ELSEVIER
Journal of Cultural Heritage 3 (2002) 299–308
Journal of Cultural Heritage
www.elsevier.com/locate/culher

Characterisation of painting materials from Eritrea rock art sites with non-destructive spectroscopic techniques

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Abstract

Rock painting samples from Eritrean archaeological sites were studied by means of micro-Raman spectroscopy and proton-induced X-ray emission technique (PIXE). Hematite and manganese oxides/hydroxides were determined in red and black paints, respectively. Since colours do not contain carbon, the paintings cannot be dated with ^{14}C. Moderate amounts of calcium carbonate or sulphate were also observed in most red drawings, while traces of phosphorus were found by PIXE only in a few red and black samples. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Non-destructive analysis; Micro-Raman; PIXE; Rock art; Pigments; Manganese oxides; Hematite; Eritrea

1. Research aims

The object of the present study is a group of rock painting samples, now belonging to the *Museo Fiorentino di Preistoria "Paolo Graziosi"*, collected from a number of sites in Eritrea (formerly, northern Ethiopia) around 1960 [1,2].

Despite the large number of caves and shelters that have been discovered in the Horn of Africa since 1842, our knowledge of Eritrean rock art is still rather poor. It is generally recognised [3] that this art is the expression of cattle herders, peoples who made domestic bovids the main subject of their paintings—even though images of wild animals occur occasionally. Determining the age of this material is extremely difficult, since archaeological documentation is incomplete and the objects which can be dated on an absolute scale are too few for an accurate timeline of styles to be drawn; thus, the only available dating method is comparison with works from other areas for which an established chronology exists. The absence of images linked to the culture of archaic hunter peoples, together with the prevalence of representations of bovids, suggests that rock art developed concurrently with the oldest food production activities, and especially with cattle breeding; however, the localisation in time of this event is still unclear. Furthermore, the association of the four main styles recognised by scholars with four distinct chronological phases ranging from the third millennium BC to first millennium AD or later, with an increasing degree of stylisation, is essentially tentative and needs to be corroborated by independent evidence [4,5].

In this scenario, the analysis of painting materials appears as a rather valuable tool for the study of Eritrean rock art. In fact, physical investigation of pigments can complement stylistic analysis in many instances, for example by testing the existence of connections between different paintings depending on the use of a common "palette" [6]. Furthermore, if carbon of organic origin (such as in charcoal) is detected on the painted surface, radiocarbon dating techniques can be applied in a subsequent investigational step.

Many non-destructive methods are available for the analysis of rock art paints. In the case of our samples, micro-Raman spectroscopy and Proton-Induced X-ray Emission (PIXE), which have been successfully used in the recent past (often in conjunction) for the investigation of historical objects or works of art, appeared to be the most suitable techniques. In fact, the identification of red and black pigment grains was accomplished by means of micro-Raman spectroscopy, while a more detailed characterisation

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of materials on the painted layer was possible thanks to PIXE element analyses.

2. Description of the samples and archaeological sites

We analysed 14 painted stone fragments, which were approximately 3–10 cm in diameter—but no greater than 2.5 cm in the direction orthogonal to the painted surface, since samples thicker than this cannot be easily accommodated under the microscope.

The samples are from nine different sites which can be considered as representative of Eritrean rock art (Figs. 1 and 2): *Zebàn Kebesà I*, *Zebàn Kebesà II*, *Cohè Edagà*, *Ba'attì Meshùl*, *Mesbàr Gueibì*, *Hulùm Barèto*, *Meteccà Arè*, *Mehbà Eclì*, *Addì Alautì*. One stone from an unknown site was tagged generically *Eritrea*; the one named *Zebàn Kebesà* originates from either *Zebàn Kebesà I* or *Zebàn Kebesà II*. Note that samples coming from the same site are further labelled *(A)* and *(B)*.

In these archaeological sites, paintings are found on the walls of caves or shelters. Animals are the main subject of the drawings, especially cattle (*Bos t. prim. macroceros*, *Bos t. prim. indicus*), but antelopes, horses, lions, panthers, camels are also represented, often in herds. Human figures, sometimes armed (*Hulùm Barèto*, *Meteccà Arè*), or on horseback (*Zebàn Kebesà I*), are usually rather schematic. There are also many geometric and “abstract” shapes most of which are interpreted as stylised animals or humans.

Pictures of different styles are often present in the same site, thus indicating that a superimposition of layers took place in time. The colours used in these paintings range from black to white, yellow or red in many different hues.

3. Experimental

The investigation of pigments and binders in archaeological rock paints has long been accomplished by means of electron microscopy (SEM) and X-ray diffraction (XRD) [6,7]. Powder granulation and grain morphology studies have also been shown to be effective for elucidating the painting technique and the accessories used in the preparation and spread of the paint [6]. PIXE has been applied to rock paintings in a few cases [8], while the utility of Raman microscopy in this field has been recently demonstrated [9,10]. PIXE and Raman spectroscopy, on the other hand, have been successfully tested together as an investigative method for pigments on manuscripts [11] These two techniques, which can provide information on both the atomic and molecular composition of materials located on the surface of objects of medium to small size, with no consumption of matter, are ideal candidates for the analysis of rock painting samples like the ones in the present investigation.

3.1. Methodologies

Micro-Raman spectroscopy and PIXE perform a mostly superficial and local analysis by way of probing, respectively, with a visible laser beam and a proton particle beam, a small area of the sample. The dimensions of the beam spot are determined by the nature of the probe beam, as explained below.

Raman microscopy is based on the focalisation of a visible laser light beam by means of a microscope magnification lens, which reduces the inspected area to a few square micrometres; measurements on single pigment or crystal grains can in general be made separately from the surrounding. The information supplied by Raman spectroscopy, that involves molecular vibrations, is such that the nature of chemical compounds and chemical bonds can be easily revealed, leading to a rather straightforward characterisation of the crystalline grain that is irradiated.

In the PIXE technique, the atomic species present in a sample (except those of low atomic number—such as carbon, nitrogen and oxygen) are detected through the X-rays that are emitted when it is hit by a proton beam produced by an accelerator. The proton beam diameter may be varied from about 2 mm down to 1 μm. To average out the local inhomogeneities, a 1 mm diameter beam (approximately 200 times wider than with micro-Raman) was used in this case. After travelling through the paint on the surface, the beam also penetrates into the material underneath; X-rays produced by both the coloured layer and the rock below are detected. To evaluate the rock contribution, we also performed some measurements on the uncovered rock.

It should be noted that the two experiments were carried out independently, so that the sample points that were investigated were not the same. Due to the heterogeneous nature of the rocks, and to the limited number of sample points, results are not expected to be totally consistent. Consider also that, since PIXE probes a wider region than micro-Raman, the former technique is more likely to give an indication of the average composition of the surface, where the latter usually focuses on single grains.

3.2. Experimental data

Raman spectra were acquired directly on samples under the microscope, without any preparation or cleaning. Analyses were done employing a red excitation line (647 nm) of a krypton ion laser source and an Olympus BH2 microscope equipped with 60 × long distance and 100 × magnification objectives. They provide a sample irradiation diameter of a few microns. The monochromator was an HR460 coupled to a charge-coupled-device detector cooled with liquid nitrogen. A sample power value of about 1–2 mW was set and acquisition times from a few tens of seconds to 200 s were employed. The spectral resolution was about 4 cm^{-1}. The spectra presented here were treated by baseline correction.

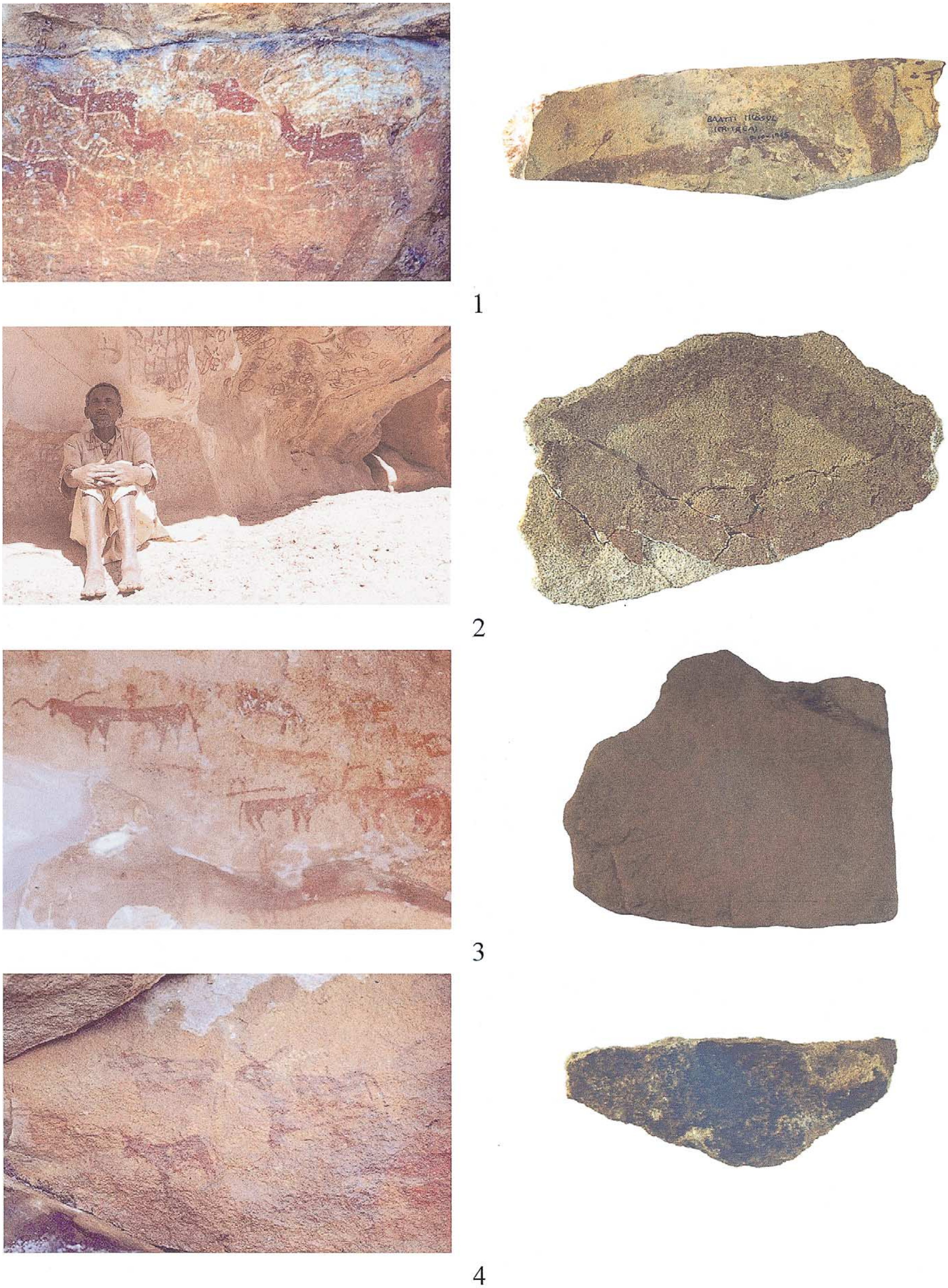

Fig. 1. Examples of paintings and rock samples. (1) *Ba'attì Meshùl*. (2) *Hulùm Barèto*. (3) *Zebàn Kebesà*. (4) *Mesbàr Gueibì* (photographs by P. Graziosi).

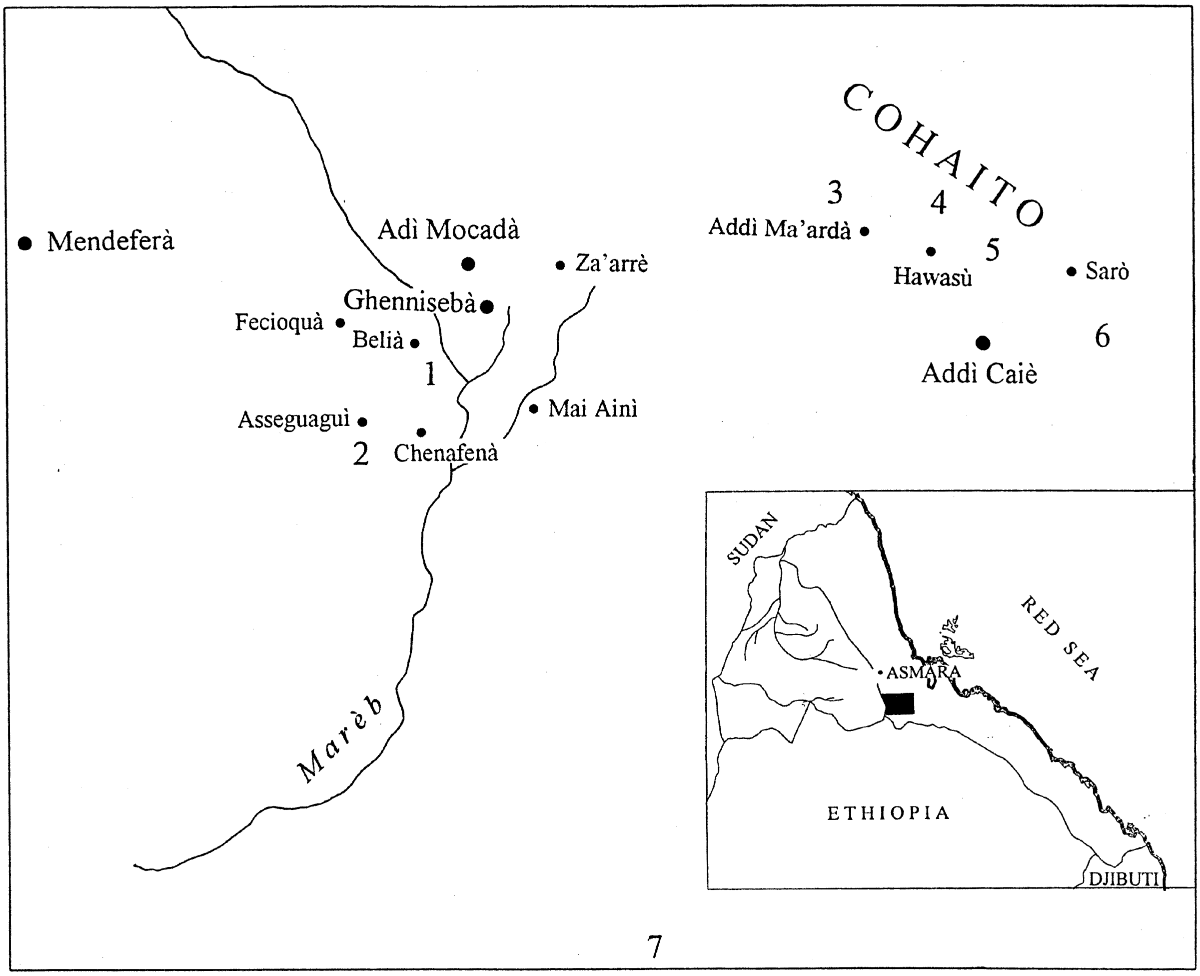

Fig. 2. Eritrea, Mai Ainì and Addì Caiè areas. Rock art sites from which rock samples were collected. (1) *Mesbàr Gueibì*. (2) *Ba'attì Meshùl*. (3) *Mehbà Eclì*. (4) *Hulùm Barèto-Meteccà Arè*. (5) *Zebàn Kebesà I* and *II*. (6): *Addì Alautì*. (7) *Cohè Edagà*.

For PIXE analysis, we have bombarded the samples with 3 MeV protons from the I.N.F.N. Van de Graaff accelerator at the Physics Department of the University of Florence, with the external beam set-up [11]. We adopted a beam spot with a diameter of 1 mm. Each sample was irradiated for about 6 min with an average beam intensity of 1 nA. The detection system consisted of two Si (Li) detectors, whose absorbers and distances were chosen so that one of them was primarily sensitive to elements lighter than Cr and the other to heavier elements. Elemental concentrations were obtained via a calibration curve from a set of thin standards of known areal density.

4. Results

Tables 1 and 2 report Raman and PIXE results for red and black drawings. We discuss each group first, then make some general remarks.

Detailed PIXE data are shown in Table 3, while Figs. 3–6 are examples of Raman spectra of the object materials.

Red drawings (*samples Zebàn Kebesà, Cohè Edagà, Zebàn Kebesà I (A), Zebàn Kebesà I (B), Zebàn Kebesà II, Ba'attì Meshùl, Mesbàr Gueibì I (A), Hulùm Barèto (A), Hulùm Barèto (B), Meteccà Arè*):

All red paints revealed the presence of hematite (α-Fe_2O_3), which gives a well-recognisable Raman signal (Fig. 3) [12]. In samples *Mesbàr Gueibì I (A)* and *Meteccà Arè*, the yellowish hydrated form goethite, α-FeOOH, which is commonly associated to native hematite, was also found by measuring its spectrum [12]. Raman results were confirmed by PIXE analyses, which measured a high content of the element iron.

Hematite is a widespread red pigment for rock paintings, whether natural or synthetic, the latter being obtained from goethite by firing (calcinating). In general, it is quite difficult to find out the origin of hematite pigment. In a recent study, an investigative method based on X-ray diffraction and morphological studies was set up and adapted to determine the natural or synthetic origin of prehistoric hematite [7].

Table 1
Micro-Raman and PIXE results for red samples

Sample	Area	Raman	PIXE
Zebàn Kebesà	Red paint	Hematite, calcium sulphate	K, Ca, Fe
Zebàn Kebesà I (A)	Red paint	Hematite, calcium carbonate	K, (Ca), Fe
Zebàn Kebesà I (B)	Red paint	Hematite, calcium carbonate	Ca, Fe
Zebàn Kebesà II	Red paint	Hematite	Fe
Cohè Edagà	Red paint	Hematite	(Ca, Fe)
Ba'attì Meshùl	Red paint	Hematite	Fe
Mesbàr Gueibì I (A)	Dark red paint	Hematite, goethite, carbon	K, Ca, Mn, Fe
Hulùm Barèto (A)	Dark red paint	Hematite, calcium carbonate, carbon (*both on drawings and rock*)	(Ca), Fe
Hulùm Barèto (B)	Dark red stripe	Hematite, carbon (*also on unpainted rock*)	Ca, Mn, Fe
Meteccà Arè	Red paint	Hematite, goethite, carbon (*also on back side*)	P, K, Ca, Mn, Fe

In almost all of the samples, Ca was also found by PIXE; the result was confirmed by Raman microscopy, which detected calcite ($CaCO_3$) in samples *Zebàn Kebesà I (A)*, *Zebàn Kebesà I (B)* and *Hulùm Barèto (A)*, and gypsum ($CaSO_4{\cdot}2H_2O$) in sample *Zebàn Kebesà*. Sulphate and carbonate may have been added to the paint mixture in order to give it a lighter hue.

Sporadic black grains were observed in some red drawings as well (*Mesbàr Gueibì I (A)*, *Hulùm Barèto (A)*, *Hulùm Barèto (B)*, *Meteccà Arè*) and were identified by micro-Raman as amorphous carbon. However, they were also observed on unpainted rock quite far from the drawing. Thus, they appeared more likely to be impurities, rather than a component intentionally mixed to red ochre to give it a deeper shade. Since they were found also on the back side of one black sample (*Eritrea*), all these impurities may well have contaminated the samples in the recent past, after the rocks had been detached from the site walls. In view of this, radiocarbon dating of black grains was not considered useful and was not executed.

PIXE also detected several metal elements (see Table 3), in particular K. These may be attributed to clay minerals, for they were commonly used mixed with pigments, according to our present knowledge of ancient colour recipes [13].

Moderate quantities of phosphorus were also found with PIXE on the *Meteccà Arè* red sample (Table 3). The simultaneous occurrence of phosphorus and calcium on painted caves was elsewhere attributed to bone fragments [6]; carbon associated with these two elements may indicate the use of bone black (a common rock art pigment prepared by burning animal bones). However, Raman revealed no signal characteristic of the phosphate ion, which is expected to be the dominant chemical species in such cases. Furthermore, no traces of bones, such as white splinters, were observed under visual microscopic inspection; and no correlation was found between carbon and phosphorus distributions on the sample surface.

Black drawings (*samples Eritrea*, *Mesbàr Gueibì I (B)*, *Mehbà Eclì*, *Addì Alautì*):

As already mentioned, one of the aims of the present research was that of checking whether the drawings contain carbon, which is the characteristic component of bone black, ivory black, carbon black or charcoal, all used in rock art as black pigments. Raman spectroscopy is quite well suited for the identification of amorphous carbon. No evidence of carbon, however, was found on black drawings; nor black iron oxides such as magnetite and manganite, also used as pigments in black colours, were detected. Instead, a broad band was observed in a spectral range, which is typical of Mn-O and Mn-OH stretching vibration frequencies. PIXE, which is not sensitive to carbon, revealed high contents of manganese (sometimes together with iron) (Table 3). The presence of manganese oxides–hydroxides was thus assumed.

The identification of such manganese compounds by means of Raman microscopy is known to be quite problematic [9]. Firstly, manganese oxides/hydroxides tend to undergo thermal transformations under high laser power values, in a manner similar to analogous iron compounds, but in a stronger way. Secondly, manganese exists in several oxidation states and exhibits a lot of hydro-oxides modifications, many of them being non-stoichiometric and disordered compounds [14]. Some difficulty was then encountered when faithful reference spectra were needed for a comparison: a certain degree of disagreement among published spectra was noticed. Unfortunately, ad hoc standards could only be recorded where pure and unadulterated manganese minerals were available. In view of all this, the assignment proposed below should not be considered conclusive.

Table 2
Micro-Raman and PIXE results for black samples

Sample	Area	Raman	PIXE
Mesbàr Gueibì I (B)	Black paint	MnOx	Mn, Fe
Mehbà Eclì	Dark brown stripe	MnOx	P, Ca, Mn, (Fe)
Eritrea	Black stripe	MnOx	P, Mn, Fe
Addì Alautì	Light black stripe	(Carbon, calcium carbonate)	(Ca, Fe)

Table 3
Elemental concentration (µg/cm²) obtained by PIXE measurements. Boldface values indicate that the element is likely to be present; boldface and underlined indicates that the element is definitely present

Sample	Area	Mg	Al	Si	P	K	Ca	Ti	V	Cr	Mn	Fe
Zebàn Kebesà	Background rock	1.5	4.3	18.9	0.0	0.0	0.2	0.0	0.0	0.0	0.1	1.9
	Red colour	0.9	3.4	4.0	0.0	**0.2**	**14.4**	1.6	0.0	0.5	0.2	**21.8**
	Red colour	1.0	5.6	16.3	0.0	**0.3**	**17.1**	0.0	0.0	0.0	0.7	**18.6**
	Red colour	1.0	4.4	7.3	0.0	0.5	**20.1**	0.0	0.0	0.0	0.4	**23.9**
Zebàn Kebesà I (A)	Background rock	1.3	1.8	5.7	0.0	0.0	0.2	0.6	0.2	0.0	0.2	1.9
	Background rock	0.6	6.3	38.4	0.0	0.0	0.5	14.8	3.9	0.1	0.1	3.2
	Red colour	1.0	3.2	5.1	0.0	**0.3**	**15.1**	0.0	0.0	0.0	0.2	**24.6**
	Red colour	0.8	3.7	6.6	0.0	**0.5**	**20.1**	1.6	0.5	0.0	0.3	**22.1**
Zebàn Kebesà I (B)	Background rock	0.5	4.1	19.2	0.3	1.2	4.4	4.6	1.2	0.2	0.9	51.4
	Background rock	1.0	3.8	17.0	0.6	0.1	4.1	1.6	0.5	0.0	0.0	3.1
	Light red colour	0.8	2.6	17.7	0.5	0.6	1.7	1.1	0.0	0.0	0.4	29.5
	Red colour	0.3	4.7	24.8	0.3	0.7	6.4	1.8	0.2	0.5	1.1	**167.7**
	Red colour	0.3	4.8	23.2	0.3	1.6	**11.3**	2.2	0.4	0.1	2.5	**254.2**
Zebàn Kebesà II	Background rock	0.3	15.2	22.9	0.0	0.0	0.2	0.0	0.0	0.0	1.3	47.2
	Red colour	0.2	14.5	25.3	0.2	0.5	0.8	0.0	0.0	0.0	0.8	**328.6**
Cohè Edagà	Background rock	2.4	6.6	13.7	0.4	0.3	3.1	7.0	1.9	0.3	0.7	45.2
	Background rock	0.6	7.0	14.1	0.0	0.4	0.8	5.8	2.1	0.2	1.0	30.0
	Red colour	1.2	5.0	18.9	0.3	0.6	**7.0**	11.9	3.0	0.3	1.7	**74.8**
	Red colour	0.2	6.7	15.6	0.0	0.8	**13.1**	10.6	2.9	0.3	1.6	**61.9**
Ba'attì Meshùl	Background rock	0.3	2.6	8.8	0.2	0.7	7.9	5.0	2.7	0.6	1.6	52.3
	Red colour (stripe)	0.3	3.6	12.0	0.0	0.7	8.9	3.5	1.6	0.5	0.6	**162.3**
Mesbàr Gueibì I (A)	Background rock	2.8	6.8	25.1	0.4	0.0	0.0	0.0	0.0	0.0	0.1	8.9
	Background rock	3.0	6.8	30.6	0.0	0.1	0.3	0.0	0.0	0.0	0.2	4.6
	Red colour	0.6	5.2	11.0	1.3	**0.6**	**19.8**	0.0	0.0	0.0	**3.2**	**77.0**
	Red colour	0.2	3.6	14.0	0.0	**0.5**	**13.3**	5.0	1.4	0.1	**2.7**	**42.9**
Hulùm Barèto (A)	Background rock	0.5	4.2	22.9	0.3	0.0	0.6	1.4	0.4	0.0	0.0	0.0
	Background rock	0.2	3.1	12.9	1.4	0.1	2.8	10.0	2.9	0.1	0.8	13.1
	Background rock	0.2	3.0	11.0	1.3	0.3	6.2	4.3	1.2	0.0	0.9	12.7
	Red colour (stripe)	0.7	3.9	7.5	0.0	0.2	**8.3**	2.0	0.6	0.2	0.5	**101.4**
	Red colour (stripe)	0.9	3.2	7.1	0.4	0.1	**7.0**	0.0	0.0	0.0	1.4	**26.3**
	Red colour (stripe)	0.6	2.9	8.3	0.0	0.4	**9.3**	0.0	0.0	0.0	0.5	**172.0**
	Red colour (stripe)	0.3	5.0	14.3	0.0	0.7	**14.0**	0.0	0.0	0.0	0.6	**124.8**
	Light red colour	0.6	4.1	7.4	0.0	0.3	8.1	0.2	0.1	0.1	0.4	31.0
Hulùm Barèto (B)	Background rock	1.8	3.1	9.9	0.4	0.0	0.0	3.5	2.1	0.4	0.2	14.9
	Background rock	1.6	3.0	26.7	0.6	0.3	2.7	7.8	2.0	0.1	0.2	9.0
	Background rock	0.2	4.3	16.1	0.4	0.0	0.0	0.0	0.0	0.0	2.1	92.1
	Red colour (stripe)	1.0	5.0	11.5	0.0	1.7	**11.6**	0.0	0.0	0.0	**11.4**	**211.6**
	Red colour (stripe)	0.8	6.5	13.7	0.0	2.6	**9.1**	0.0	0.0	0.0	**4.0**	71.5
	Red colour (stripe)	1.2	7.1	16.9	0.0	2.5	**17.3**	0.0	0.0	0.0	**16.2**	**270.2**
Meteccà Arè	Background rock	0.4	5.8	24.3	0.0	0.3	8.8	2.1	0.6	0.1	0.1	6.2
	Background rock	0.5	6.2	26.7	0.0	0.1	1.7	9.0	2.5	0.1	0.1	5.6
	Red colour	0.3	2.4	5.6	**2.2**	**0.9**	**14.6**	0.0	0.0	0.0	**1.1**	**35.5**
	Red colour	0.3	2.9	4.9	**1.9**	**0.7**	**17.3**	0.0	0.0	0.0	**0.9**	**33.1**
	Red colour	0.2	3.6	6.0	0.8	**1.1**	**11.4**	0.0	0.0	0.0	**3.4**	**37.8**
	Red colour	0.7	9.0	15.5	0.0	**1.2**	**30.7**	0.0	0.0	0.0	**2.0**	**89.3**
Mesbàr Gueibì I (B)	Background rock	2.0	2.7	10.3	0.0	0.0	0.0	4.2	1.5	0.3	1.3	80.0
	Black colour	1.5	3.7	9.7	0.7	0.0	0.0	6.5	3.2	0.1	**188.8**	**164.6**
Mehbà Eclì	Background rock	0.8	2.9	44.2	0.0	0.0	0.0	2.3	0.8	0.1	0.1	1.8
	Background rock	0.7	3.7	12.1	0.0	0.9	2.4	5.1	1.5	0.2	2.8	106.2
	Black colour	0.4	2.8	13.6	**1.0**	0.9	**10.2**	4.2	1.5	0.2	**10.3**	**72.8**
	Black colour	0.2	4.3	14.4	**1.4**	1.6	**12.2**	4.5	1.5	0.1	**32.5**	**98.7**
Eritrea	Background rock	0.6	9.3	31.9	0.0	1.7	1.5	3.6	0.8	0.4	9.2	61.5
	Background rock	0.4	1.4	10.5	0.6	0.3	16.6	0.9	0.3	0.0	0.4	10.9
	Background rock (red area)	0.8	5.2	16.2	0.7	0.5	2.6	3.1	0.9	0.0	1.9	37.2
	Background rock (red area)	0.2	2.5	10.7	0.0	0.3	2.1	2.3	0.7	0.1	1.4	31.0
	Black colour	0.7	3.4	10.2	**2.2**	0.5	16.5	0.0	0.0	0.0	7.0	**41.8**
	Black colour	1.7	7.8	23.7	**7.9**	1.1	29.9	0.0	0.0	0.0	**67.5**	**88.5**
	Black colour	0.7	4.6	16.3	**2.0**	0.8	9.9	2.8	0.7	0.1	**15.0**	**42.8**
	Black colour	0.1	3.2	10.8	**1.6**	0.5	6.2	1.5	0.4	0.0	**41.3**	**30.3**
Addì Alautì	Background rock	0.4	8.0	20.7	0.0	0.9	6.2	6.7	2.0	0.1	1.8	68.8
	Background rock	0.5	9.1	22.8	1.0	1.5	13.0	8.8	2.1	0.2	5.8	121.7
	Background rock	0.4	5.5	18.1	0.0	0.2	0.3	3.1	0.9	0.1	0.4	2.7
	Background rock	0.2	7.7	25.6	0.0	0.3	0.9	0.8	0.9	0.0	0.9	2.5
	Light black colour	0.9	2.6	5.1	0.0	0.1	6.5	0.7	0.3	0.0	0.4	**23.7**
	Light black colour	1.4	4.0	14.3	0.0	0.3	**8.7**	2.9	1.0	0.1	0.4	**24.4**
	Light black colour	0.7	3.7	10.5	0.0	0.2	**6.5**	0.2	1.2	4.5	0.3	**24.7**

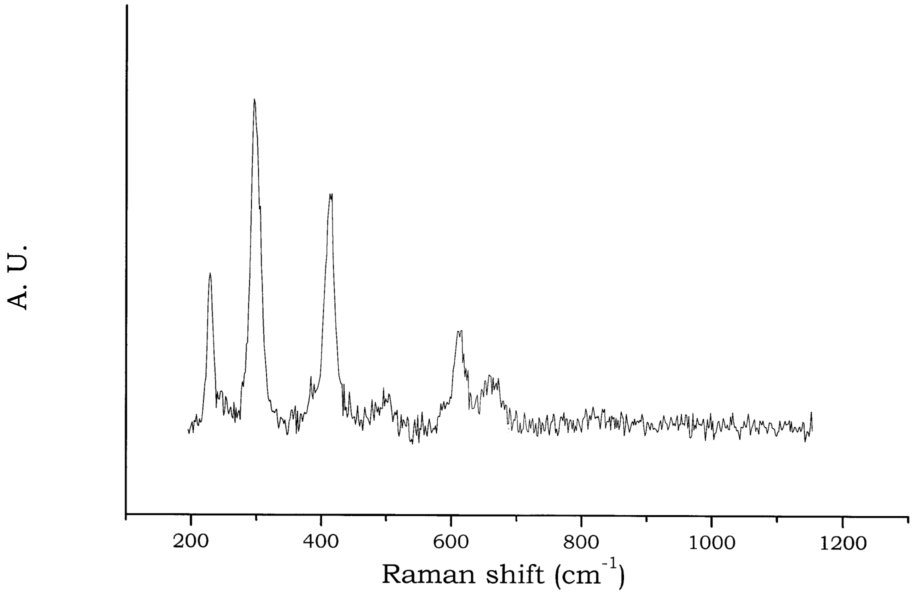

Fig. 3. Raman spectrum of hematite, recorded on sample *Meteccà Arè*.

Figures 4–6 report Raman spectra together with Lorentzian multi-peak fitting results. Three peaks were observed near 500, 600 and 650 cm^{-1}; the weak band at 492–495 cm^{-1} and the stronger one at 590–598 cm^{-1} were assigned to bixbyite (Mn_2O_3), while the presence of the Raman signal at 643–652 cm^{-1} was attributed to a variable contribute coming from a spinel structure (Mn_3O_4, haussmanite); sample *Eritrea* also showed an additional band at

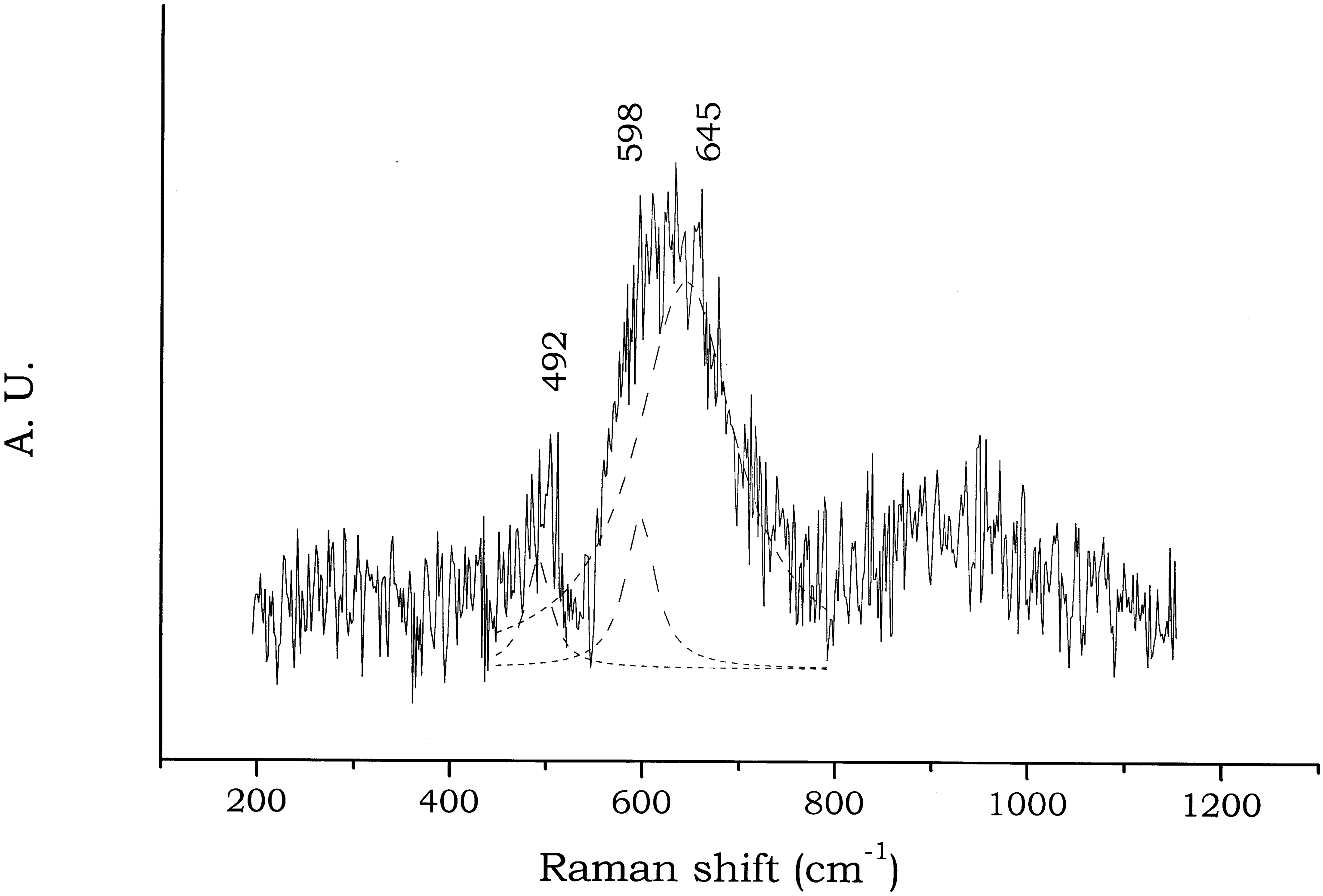

Fig. 4. Raman spectrum acquired on black drawings of sample *Mesbàr Gueibì I (A)*. Lorentzian multi-peak fitting results are shown in dashed lines.

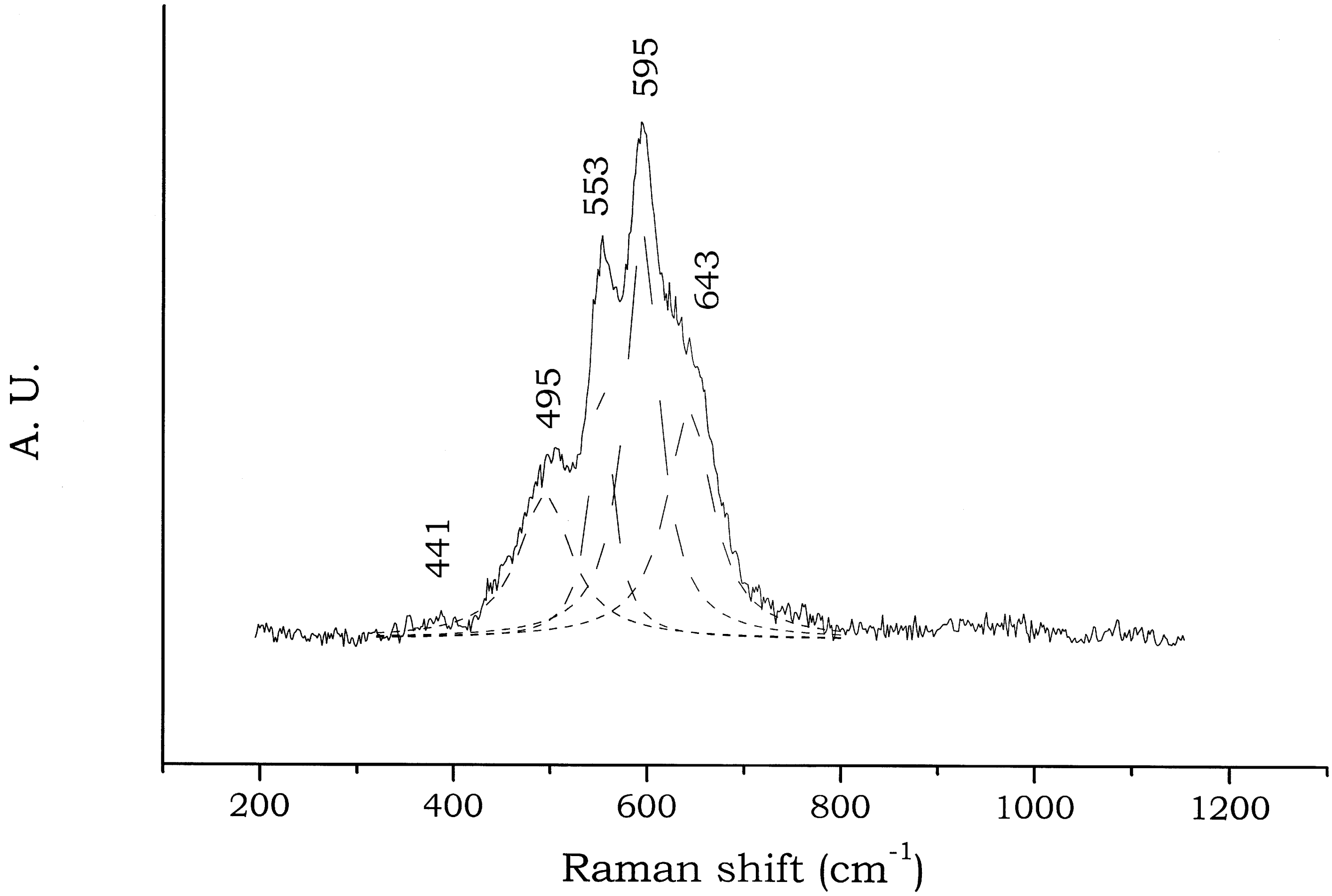

Fig. 5. Raman spectrum acquired on black stripe on sample *Eritrea*. Lorentzian multi-peak fitting results are shown in dashed lines.

553 cm^{-1} which may be ascribed to groutite sites (MnOOH) [14]. Moreover, black drawings appeared as homogeneous phases in which no distinctive grains could be observed, so that a fine mixture of different Mn^{II}, Mn^{III} and Mn^{IV} oxides and hydroxides has to be assumed.

As in some red drawings (see above), some phosphorus content was detected by PIXE analysis on *Eritrea* and *Mehbà Eclì* samples. It was, however, not confirmed by Raman microscopy, i.e. no trace of phosphate was found; amorphous carbon was not observed either. Both species are distinctive of ivory black or bone black, widely used black pigments in the prehistoric palette.

In sample *Addì Alautì*, in the area of interest (a light black stripe crossing the sample surface) the colour was so thin that no significant Raman spectrum could be recorded, in agreement with PIXE elemental analysis, which did not measure appreciable atomic contents.

5. General remarks

Moderate amounts of manganese were revealed by PIXE analyses on *Mesbàr Gueibì I (A), Hulùm Barèto (B)* and *Meteccà Arè* red drawings, but were not confirmed by Raman microscopy; on the other hand, iron was detected on almost all black paints which were characterised as a mixture of manganese oxides/hydroxides. The cause of these discrepancies is not fully clear. A tentative explanation is that the minerals used in the preparation of paints contained large fractions of impurities; the native minerals hematite and magnetite are in fact frequently found to be associated with each other.

Another question arises from the presence of phosphorus on some red and black colours. This element was clearly detected by PIXE but the expected phosphate was not revealed by Raman. Furthermore, phosphorus on the surface of rock artefacts is usually derived from animal organic matter (e.g. bones, guano), but no traces of such matter were observed.

The difference in the spatial resolutions and penetration fields of PIXE and Raman can account, at least partially, for the discrepancies in the observed compositions. It must be recalled also that the two sets of measurements were performed separately, so that results do not refer to the very same points.

6. Conclusions

This study confirms that micro-Raman and PIXE, in conjunction, can be used for the identification of rock art pigments. The main components of the red and black paints

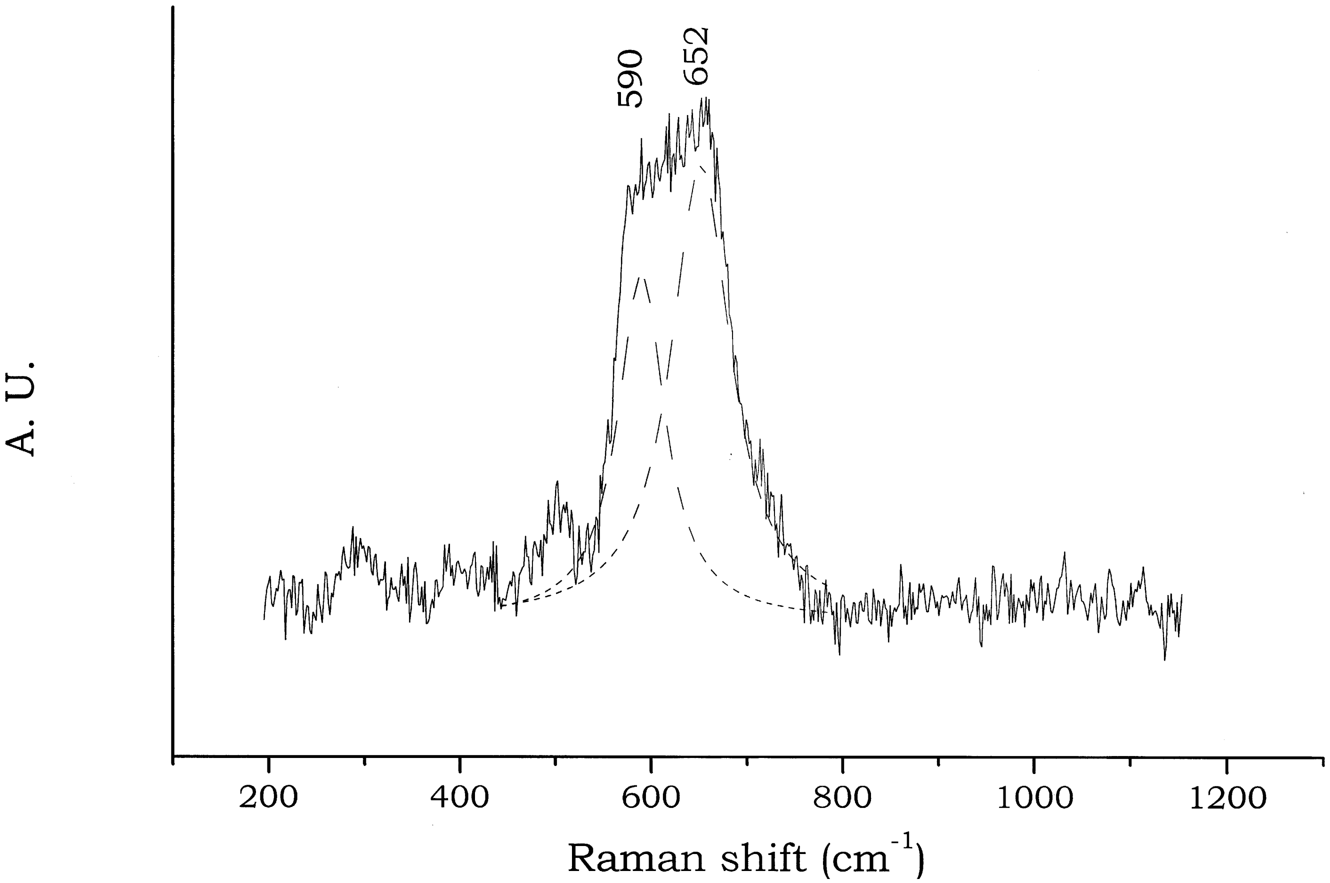

Fig. 6. Raman spectrum acquired on black stripe of sample *Mehbà Eclì*. Lorentzian multi-peak fitting results are shown in dashed lines.

were clearly identified in all the samples. The presence of hematite and manganese hydro-oxides in red and black paints, respectively, was revealed by means of Raman analysis, and was confirmed by PIXE measurements. These are known to be widespread colours for rock art, being found also in prehistoric sites. No clear difference in the composition of the paints among the various archaeological sites was observed, so that there is not enough evidence to support the existence of different painting techniques or recipes—which may in turn be related to different cultural areas or chronological phases.

Carbon grains detected on red samples are likely to be due to recent pollution, so a radiocarbon dating was not performed. The presence of Fe on black drawings, Mn on red drawings, and P on both red and black ones was not confirmed by Raman analysis. Further investigation is needed on all these aspects. Even if non-destructive techniques would be preferred, complementary methodologies, such as X-ray diffraction, X-ray fluorescence and Mössbauer spectroscopy, could be adopted for a more detailed investigation on inorganic components, while the presence of organic species could be tested by means of FT-Infrared spectroscopy.

In further studies, the opportunity of working in situ should also be considered: a portable micro-Raman instrument coupled to a movable probe through optical fibres could be used to take measurements directly on painted rocks inside a cave. This would be an improvement, as no sampling procedure would be necessary and an immediate comparison between meaningful areas under investigation could be possible. In situ elemental analysis is also possible with a portable PIXE instrument, now available; alternatively, a portable X-ray fluorescence system may be used (but with limitations with respect to standard PIXE analysis).

Acknowledgements

This work was supported in part by the Cultural Heritage Committee of Italy's CNR. Authors express their gratitude to the Director of the *Museo Fiorentino di Preistoria "P. Graziosi"*, Prof. ssa Alda Vigliardi, for supplying the rock painting samples, and Prof. Emilio Castellucci for precious suggestions and advice. We are also grateful to the Museo di Mineralogia of the University of Florence and to the Fondazione Scienza e Tecnica of Florence for kindly providing standard manganese minerals.

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