

Characterisation of Materials and Techniques in First Archaeological Findings of Nasca Wall Paintings

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Abstract

The pre-Colombian wall paintings in Peru were already known from north and central coast sites, but little information exists on the southern coast corresponding to the Nasca region. The recent excavations on Cahuachi site supplied fragments of plaster with paint layers found near Great Pyramide, corresponding to phases III and IV of the construction of the site, and dating back to the Early Intermediate Period (from 200 BC to 350 AD). A series of fragments from three locations from these two respective periods were transferred directly from the excavation to the laboratory and analysed. A panel of observation and analysis methods was applied in order to describe the stratigraphy and materials used for these paintings, with special attention to the paint layer. The stratigraphy was observed by optical and electron microscopies and X-ray fluorescence, Raman and infrared spectroscopies were employed for elemental and molecular characterization of the plaster and paintings. The obtained results show the large use of iron oxides and copper based pigments, as well calcium sulfate, siliceous and clay materials and graphite. Although the most of pigments could be provided by local deposits, the provenience of graphite remains undetermined. The differences of painting materials between phases III and IV are related to the palette of colours and pigments. The colors for phase III seem limited to the red and yellow ochre pigments, unidentified black and gypsum white. During phase IV, additional pigments were identified such as: paratacamite, malachite and chrysocolla for greens, hematite for purple, graphite black and siliceous white, which replaced gypsum white. The paintings were sometimes applied in several layers separated or not by white coating layer. The painting materials and techniques identified on Cahuachi site, and especially the differences between the phases observed, constitute a new insight in the knowledge of wall painting tradition in Southern Peru.

Introduction

Wall painting has a very ancient tradition in the Andean area [1]. The oldest examples are those of the Cerro Ventarrón religious sanctuary, the only ones known from Pre-Ceramic period, dated back to over 4000 years. This pictorial tradition was developed through the pre-Hispanic centuries. It is worth noticing that the first paintings appear on the north coast of Peru (Cerro Ventarrón, Kotosh and Cerro Sechín), then on the central coast (Garagay). The wall decoration patterns were at the beginning very simple and schematic, and then become more complex. During the period of the Early Horizon (900 – 200 BC) the polychromy on monuments was developed, with in particular the paintings and painted reliefs of the temples of Puncurí and Cerro Blanco, in the Nepeña Valley in the north of Peru.

During the Early Intermediate Period (200 BC – 700 AD), the mural art flourished. Two major styles coexist: the "Lima" style on the central coast, and the "Mochica" style in the north. Both styles continued during the Middle Horizon (700–1000 AD). The first style is characterized by the repeated use of a pattern of intertwined snakes. In the "Mochica" style, real scenes were painted, with incisions used as preparative drawings. Several archaeological sites illustrate this style and Mochica iconography including the Huaca de la Luna (Moche valley), the El Brujo complex (Chicama valley), La Mina (Jetepeque valley), Pañamarca (Nepaña valley) and the Huaca Pintada (Lambayeque valley) on the northern coast. For later

periods, little evidence has been preserved but no major variations seem to have been introduced. The Mochica style was divided into five phases. Most of the known Mochica murals belong to phase IV (Early Intermediate Period) or to phase V (Middle Horizon). The paintings of the Middle Horizon are characterized by the splitting of the scenes into several square surfaces which follow each other. To the south of Peru, on the highlands, in the large urban center of Tiahuanaco, several large stone temples were built between 700 A.D. and 1200 A.D. There were also adobe walls, some of which were painted [2]. Few examples remain from the Late Intermediate Period (900–1440 AD). Also, few murals are dated from the Late Horizon during which the Inca Empire prevailed. Vandalism, the rainy climate in the Sierra and the iconoclasm of the colonial era all contributed to the massive destruction of these paintings, which were probably much more numerous. However, in the south coast, among the archaeological sites belonging to this period, La Centinela in the Chincha valley, Incahuasi and Guarco in the Cañete valley and Tambo Colorado in the Pisco valley, have preserved inca-style paintings [1]. Several other sites were found on the central or northern coast, like La Fortaleza, but very few in the interior of the country. However, some historical writings like the chronicles of Garcilaso de la Vega [3] testify to Inca murals but unfortunately they have disappeared.

In summary, the oldest examples of mural painting were discovered on the north coast, where presumably the pictorial technique appeared in the Pre-Ceramic period. Mural painting was then developed during the Early Horizon through the Chavín style on the north and central coast. On the other hand, in the south, except for the few fragments of mural painting recently discovered in Cahuachi, and some others on an Early Horizon site that is now destroyed [1], no other vestige bears witness to murals on the south coast. Consequently, according to these archaeological data, it seems that the technique of mural painting was adopted and mastered very early by the cultures of the north, while the Paracas and Nasca cultures in the south do not seem to have had a predilection for this type of polychrome architectural decoration.

The Nasca, whose culture appeared on the south coast of Peru in the 2nd century BC and disappeared around the 7th century AD, have left many vestiges that testify to the importance of the development of polychromy in cultural expression. In particular, objects of worship such as ceramics and textiles were produced by them on a large scale. Indeed, the Nasca seem to have been masters in the art of rich polychromy on ceramic [4, 5] and on textile [6, 7]. Ceremonial buildings also seem to have been a favorite support for developing polychromy, precisely at Cahuachi, the major ceremonial center of the Nasca during the beginning of the Early Intermediate Period (200 years BC to 350 years AD). Archaeological excavations carried out in 2006 by Giuseppe Orefici revealed the existence of fragments of paintings on the walls of the great pyramid of Cahuachi. These are, up to now, the first examples of mural painting discovered on the site. They are one of the few murals discovered on the south coast.

The Cahuachi site is located in the center of the Rio Grande basin, 42 km from the Pacific coast (Fig. 1). It was erected on the south bank of the Rio Nasca, in the middle of the valley and of natural mounds. The presence of water, rare in this arid region, made it a sacred place: a *huaca*. The occupation of the site was very extensive since the site surface is estimated to be 24 km². Excavations have continued since the 1950s, started by W. Strong, then continued by H. Silverman and finally, since 1982 by CISRAP (Centro

Italiano Studi e Ricerche Archeologiche Precolombiane) team. Until now, only part of the site has been excavated: the area where the most imposing buildings are concentrated.

The central sector of Cahuachi is made up of monumental ceremonial buildings, with the "Great Pyramid", the "Great Temple", as well as other major structures. The monumental district extends east and west, linearly, with a high density of construction. Oldest buildings were constantly covered by new structures, until the abandonment of Cahuachi (around 400 AD). In general, the walls of the structures of the old platforms were dismantled and their surfaces were covered with embankments in order to reconstruct new platforms on the top.

We can thus identify four construction phases and a fifth phase during which the abandonment of the site was ritualized [9, 10]. The most monumental structures were erected during the phases 2 (200 BC to 0) and 3 (0 to 250 AD): they consisted of several platforms two to three meters high, superimposed on each other. Phase 3 coincides with the peak of the Cahuachi ceremonial center activity. The oldest traces of wall paintings date from the third phase of construction, then other painted decorations were applied during the fourth phase (250–400 AD) [11, 9]. During the phase 4, the interior of the Great Pyramid changed of use and space was divided with narrower passages [10, 12].

Some fragments of wall paintings taken from the Cahuachi site were analyzed in the laboratory in order to characterize their materials and techniques [13]. This was the first analytical study on Cahuachi murals and on fragments directly transferred to the laboratory from an excavation site, which permitted to avoid any conservation treatment or museum collection storage.

2. Archaeological Context And Sampling

The central area of Cahuachi is made up of predominant monuments such as the Great Temple, the Orange Pyramid, the Temple of the *Escalonado* and the Great Pyramid. They are connected to each other and to several other minor temples by squares, enclosures, passageways, staircases.

The Great Pyramid, 30 m high, is the tallest building. Its stepped architectural form and the abundant vestiges of ritual objects seem to indicate that it was the focal point of religious activity. The first fragments of mural paintings were discovered in this building.

The state of conservation of the paintings is poor, because the coating detaches from the wall and falls. As a result, the remains of wall paintings splitted into small fragments of painted plaster were found at the base of the walls (Fig. 2.a).

They are rare and too fragmentary to allow the original motifs to be reconstructed. In the upper part of the pyramid (phase 3), only fragments of red paint were found, while in a lower area (phase 4), several colors were present: yellow, orange, red, green, white, black and purple. Black or white lines seem to emphasize the outlines of patterns. Some sections of the walls may have been painted in only one color while others may have been decorated with polychrome patterns or scenes.

According to the first observations in situ, the preparation of the support and the pictorial technique seem to be relatively close to the contemporary cultures of the central and northern coast: the surface of the *adobe* walls is covered with mud-based coatings [14]. This plaster is generally thick because it was used to even out the surface of the walls by filling in the hollows between the *adobes* (Fig. 2.b).

On the fragments of paint found in the lower part of the Great Pyramid, we note the presence of large incisions, generally underlined by a black line which was employed to separate two colors. The paint was applied after the incision on the clay plaster. Among the Great Pyramid paint samples, we found some with a thin white layer (plaster or whitewash) applied to the base plaster, and on which the pictorial layer was executed. In some cases, several layers of paint overlap one another or are separated by a layer of plaster. This recalls the painting practices used by northern cultures. The samples were chosen among the many fragments detached from the wall. We have chosen them with the aim of getting the most complete paint stratigraphy as well as the different colors and types of coatings.

The samples from our study were taken from four areas of Cahuachi (Fig. 3). All the fragments of mural painting were taken from three distinct areas of the Great Pyramid (Y8): two sectors belonging to the upper platforms of the pyramid (samples 16N, 17R, 18J, 19R) and a sector in the lower part of the pyramid (samples 01V, 02V, 03J, 04R, 05R, 06R, 07R, 08N, 08J, 09N, 10N, 11N, 12N, 13V).

Finally, two plaster fragments (14G and 15G) come from the *Escalonado* temple.

By observing the thickness of the coating of the fragments taken on site, we can distinguish a thin layer on the surface for the majority of the samples. The stratigraphy generally displays a first, coarser layer, which essentially has the function of equalizing the surface of the wall, and a second one, thinner and smoother, intended to receive the paint.

Methodology

Stratigraphic sections

The observation of samples in the form of stratigraphic sections was done first. Thus, tiny samples (about 1 mm) were taken from the fragments in order to observe the different superimposed layers of paint and coating. The samples were included in a non-pre-accelerated polyester resin (H59). The resin was then eroded gradually until the sample was flush.

Because many fragments easily disintegrate, sometimes two complementary samples were taken to obtain the whole stratigraphy. Some painted plaster fragments have two juxtaposed colors easily separating from each other, therefore, they have been also prepared as separate fragments (04R and 04N; 08J and 08N). Only sample 01V containing the two pictorial layers was successfully included in the polyester resin without splitting.

All the samples were studied under an optical microscope and at the SEM-EDS, which made possible to visualize the stratigraphy and to obtain the elementary composition of each paint layer and that of the

support coating of all the samples.

Scanning electron microscopy and elementary analysis by EDX

The nineteen stratigraphic sections were observed and then analyzed using a scanning electron microscope (SEM-EDS).

The electron microscope used was a JSM 5600 LV (JEOL) coupled to an EDX Pentafet Link 6587 probe (Oxford Instruments). The observation of the pictorial layers in backscattered electrons was carried out without the use of metallization by working with a partial vacuum (pressure of 17 Pa) at an accelerating voltage of 15 KV. The obtained data was processed with Inca software (Oxford Instruments).

Raman micro-spectroscopy

For the Raman spectroscopy analyzes, carried out directly on the raw samples, we used two complementary devices.

The first of them was a RM 2000 Raman dispersive microspectrometer (Renishaw) with two monochromatic sources (633 nm and 785 nm) and the second was a Labram IB microspectrometer (Horiba Jobin-Yvon) with a monochromatic source of 532 nm. Both devices are equipped with a barrel fitted with density filters to attenuate the power of the incident laser beam received by the sample. With the 100x magnification used, the spot size was 1 μm^2 . Spectra are obtained with an acquisition time of 30 s and an accumulation of at least five spectra for the 532 and 633 nm lasers, and up to 20 spectra for the 785 nm laser. For each type of particle ten analysis points were analysed on areas with the same microscopic characteristics. No filter was used for the acquisition of spectra of reference pigments.

Fourier transform infrared spectroscopy

The FTIR analyzes were carried out with the IR 2000 spectroscope (Perkin-Elmer) equipped with DTGS detector. The analyses were performed in transmission mode after preparing the pictorial layer samples in KBr pellets. The acquisitions of spectra were done in the spectral interval from 4000 to 400 cm^{-1} with 4 cm^{-1} resolution. The Spectrum software (Perkin-Elmer) was used to control the instrument and process the data.

4. Reference pigments

Several mineralogical studies were carried out in Peru [15, 16, 17]. They give localizations of deposits of ores and determine the various minerals present on the territory. These studies also indicate the mineral compounds which could have been exploited by pre-Hispanic civilizations, in particular the pigments [13].

Five local pigments, extracted from different deposits in the region and used to make copies of old polychrome ceramics, were obtained from a potter in the town of Nasca. They were a green stone, a black stone, and a second black speckled with red, as well as reddish orange and yellow powdery earth. Each pigment was analyzed in Raman spectroscopy and in elementary energy dispersion analysis (EDS).

According to the results obtained from Raman spectroscopy, the green stone was identified as clinoatacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$ (monoclinic), characteristic of the Peruvian and Chilean coastal desert. It is often associated with the atacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$ (orthorhombic) and the paratacamite $\text{Cu}_3(\text{Cu}, \text{Zn})_2(\text{OH})_6\text{Cl}_2$, typical of the region which is found in particular in the copper deposits of the Mina Justa in Marcona [18]. Clinoatacamite is attested at Lily's mine in the Pisco region [19].

The black and red stone was found to be hematite, containing a few grains of quartz. When it was ground to powder for analysis, it turned purple. Black stone is a complex rock made up of quartz, feldspar, clay and hematite. The yellow powder seems to correspond to a kind of limonite: a combination of several minerals with goethite, iron oxides and feldspar. The orange-red powder is clay containing hematite and sparse grains of sand.

Results

5.1. Stratigraphic observations

The majority of samples have a single pictorial layer (Fig. 4.a) but those from sector Y8 Exp135 present the direct superimposition of colored layers (Fig. 4.b).

The superimposition of the pictorial layers suggest the presence of repaints which would not correspond to the initial pattern but it could simply be juxtaposed paintings which overlap at the color junction. In the case of the red paint spot on a black background of sample 06R, it could correspond to a detail directly painted on the surface of an initial drawing.

On the other hand, for the samples from sectors Y8 Exp 133 and 138 (16N, 17R, 19R), some have been repainted, this time applied to a new layer of plaster (Fig. 5).

These two sectors are located in the upper part of the Great Pyramid while the Exp135 sector is more eccentric. It is possible that this difference in the technique of applying the pictorial layers (with or without intermediary layer of a coating) may correspond to different construction phases, since the samples taken from the first two sectors correspond to the third construction phase and that the samples from the Exp 135 sector belong to phase 4.

On the other hand, upon observation, there is a difference in texture of the white pictorial layers depending on the sector to which the samples belong. In the samples of the Exp 135 sector, the white layer always applied under the black layer, is homogeneous and consists mainly of white transparent crystals. On the contrary, in the samples from sector 133, the white layer has a cream color and contains many aggregates of various colors. The other pictorial layers do not present any major differences between the sectors.

5.2. Support

The elementary analyzes of the support plaster of each sample have the same characteristics, whether the plaster belongs to the first or second application.

It generally consists of a matrix based on silicon and aluminum, accompanied by low and slightly variable concentrations of other elements, like sodium, magnesium, chlorine, potassium, calcium and iron. This composition corresponds to the montmorillonite silt already identified in Cahuachi in building construction materials such as adobe and unpainted plaster [20]. It acts as a binder for the layers of the coating. Large and medium inclusions of various kinds are added to this clay matrix: silica (quartz), calcium-sodium or potassium, calcium, sodium aluminosilicates (probably feldspars or micas), iron oxides as hematite $\alpha\text{-Fe}_2\text{O}_3$, maghemite $\gamma\text{-Fe}_2\text{O}_3$ and magnetite Fe_3O_4 .

5.3. Green paint

The green paint was analyzed on three samples (01V, 02V, 08J), belonging to sector Exp 135, eccentric sector of the Great Pyramid. The grains in this paint are quite large (from 20 to 400 μm).

The SEM-EDS analysis shows for these layers the systematic presence of copper, sometimes associated with chlorine, sometimes with silicon. So, the detected compounds could be copper chloride (paratacamite, clinoatacamite, atacamite) or copper silicate (chrysocolla) or a mixture of these compounds.

The Raman spectroscopy analysis completes these first results by highlighting three distinct minerals (Fig. 8): the paratacamite (119, 142, 364, 421, 511 cm^{-1}) [21], the malachite (153, 177, 216, 356, 432 cm^{-1}) [22] and the chrysocolla (160, 194, 338, 410, 671 cm^{-1}) [23]. It is possible that these minerals may come from the same copper deposit.

Figure 6. Raman spectra obtained on three green grains distinct from the green paint in sample 02V. The purple spectrum corresponds to malachite, the blue spectrum to paratacamite and the dark blue spectrum to chrysocolla. Laser: 785 nm.

5.4 Red, yellow and purple paints

The elemental compositions of red, orange and yellow paints are similar.

The major presence of aluminum and silicon can correspond to clay or an aluminosilicate (feldspar). Other minor elements have been identified by EDS: Fe, Ca, S, Na, K, Mg, Cl, .

The presence of these elements, and in particular iron, may indicate that it is a clay more or less charged with iron oxides, such as goethite and hematite (Fig. 7) which are the source of the coloration. The detection of other elements points out the presence of other compounds in that colours, like anhydrite or gypsum, calcite, etc.

The colour of the pigments purple, red, is probably due to the presence of hematite but of different particle size.

Raman spectroscopy analysis of the 13V violet paint, for which the iron concentration is higher, revealed the presence of hematite as a major compound (Fig. 8).

5.5. Black paint

Elementary analysis of black paint samples shows a composition a bit similar to the reds and yellows: Al, Si, K, Na, S, Ca, Mg, Cl, Fe. The absence of manganese shows that manganese oxide is not the source of the black color. On the other hand, the black pigment could be a black iron oxide such as γ -Fe₂O₃ maghemite or magnetite Fe₃O₄. It could also be carbon black. For sample 06R, no iron oxide was identified in Raman spectroscopy, but graphite was identified on the black particles (1335, 1581, 2457, 2676, 3236 cm⁻¹) as well as quartz for many white transparent particles (205, 264, 355, 392 and 460, 806 cm⁻¹) (Fig. 9).

5.6. White paints

With regard to white paint, the study made it possible to distinguish two pigments of different nature. The first concerns the samples from the Exp 135 sector (06R, 09N, 11N) and consists mainly of silicon (Fig. 10.a): it is probably a siliceous material (quartz, flint, diatomite or celite?) but it was not identified precisely in Raman spectroscopy.

Also, few particles of andesine (Na, Ca)[Al(Si, Al)Si₂O₈] and of feldspar, such as sanidine (K,Na) [(Al,Si)Si₂O₈] were identified in Raman spectroscopy.

The second white pigment, found in sample 16N, could correspond to an aluminosilicate mixed with a little calcium sulphate. Iron was also identified and could be naturally present in this rock or come from neighboring red and yellow paints. These compounds were identified on two samples (16N and 17R) which belong to the Exp 133 sector (Fig. 10.b.).

All of the analyzes allowed us to draw up a list of pigments in the paint layer and the composition of the preparation layers present in the samples of wall paintings in Cahuachi (Table 1).

Table 1
Identified mineral materials.

Stratigraphy	Identification	Samples
Green paint	Paratacamite, malachite et chrysocolla	02V, 08J
Yellow paint	Yellow ocher	03J
Orange paint	Orange ocher (hematite and clay)	07R, 19R
Red paint	Red ocher (hematite and clay)	04R
Purple paint	Hematite and clay	13V
Black paint	Graphite, aluminosilicate and quartz	06R
Preparation/ white paint	White clay and calcium sulfate	16N, 17R
	Siliceous material	06R
Grey coating	Clay loam	All samples

Discussion

6.1 Origin of pigments

The samples from this study are among the few examples of murals on the south coast of Peru and are among the oldest in the region. Indeed, only D. Bonavia mentions the presence of murals on a site dated from the Early Horizon that has now disappeared [1].

The pigments were probably extracted from deposits close to the Nasca sites. Previous archaeological research has shown that mining was already been practiced during the Nasca era, notably Mina Primavera and the Mina Ballena (Fig. 1). Nasca people extracted hematite from Mina Primavera [24]. Excavations near the Ballena mine reveal the existence of mining from the Early Nasca to the Late Horizon. This site was occupied by small groups of miners for short periods of time, when they mined and extracted minerals from local deposits in the vicinity [25]. Given the quantity of mines or deposits in the lower part of the Andean foothills, relatively close to Cahuachi and other archaeological sites, it is possible that other sites had the same function as that of La Ballena. The proximity of these deposits has certainly facilitated the use of pigments by pre-Hispanic painters as they still are today for traditional Nasca ceramists.

According to the results, the red and yellow paintings of Cahuachi were probably made with earth rich in iron oxides: hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$). Indeed, sources of hematite and red and yellow ocher are abundant in the Nasca region. Sources of limonite, hematite and ferruginous clays are known near the city of Ica [15, 16], as well as sedimentary rocks intensely colored by iron oxides in the lower valley of Ica [26]. Further to the south, ochres and iron oxides are abundant in and around the Marcona mine, one of the largest deposits of iron on the coast [27, 28, 18]. Between Ica and Marcona, the Nasca region has its own deposits. In fact, in the north of the department, there are significant deposits of

ferrous minerals including hematite and limonite [26]. It is in the north of the Ingenio valley, at the foot of the first Andean mountains that is located the Mina Primavera, a hematite mine, which has been exploited since the Nasca era [24]. Thus, it seems that ancient civilizations were able to easily obtain red and yellow pigments thanks to the abundance of ochres and iron oxides in the region.

On the other hand, the analysis of samples of Cahuachi green paint shows that painters used several copper compounds such as paratacamite, malachite, chrysocolla. Indeed, copper ores are abundant on the coast, present in the form of carbonates, silicates and chlorides, and are sometimes intimately mixed, as it is the case in the mines of Canza and Tingue (Ica) [15] (Fig. 1). The presence of this type of composite deposits in the region could explain why thanks to the Raman analysis we identified three distinct minerals for the same fragment of paint. Other copper deposits with their secondary minerals are known near Pisco (Lily Mine, Mina Eliana, Cincocruces), Marcona (Mina Justa) and between Ica and Palpa (Proyecto Chavez) [29]. But the deposits of copper ores are concentrated in particular in the “copper fringe south of the Pacific slope”, which borders the basin of the Rio Grande de Nasca. There, one finds green copper minerals (malachite, atacamite, clinoatacamite, paratacamite, chrysocolla) which could be used as pigments once reduced to powder [17, 26].

Black paint could not be identified precisely: the composition of the material remains complex. The black coloration may be due to the presence of graphite or carbon black identified on the black particles. It could be graphite mixed with a rock composed of many chemical elements but sources of graphite are not known in the Nasca region. This rock is reminiscent of the reference black stone used by the Nasca ceramist as a black pigment: a complex of quartz, feldspar, clay and hematite.

Finally, the analyses made it possible to differentiate two types of white paint: a siliceous material and an alumino-silicate - probably a clay - mixed with calcium sulphate. The latter could be present naturally in the extracted white rock or be added a posteriori as filler. On the southern coast, calcium sulphate can be found in the form of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and anhydrite CaSO_4 in several places, in particular between Pisco and Ica [15, 16].

Among the pigments identified, several of them were used by the other pre-Hispanic cultures of the coast, in particular red and yellow ochres, hematite and goethite as well as copper green pigments (chlorides, carbonates, copper silicates).

The nature of black and white pigments differs more depending on the region and cultures. With regard to black paint, the use of graphite is only mentioned once on the site of Chornancap (700–1532 AD) [1] and magnetite was identified at Pañamarca (500–900 AD) [30], both on the far north coast. For white paints, clay has been used several times alone or with a filler, notably at Huaca de la Luna (north coast, Early Intermediate Period, Middle Horizon) and Tambo Colorado (south coast, Late Intermediate Period), but no results have demonstrated the use of a siliceous material [1, 31]. This pigment could then be considered characteristic of Cahuachi.

6.2 Technical considerations

This preliminary study, carried out on the Cahuachi murals, allowed to identify some of the main materials used (Table 1) by the Nasca painters but also to partly understand the pictorial techniques used to adorn the buildings of Cahuachi.

The first observations of the fragments seem to confirm the hypothesis of a painting *a secco* (on dry support): the low calcium content in the coating and the poor adhesion of the layers allow ruling out the hypothesis of the fresco. However, the FTIR analyses did not reveal the presence of any organic binders. On the Mochica site the Huaca de la Luna, decorated with paintings dating from the 3rd to the 8th century AD, analyses of binders revealed the use of cactus gum and another binder of unprecised animal origin [32]. In that case, the technique used was a distemper. For the moment, this is the only identification of a binder in the murals roughly contemporary with those of Cahuachi, but this is a site on the north coast and it is difficult to say whether the technical knowledge could have been similar or not.

Based on the observations and analytical results, the preparation of the support wall was simple. In most cases, the walls were simply smoothed using the same silt material used for the adobe, then the paint was applied directly. However, five fragments (06R, 09N, 11N, 16N, 17R) from the upper and lower parts of the Great Pyramid have a white coating which was applied to the surface of the walls before painting. Finally, in sector Y08 Exp 135 (phase 4), fragments attest to the making of incisions inscribed on the painted walls. These incisions seem to constitute a first engraved sketch. It generally delimits two distinct colors which will be applied afterwards. On these incisions black lines were applied, covering or underlining them. The color palette of the paintings in sector 135 seems to be as varied as that of contemporary cultures in the north or that of the Inca paintings of the southern coast.

Finally, the study of the fragments of mural painting highlighted differences according to the areas of discovery of the samples (Table 2). Thus, the nature of the white coating constitutes a distinctive feature. Indeed, on the walls at the feet of the pyramid (part 4), the white coating used is a compound with a high silica content, perhaps a hydrated silicate, while the white coating used for the upper part (phase 3) is based on clay and gypsum. This difference may be due to the depletion of white clay resources or change in painting materials due maybe to their properties.

In addition, some paints were repainted with a coat of plaster that completely covered the old paint. These repaints are present only on two fragments (samples 17R, 19R) of the sectors located in the upper part of the pyramid (Exp133 and 138). These areas were probably the first to be painted during construction phase 3, and were subsequently repainted.

Finally, there is a limited use of colors for the upper sectors, but the very small number of fragments discovered in sectors Exp133 and 138 does not allow us to know the number of colors originally used. According to the few fragments found, the palette consists of red (sector Y08 Exp138), yellow and black (sector Y08 Exp133). If we consider the dating of the paintings, with those of the Exp138 and Exp133 sectors older than the paintings of the Exp135 sector, it seems that the color palette has been enriched over time.

Table 2
Major differences observed on the murals in each sector.

Distinctive features	Phase 3		Phase 4
		Y08 Exp133 16N, 17R, 18J	Y08 Exp138 19R
Repaint with coating layer	Yes	Yes	No
White coating	Clay and gypsum	Clay and gypsum	Siliceous material
Colors	Red, yellow, black	Red	Black, wight, red, orange, yellow, green, purple
Identified pigments	Red ocher, unidentified black	Red ocher	Graphite, white siliceous material, red ocher, orange ocher, yellow ocher, paratacamite + malachite + chrysocolla, hematite

We also note another difference among the pigments composition: in fact, some paint samples contain calcium sulphate in small quantities (reds 17R, blacks 16N, 10N, yellows 8J, 3J, whites 16N, 17R). This compound can be found in certain paintings in phases 3 and 4, located in the upper part of the pyramid (Exp 133) and in the paintings in the lower part (Exp 135). Gypsum or anhydrite are both natural calcium sulfates, which may have been added by the painter as a filler or as a "diluent" to obtain light tones, but they can also naturally occur in the deposits of minerals that served as pigment.

During the 2007 excavation campaign, new pieces of painted walls (green, emerald green, blue, black, red, and brown) were discovered at the feet of building walls. Among these fragments, two colors appear for the first time: blue and brown. On the other hand, rags impregnated with paint were also discovered with the painted fragments fallen at the foot of the walls. They were probably used to paint the walls, like the large cotton pads (broquel) used to brush the walls in Pachacamac site [1, 32].

Conclusion

The present study showed the first approaches to characterization of Nasca wall paintings from the Early Intermediate Period, on the site of Cahuachi.

These paintings are among the most ancient found in South Peru. The studied fragments dated from the 3rd phase (from 0 to 250 AD) and 4th phase (from 250 to 400 AD) of occupation period show many similarities between them, concerning their stratigraphy and the majority of pigments. The pigments are

mostly originating from local resources like clays, iron oxides and copper minerals. However, the difference of composition of the white pigment between samples from respective constructive phases was observed on several samples and it may be therefore considered as a possible chronological marker. Also, copper minerals were found in green painting only from the 4th phase. The presence of copper minerals may be an additional marker, because up to now, we have found in the 3rd phase paintings only clays and iron oxides. This information needs to be further confirmed, exploring more widely the Cahuachi site or looking for painted plasters from future discoveries in South Peru.

Although the studied fragments are few, they constitute an important insight into the knowledge of pre-Columbian art in Peru in general and especially in wall painting history, because some already known examples of wall painting are remote from a geographical point of view, on the North or Central coast, or from a chronological point of view, being dated mostly from the Middle Horizon and Late intermediate Periods. The Cahuachi murals have similarities with the other pre-Hispanic murals known in Peru but they also have their particularities. For example, pigments of hematite, ochers and copper chloride or carbonate have been identified in many other sites. On the other hand, we recognize a greater variability in the use of white and black pigments according to the sites. For instance, the white pigment could be limestone (Tucume, Huaca Licapa, Pañamarca, Chornancap and La Mayanga in north coast), clay with lime (Tambo Colorado in south coast), or clay with gypsum like in the Huaca de la Luna (north coast) and Cahuachi. In addition, another white pigment was identified only in Cahuachi: a siliceous material. The black pigments used in pre-Columbian paintings could be: charcoal mixed both with quartz and feldspars (Huaca de la Luna), magnetite (Pañamarca), graphite and chalcocyanite (Chornancap), pyrolusite (La Mayanga), hematite (Pachacamac) and graphite with quartz as appears to be the case in Cahuachi. The observations and analyses made in this study give first elements of knowledge on Cahuachi paint materials and techniques, but they need to be completed in the future by new discoveries to give a more complete view on the ancient wall painting art of the south coast of Peru.

Declarations

Availability of data and material

Please contact the corresponding author for reasonable data requests.

Competing interests

There are no financial and non-financial competing interests.

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Authors' contributions

Nathalie Boucherie participated in the sampling, carried out the analyses by Raman spectroscopy and wrote the text; Nathalie Pingaud prepared and analysed the cross-sections and contributed to the revision of the manuscript; Witold Nowik supervised the work, discussed the obtained results, structured and revised the manuscript.

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Figures

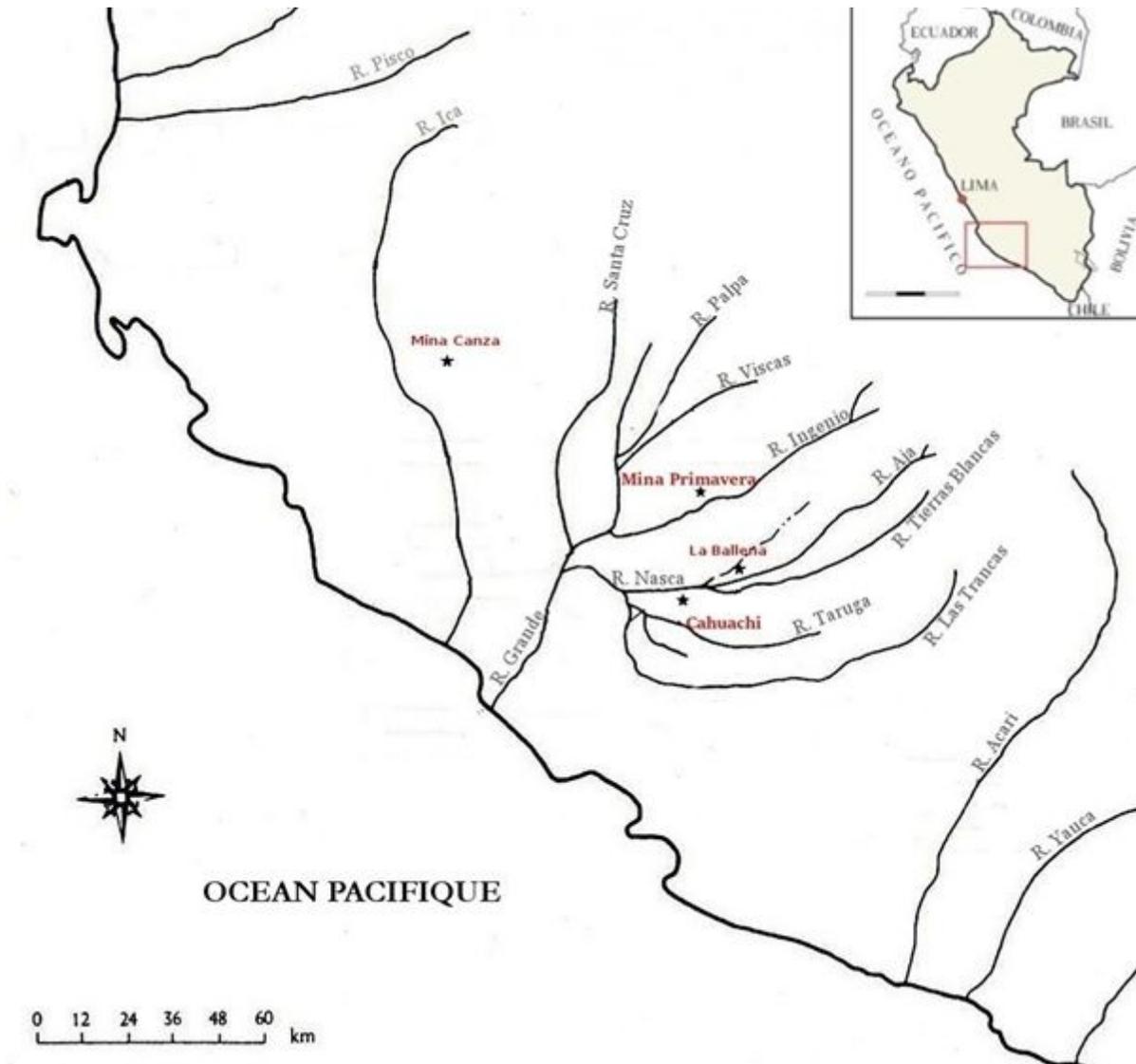


Figure 1

Map of the southern coast of Peru with the site of Cahuachi and the Primavera, La Ballena and Canza mines. According to [8].



Figure 2

a. Fragments of wall paintings discovered in the lower part of the Great Pyramid. b. A corner of the wall in sector Y2 Exp136 with the evident presence of a thick layer of plaster on the right wall and a thinner plaster showing adobes on the left. Photos: N. Boucherie.

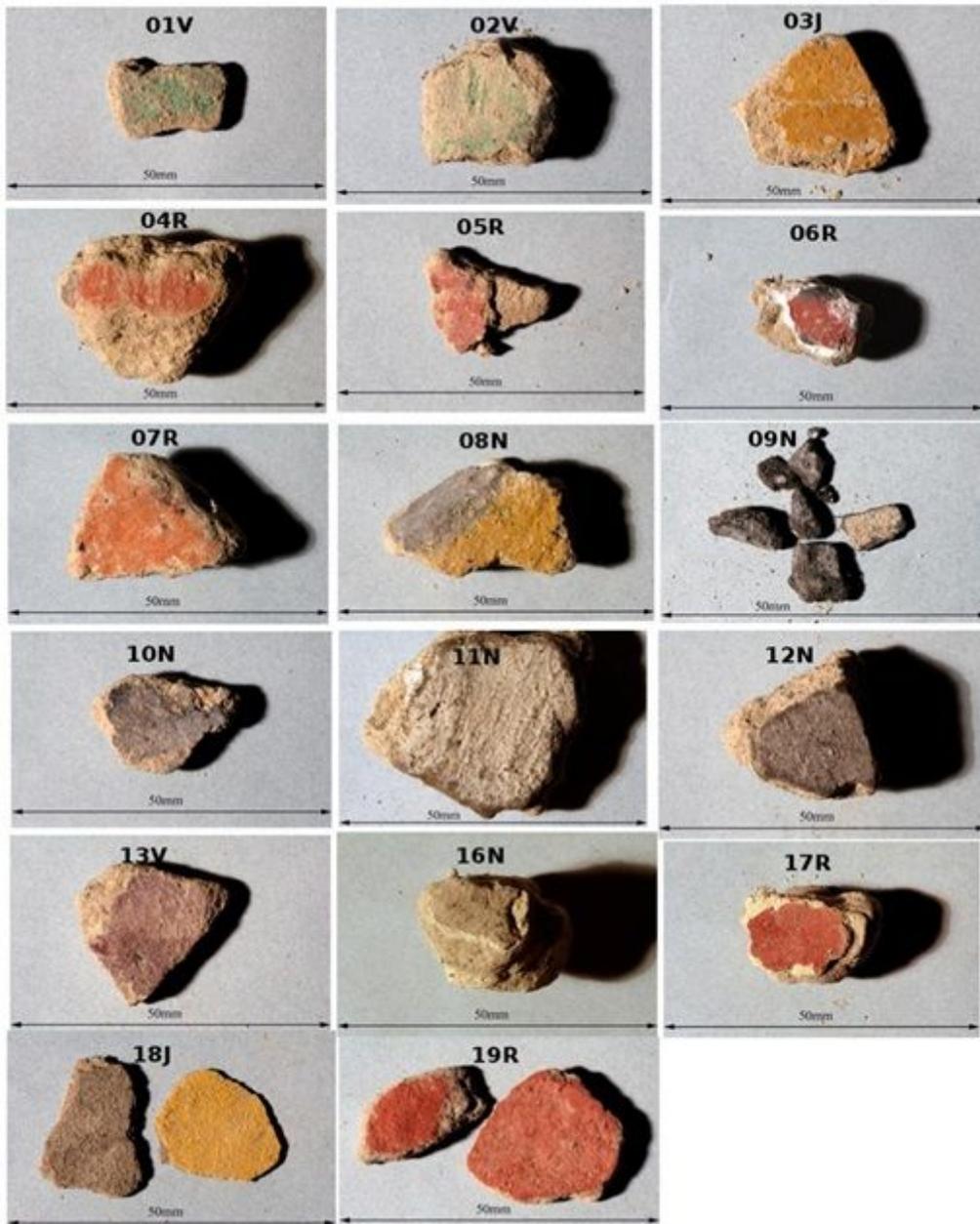


Figure 3

Samples of mural painting taken at Cahuachi, Nasca. Photos: Dominique Bouchardon (LRMH).

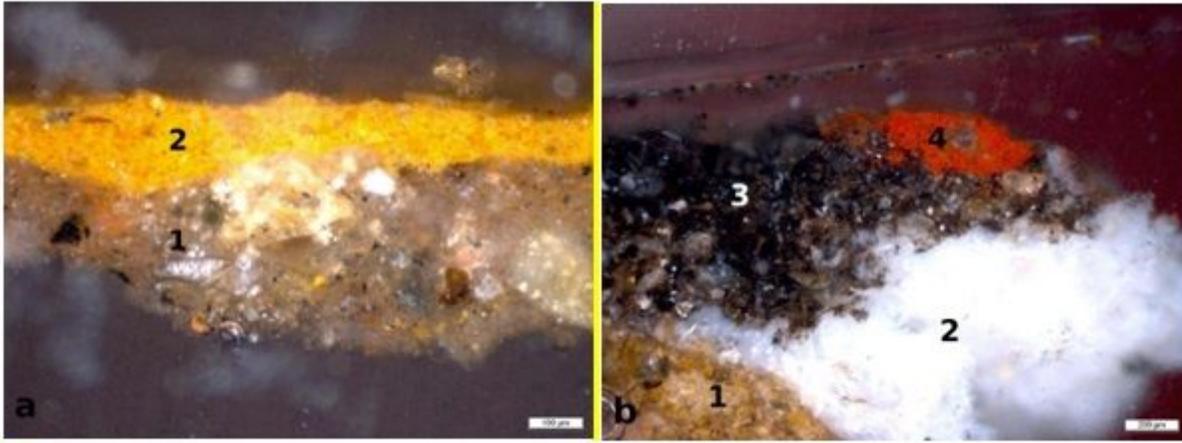


Figure 4

a. Cross-section of the 03J yellow paint sample with a thick yellow pictorial layer (1) applied on the coating (2). b. Sample 06R, with a red pictorial layer (1) on a black pictorial layer (2), itself on a white layer (3).

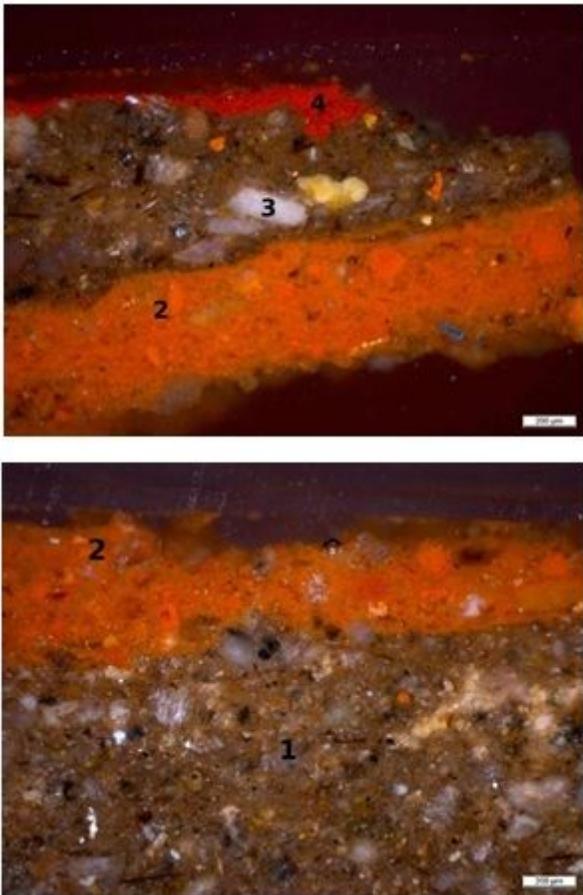


Figure 5

Sample 19R, sector Y8 Exp 133. For reasons of cleavage between the layers, the complete stratigraphy was reconstructed using two complementary cross-sections. They display the application to a coating (1) of a thick orange-red layer (2) to which a layer of coating (3) has been applied again and then a thin red layer (4).

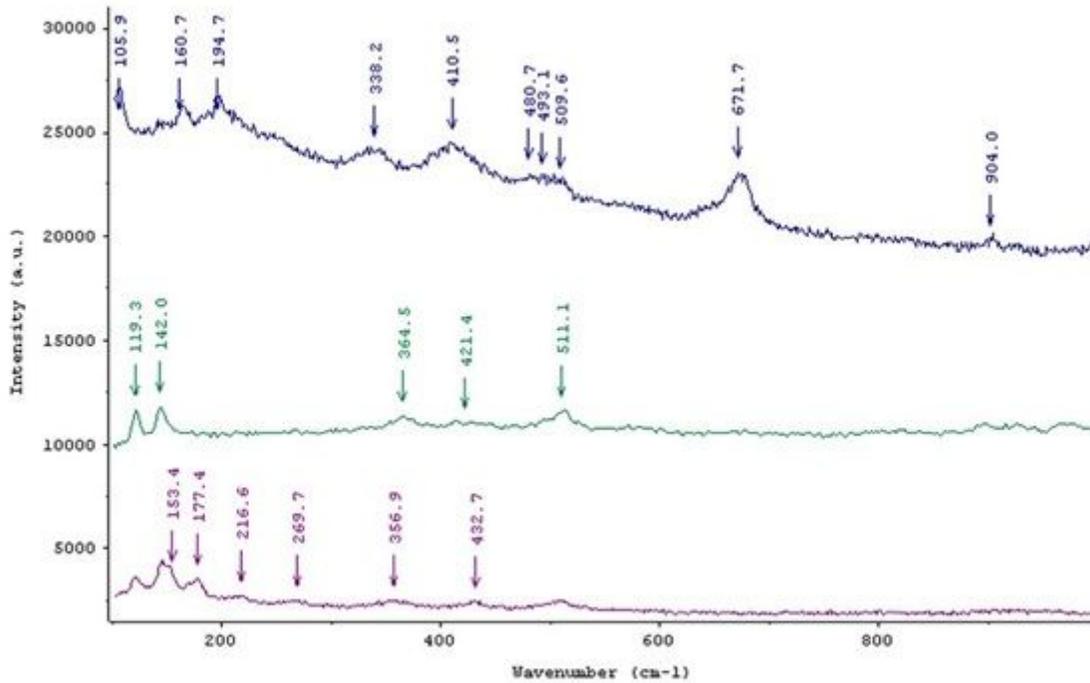


Figure 6

Raman spectra obtained on three green grains distinct from the green paint in sample 02V. The purple spectrum corresponds to malachite, the blue spectrum to paratacamite and the dark blue spectrum to chrysocolla. Laser: 785 nm.

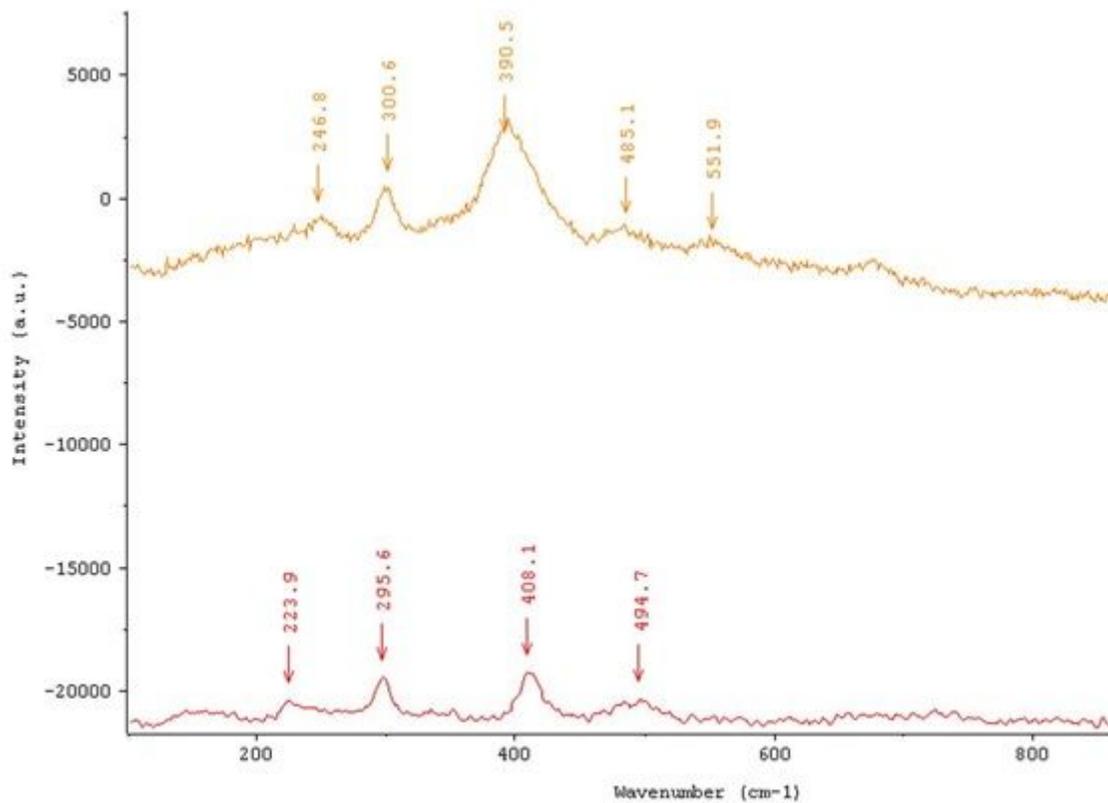


Figure 7

Raman spectra obtained on a red grain and a yellow grain of yellow paint 03J: orange spectrum corresponds to goethite, red to hematite, laser: 532 nm.

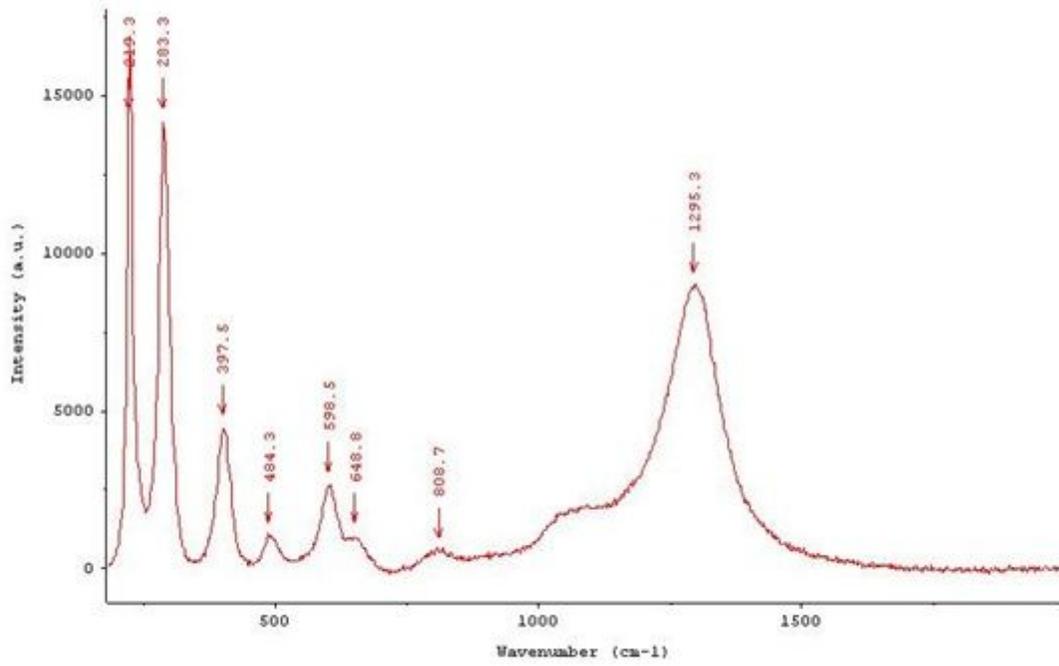


Figure 8

Raman spectrum obtained on the red pictorial layer of the 13V sample and corresponding to the hematite, laser: 785 nm.

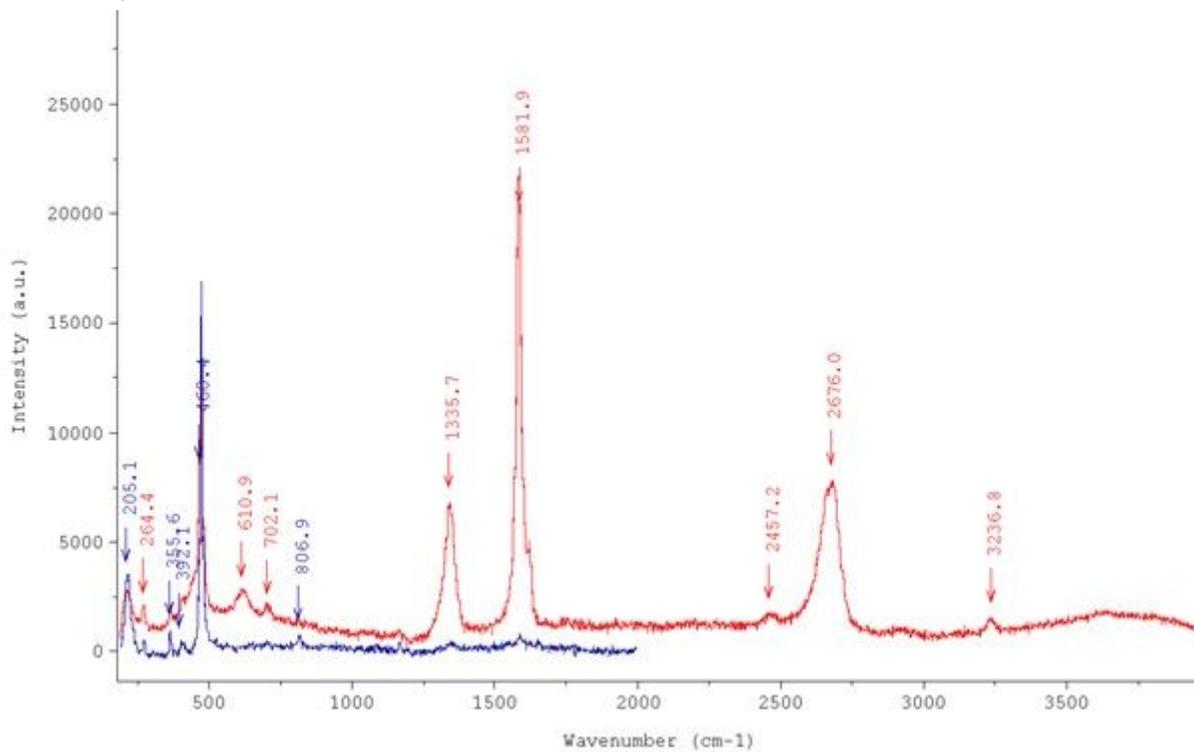


Figure 9

Raman spectrum obtained on the black spots of black paint 06R. Red spectrum corresponds to graphite, laser 514 nm. Blue spectrum corresponds to quartz, laser 785 nm.

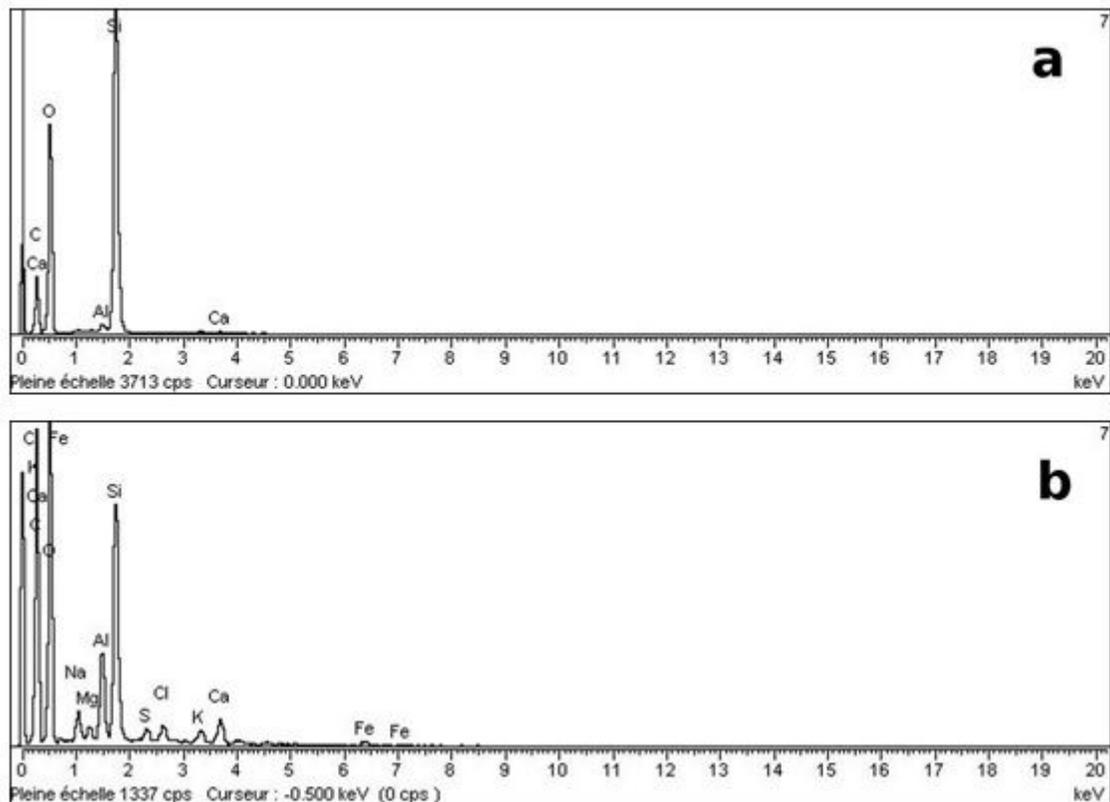


Figure 10

a. Typical EDS spectrum of the white layer of sample 06R. b. Typical EDS spectrum of the white layer of the 16N sample.

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