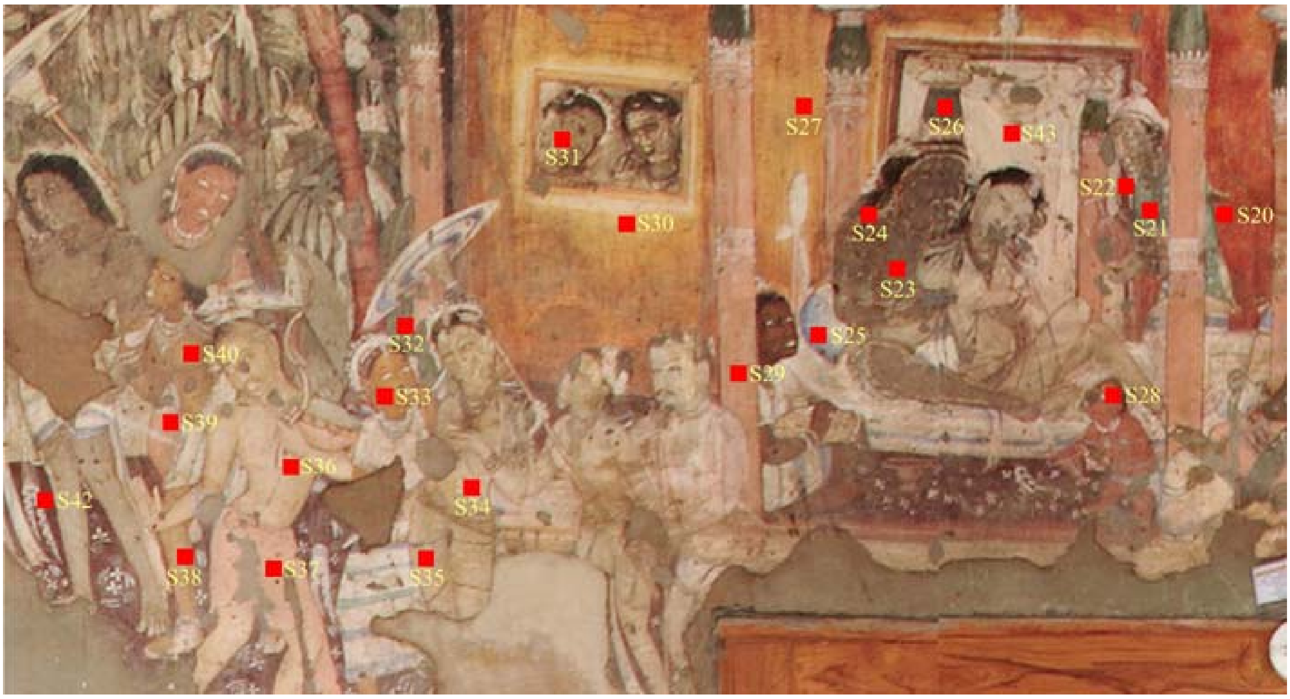


Figure 1. Ajanta cave 1,7 external porch. Areas submitted to XRF and spectrocolorimetric analyses

Results interpretation and hypothesis formulated have also considered all the results obtained from the other XRF measures and from micro-destructive analyses, in particular to evaluate the composition of preparatory layer which influence the XRF measure, but not the colour.

In table 1 it is evident that in all areas investigated the elements iron and calcium are present with minimum counting ranging between 25 and 30. On the basis of evidences from XRF and micro-destructive analyses we hypothesize that this does not represent contribution of the paint layer but of preparatory layers, thus we have assumed that iron or calcium are associated to a pigment present in the paint layer only when their counting is greater than 30.

Point measured colour	L	a	b	XRF counting
S43 white background	73,73	4,75	15,49	Ca(36) Fe(23)
S20 orange	46,63	24,45	22,60	Fe(38) Ca(32)
S33 orange face	53,83	14,85	26,35	Fe(99) Ca(44) As(29)
S28 red face	45,62	14,79	16,51	Fe(45) Ca(32) As(23)
S22 red background	49,28	11,31	10,29	Fe(83) Ca(38)
S42 red background	37,00	8,00	6,87	Fe(74) Ca(25)
S39 pink leg	58,31	14,30	18,69	Fe(32) Ca(32)
S37 pink skirt	63,58	13,86	21,04	Fe(33) Ca(24)
S29 pink column	58,38	16,14	21,10	Fe(60) Ca(45)
S36 pink complexion	66,15	8,94	20,51	Fe(46) As(43) Ca(27)
S27 yellow background	57,73	17,61	33,22	Fe(49) Ca(24)
S30 pale yellow background	65,40	12,79	35,52	Fe(37) Ca(31)
S38 yellow leg	57,98	8,72	22,17	Fe(72) As(41) Ca(21)
S40 yellow body	53,55	8,84	19,11	Fe(82) Ca(48) As(26)
S26 green capital	42,41	-0,67	6,77	Fe(56) Ca(34) As(24)
S32 green leaf	48,18	-0,82	9,62	Fe(97) Ca(45) As(17)
S23 dark-green body	*46,94*	*3,72*	*9,80*	*As(281) Ca(34) Fe(24) Sr(24)*
S31 green face	*49,25*	*3,08*	*13,84*	*As(119) Fe(78) Ca(46)*
S24 green shoulder	*48,19*	*4,29*	*13,66*	*As(148) Fe(34) Ca(33)*
S34 yellow-green belly	*66,69*	*5,08*	*24,03*	*As(180) Ca(34) Fe (26)*
S35 yellow-green leg	*59,60*	*4,08*	*18,54*	*As(181) Ca(38) Fe(30)*
S25 blue pillow	60,41	-1,65	-3,07	Ca(48) Fe(40) Sr(25)

Table 1. Colour (Lab space ill D65 10°, SCE) and XRF analyses results for areas investigated on the porch. To simplify data reading elements with counting below 16 have not been included in the table.

Whites

In the white point (S43) investigated, only iron and calcium are present with counting around 30, this suggests the use of kaolin as white pigment. The slight yellow tone measured (b=15,49) is due to the presence of altered superimposed materials.

Oranges

Two orange areas have been analysed. Point S20 has a bright red tone of orange (a = 24,45), but the iron counting is only a little higher than the value coming from the preparatory layers and elements indicating red or orange pigments are not present. Therefore this red colour and its intensity are due to the presence of a red colorant such as a red lake[1], characterized by good covering properties and bright tones. Micro-destructive analyses executed on sample P13 confirm this hypothesis. The other orange point (S33) has a lower red and a greater yellow tones. The presence of iron and arsenic suggests the mixing of an ochre with orpiment and/or realgar.

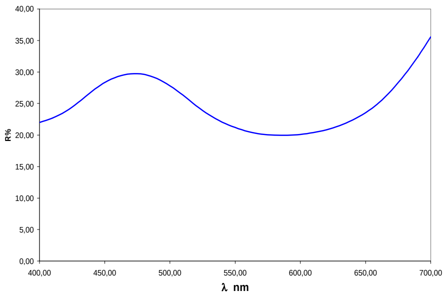
Reds

Iron is found in the three red areas investigated suggesting the use of a red ochre. Point S28 contains also a little amount of arsenic showing the use of orpiment and/or realgar. In point S28 the greater red component is associated with the lower iron content suggest the use of a red lake to reinforce the colour of the red ochre.

Pinks
Pigment attribution in pink areas is more complicated since pink is always a mixture of colours. Points S39 and S37 have low iron counting but quite a high value of red (a coordinate). This suggests the use of a red colorant mixed with a white pigment such as kaolin (low calcium counting). In points S29 and S36 iron counting is higher, the use of red ochre is very likely. Point S36 contains also arsenic suggesting that the pink tone has been obtained adding orpiment or realgar.

Yellows
Four different yellows have been observed. Points S27 and S30 have a bright yellow colour with an orange component and do not contain high amount of iron. We assume that in those points the tone of the yellow ochre has been reinforced with a yellow colorant[2] Points S38 and S40 have a less intense yellow tone, the presence of yellow ochre and orpiment is shown by the counting of iron and arsenic.

Greens
Seven different green areas have been analysed on the porch. Green points S26 and S32, measured on a leaf and on a capital, contain iron and little amount of arsenic. It is thus likely that those areas contain green earth (pigment identified also by micro-destructive tests) and orpiment. The other green points have been measured on the skin of figures. Skin greens, differently than those of dresses, trees or architectures show a more yellow-grey tone and contain arsenic as the main element. Visual and micro watch observation evidenced that two layers are present on green skins: a light-yellow layer and a greenish layer over it. In the micro-watch image for investigated point a faded yellow layer is visible in an area where a part of the green layer has fallen. Arsenic is present also in the light yellow layer below, because it has been observed by XRF in correspondence of fallings of the upper layer. While only in point S31 (figure 2) green earth has been found by XRF, in other green areas is difficult to justify the green colour observed in the upper layer. A possible hypothesis is that yellow layer is made by orpiment mixed with a white pigment like kaolin, whereas the upper layer contains orpiment mixed with a pigment not investigable with XRF technique (an organic blue colorant [3], lapis lazuli or organic black[4][1]) to obtain a colour which could resemble to a olive complexion. Unfortunately it has not been possible to obtain a sample in one of those areas and this hypothesis is left without a confirm.



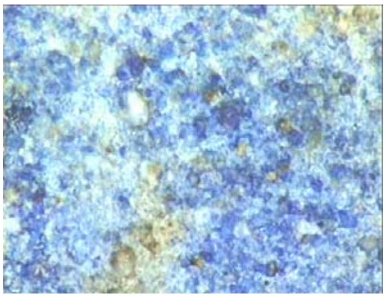


Figure 2. S31, micro-watch image (70x) Figure 3a. S25 reflectance spectrum
Figure 3b. S25 micro-watch image (175x)

Blues
The blue area analysed in the porch contains iron and calcium with counting attributed to the preparatory layers. The following evidences confirmed the employ of lapis lazuli: the absence of elements indicating a blue mineral pigment, the reflectance spectrum (figure 3a) of the blue

colour containing the red tail component, typical of lapis lazuli, the morphology of blue crystals (Figure 3b), micro destructive analyses and the bibliographic data.

General Results from Non Destructive Test in all Cave 17

The comparison between the results of the 350 XRF measures carried out inside the cave and on the porch, micro analyses and bibliographic data enabled us to identify the palette of pigments employed for the paintings. The results are shown in table 2. The work of different artists could be assumed on the basis of the different styles of painting and the difference of pigments used in diverse zones of the cave. Some colours have been obtained by a mixture of pigments. For example pink tones have been obtained by a mixture of a white (kaolin or calcium carbonate) with a red colour (red ochre and/or red lake). Orpiment and/or realgar is added to the pink to obtain the flesh complexion. For olive complexion, instead a complex mixture of orpiment and celadonite and/ or an organic pigment was used.

colour	Pigment	location
yellow orange	yellow ochre organic yellow orpiment and/or realgar	backgrounds, figures dresses animals probable presence in bright yellows with loo Fe animals, dresses, decorations, tools, aureoles, complexion
white	kaolin calcium carbonate shell white [5] lead white	all around dresses, architectures shields, lips, necklaces, women decorations dresses, highlights and woman decorations
red	red ochre red lake minium cinnabar	all around elephants, red pigment brightener all around elephants, dresses, inscriptions, architectures, tools blood (only west wall)
black	organic black	all around
blue	lapis lazuli	all around
green	green earth orpiment with blue or organic black	background, architectures, leaves, dresses figures of olive complexion (no est wall)

Table 2. Overall cave 17, painting board of pigments

MICRODESTRUCTIVE TESTS

With the aim to complete the information obtained by non destructive tests a campaign of micro sampling has been carried out. Sampling were of three types:

1. Micro-fragment of paint and preparatory layers to recognize constitutive materials the and succession of layers. Samples were submitted to microscopic, micro-FT-IR, Raman and SEM analyses. Three samples are shown as example in the following section.
2. Samples of plaster for the study of preparatory layers and fillings. Those samples have been analyzed by XRD and FTIR.
3. Samples for analysis of superimposed conservation materials from previous conservation interventions. Such samples have been analyzed by FT-IR.

Microanalyses evidenced that: The paint layer has been applied onto dry plaster with pigments of organic and inorganic nature. The binder is certainly of an organic nature and it is probably a vegetable gum. In the paint layer pigment is mixed with kaolin and often also with gypsum. Two preparatory layers are present in the first 500 μm below the paint layer. The first from the bottom is a preparatory layer made of mud, vegetable fibres, dung, grinded local rock (containing quartz, feldspars, pyroxenes, olivine, celadonite, iron oxides and iron titanate). The second is a calcium carbonate preparatory layer with thickness ranging from 80 to 200μm, which probably has the function of rendering the pictorial surface flat and homogeneous in colour in order to better receive the pigment layer. The pictorial surface is always covered with superimposed materials such as dirt, smoke, oxalates and materials introduced in past and recent conservation treatments. Two types of fillings have been analysed: white fillings principally made of gypsum, grey fillings contain gypsum and silicate minerals from local rocks. Plaster used by Indian personnel for conservation interventions has the same composition (mud, dung, fibres, grinded rock) of the first preparatory layer.

Micro-destructive Analyses on Paint Layer Samples

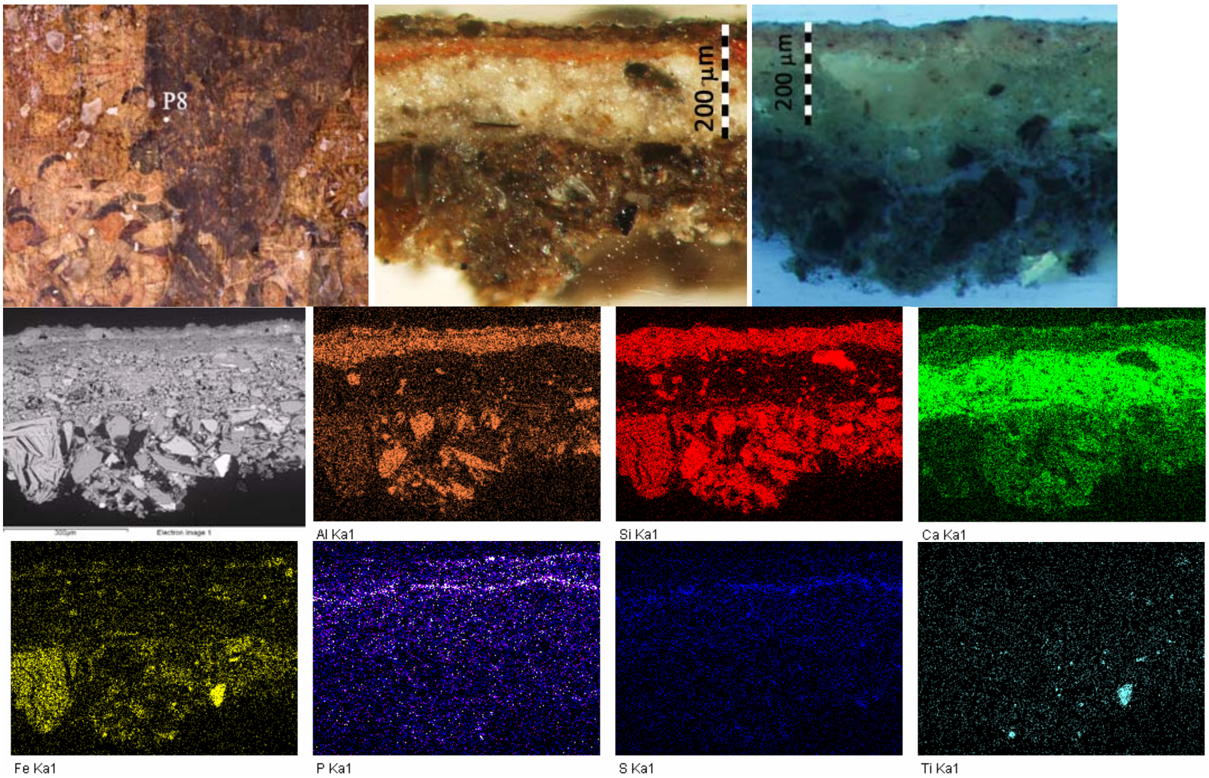


Figure 4. Sample P8, west wall. Area of sampling, micro-picture of the cross section under white reflected and UV light. SEM image and X-ray mappings.

In figure 4 are shown the cross section and SEM images from sample P8 collected on the west wall in an area adjacent to a cleaning patch executed by the Indian personnel. The sample has been collected where the black deposit still exists. Sample is made of different superimposed layers: a brown preparatory layer made out of mud, fibres and grinded rock, a whitish layer of about 150 µm containing calcium carbonate and silicate inclusion. The orange paint layer contains kaolin mixed with gypsum, ochre and probably a red organic colorant. The black layer contains oxalates, polyvinyl acetate and residues of altered shellac. The presence of phosphor in the superficial layers probably comes from vegetable extracts with the function of binders of the paint layer.

The cross section and SEM results from sample P13 are shown in figure 5. The surface of the sample is covered by a fluorescent layer of organic material. In this area a natural resin, oil, oxalates and gypsum have been evidenced by micro FT-IR. The presence of a synthetic polymer is also possible. The orange paint layer contains kaolin mixed with gypsum. On the surface is evident a very thin layer of iron (red ochre), whereas the orange colour for all the thickness of the paint layer could be attributed to an organic colorant.

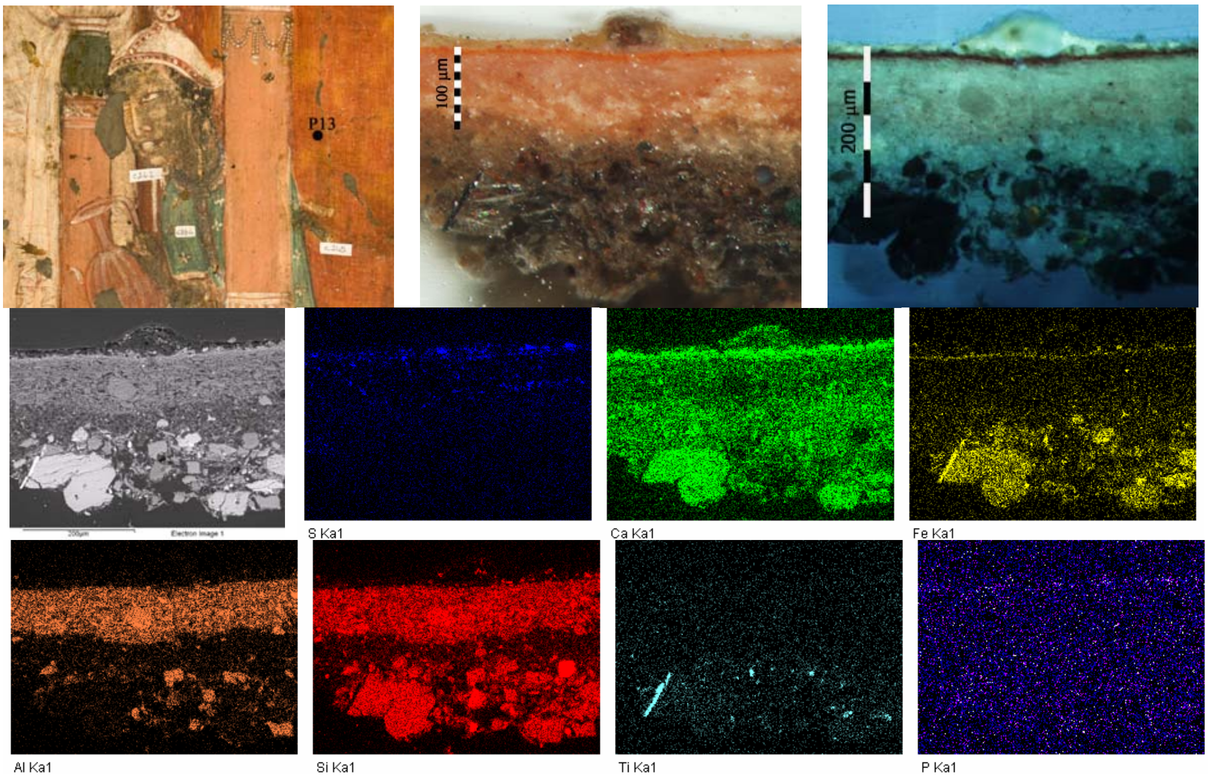


Figure 5. Sample P13, orange curtain (external porch). Area of sampling, micro-picture of the cross section under white reflected and UV light. SEM image and X-ray mappings.

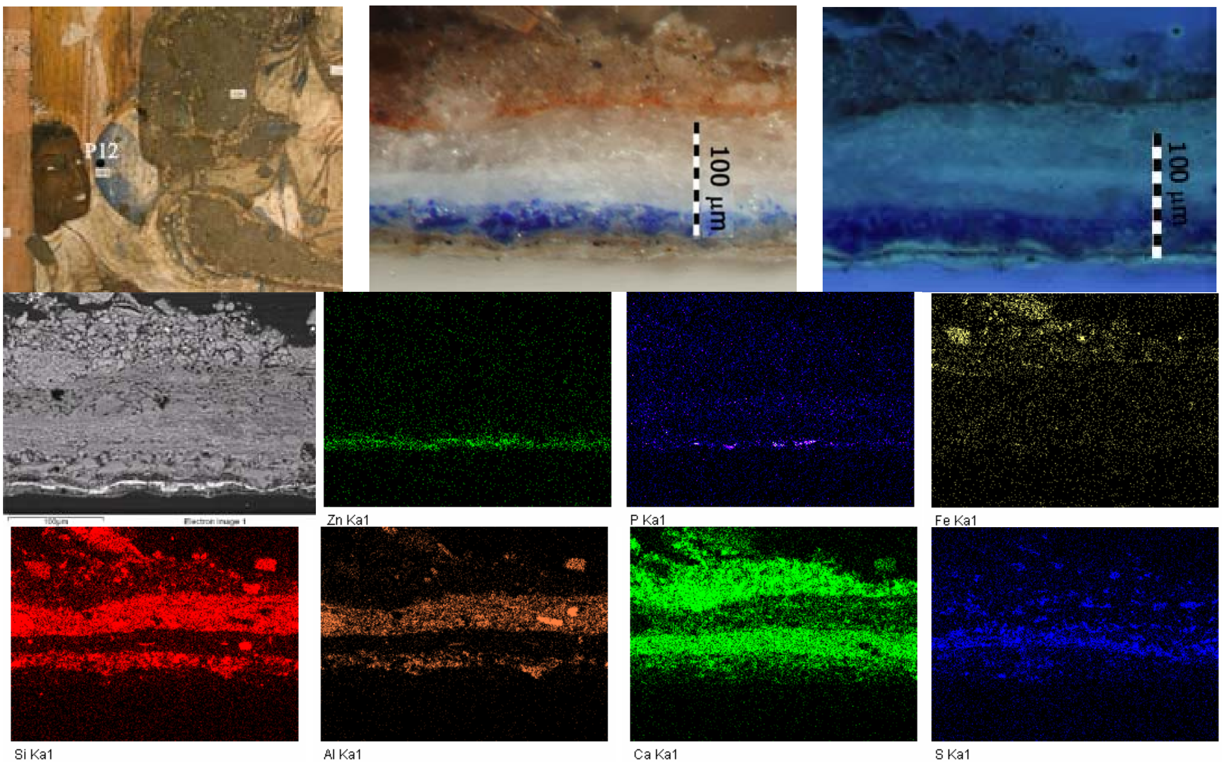


Figure 6. Sample P12, blue pillow (external porch). Area of sampling, micro-picture of the cross section under white reflected and UV light. SEM image and X-ray mappings.

The latter sample is P12 collected from the blue pillow of the external porch. In this sample the succession of layers is more complicated. The two preparatory layers are the same as those shown for the other samples. First layer is the brown preparatory layer made by mud and grinded rock, over which there is the calcium carbonate preparatory layer. Then a white layer is observed of about 100 μm thickness, which is actually made by two distinct layers: a kaolin layer and a gypsum layer. Between calcium carbonate and kaolin layers a red ochre preparatory drawing is evident. The blue layer (about 20 μm thickness) contains kaolin and lapis lazuli. On the surface of the sample an organic layer with yellow UV fluorescence is evident. Zinc is present in correspondence of this area, probably related to a recent conservation intervention realized with a synthetic polymer added with zinc white.

Microdestructive Analyses of Superimposed Materials

The results obtained from two samples for analysis of superimposed materials, are recorded below: one relating to an extract obtained from a swab used for solvent cleaning (T1) and the other to the drip stain of a superimposed substance taken from a fill on the east wall (P11). In sample T1 as shown in the FT-IR spectrum (figure 7) the principal component is polyvinyl acetate (PVA), a material widely used by the Indians in recent surface consolidation treatments. In sample P11 (figures 8, 9), comparison with the reference spectrum of shellac enabled us to identify the latter as the main component. UV light picture (figure 8) evidenced two types of fluorescent materials: shellac evidenced by its orange fluorescence is present in dripping P11 and over the grey filling on the top left. The other type of dripping with a yellow UV fluorescence, not soluble in water and in acetone is probably a mixture of oil and a natural resin like dammar.

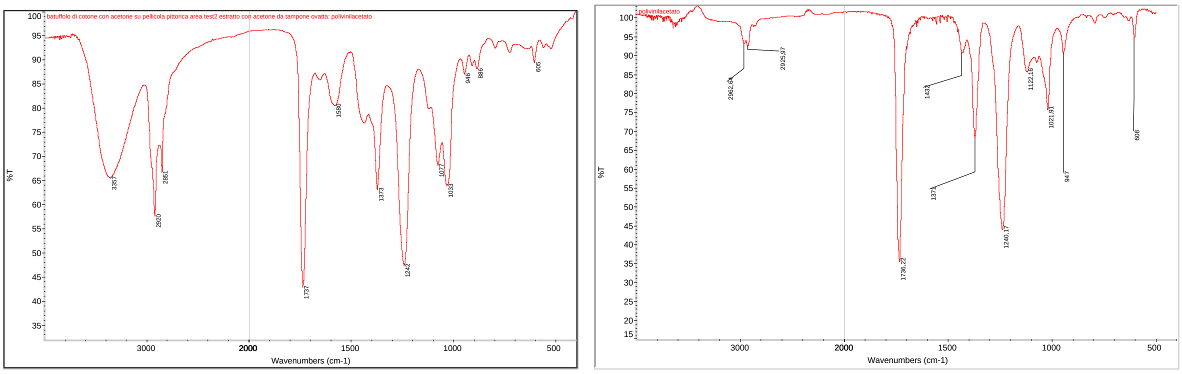


Figure 7. FT-IR spectrum of the extract from sample T1 (left), FT-IR spectrum of the polyvinyl acetate (right).

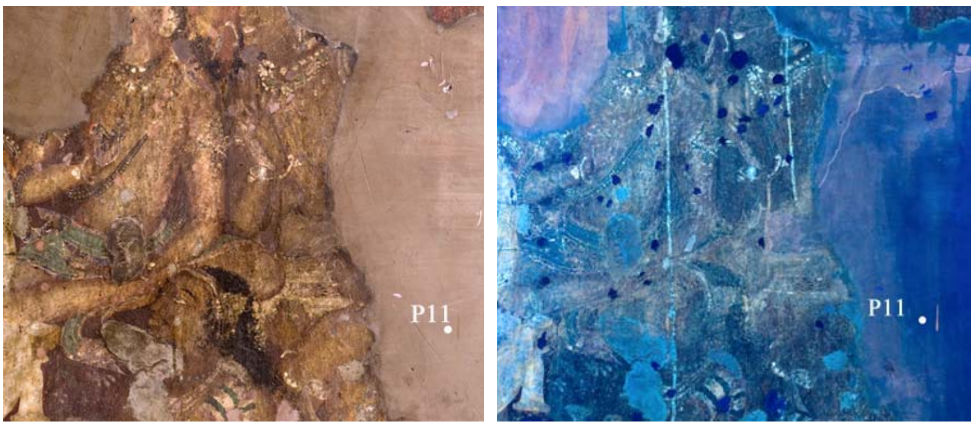


Figure 8. Est wall area of sample P11, picture under visible and UV light.

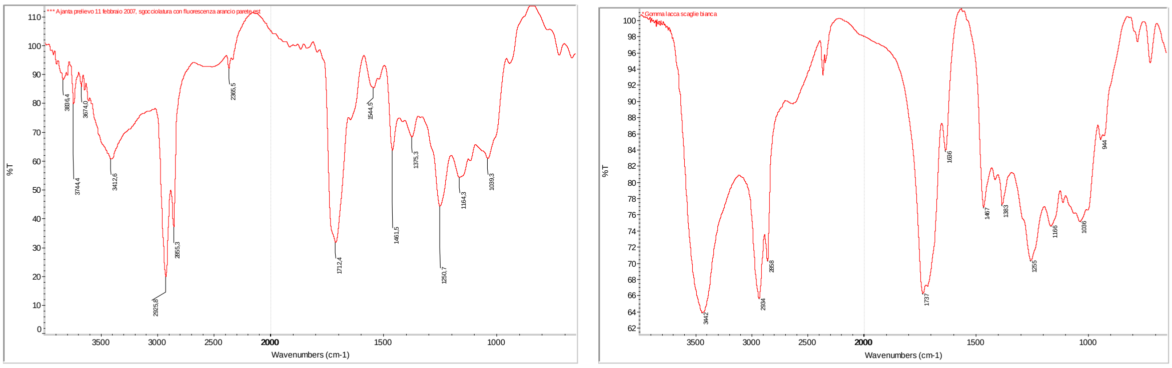


Figure 9. FT-IR spectrum of fluorescent portion of sample P11 (left) and FT-IR spectrum of shellac (right)

CONCLUSIONS

The scientific analyses carried out in Ajanta cave 17 by either non-destructive and destructive techniques evidenced that the paint layer has been applied onto dry plaster with pigments of organic and inorganic nature. Some differences in the pigments used and in the style of painting were evidenced between the different walls of the cave, suggesting the presence of different artists. Painting board can be summed up as follows. Red pigments used were red ochre, red lake, cinnabar, minium. Yellow and orange pigments were yellow ochre, orpiment and/or realgar and a yellow organic dye. Kaolin, calcium carbonate, shell white and lead white were used as white pigments. Blue areas were always painted with lapis lazuli, black areas with an organic black. Green areas were painted with green earth or with a mixture of orpiment and green earth and/or a pigment of organic origin. In the paint layer pigment is mixed with kaolin and often also with gypsum. The binder is certainly of an organic nature and it is probably a vegetable gum. Two preparatory layers are present: a preparatory layer constitute of mud, vegetable fibres, dung and grinded local rock; a calcium carbonate preparatory layer, which probably has the function of rendering the pictorial surface flat and homogeneous in colour in order to better receive the pigment layer. The pictorial surface is covered with a thick layer of different superimposed materials such as lamp black or charcoal, calcium oxalate, altered shellac, oil, natural resins, polyvinyl acetate. The presence of such a large variety of superimposed materials which sometimes do not allow the clear reading of the details of the paintings renders particularly difficult the cleaning operations.

ENDNOTES

1. Between red colorants the more common in India was the red of the gum named *laksa*, also named shellac. The colorant substance contained in shellac is constituted of four different types of laccaic acids, which precipitated as calcium salts produce a bright red, more stable than red of *cochineal* which has a similar chemical composition. (from *I colori degli antichi* Nardini Editore, Firenze 2003 pag 107-144).
2. For example turmeric, saffron, *gomma gutta*, indian yellow (from: *I colori degli antichi*, Nardini Editore, Firenze 2003 pag 107-144)
3. indigo
4. organic black come from combustion of organic material such as vegetable residues (vegetable black), bones (animal or bone black) oils (charcoal, lamp black)
5. shell white is characterized by the presence of high amount of strontium associated to calcium

BIBLIOGRAPHY

1. Agraval, O. P. "Problems of conservation of the wall paintings at Ajanta", in *International Symposium on the Conservation and Restoration of Cultural Property*, Tokyo (1997).
2. D'Monte, D. "Conservation questions at Ajanta", *Frontline*, November 20, (1998) pp 65-70
3. Ghosh A. in *Ajanta Murals*, New Delhi (1996), pp. 53-55;
4. Meilunas, R. J. Bentsen, J. G.; Steinberg, A. "Analysis of aged Paint binders by FTIR spectroscopy", *Studies in Conservation*, 35 (1990) 33-51
5. Schlingloff, D., *Studies in the Ajanta Paintings*, Delhi (1988); *Guide to the Ajanta Paintings*, Delhi (1996).
6. Sharma, N. S.; Venkateswaran, Singh, S. K. "Solvents used for the removal of shellac and other accretionary deposits" in *Symposium on Mural Paintings* , Dehera Dun (1980)
7. Sharma, R. K.; Gupta, H. O. "Restoration of some Important Wall Paintings in India: Specific Problems and Measures", in *Researches in Archaeology and Conservation*, New Delhi (1999).
8. Singh, M. Trambake R. S.; Gupta D. A. "Chemical Conservation of Hinyana Paintings (2nd century B.C.) cave n° 10 Ajanta", *ASI Report*
9. Spink W. "Ajanta and Ghatotkacha: A preliminary Analysis", *Ars Orientalis*, 6, (1966), pp. 135-55; "Ajanta's Chronology: The Problem of Cave Eleven" *Ars Orientalis*, 7, (1968), pp. 155-68; "Ajanta's Chronology: The Crucial Cave", *Ars Orientalis*, 10, (1975), pp. 143-69; "Ajanta's Chronology: Politics and Patronage, in *Kaladarsana*, *American Studies in the Art of India*, ed. By J. Williams, New Delhi-Bombay-Calcutta (1981), pp. 109-126; "The Archaeology of Ajanta", *Ars Orientalis*, 21, (1991), pp. 67-94.
10. Tandon, P. N. "Indian Pigments and their Problems of Preservation", *Conservation of cultural Property in India*, IAFSCCP, (1988) New Dehli
11. Trambake, R. S.; Raghavendra V. S; Mishra, Srikant; "A note on some conservation problems and treatments of mural and stone art Ajanta", *Conservation of cultural Property in India*, IAFSCCP, (1996) New Delhi

Back to Top