



# The compositional and mineralogical analysis of fired pigments in Nasca pottery from Cahuachi (Peru) by the combined use of the portable PIXE-alpha and portable XRD techniques

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## ABSTRACT

An analytical protocol based on the combined use of the portable PIXE-alpha (Particle Induced X-ray Emission) and XRD (X-ray Diffraction) non destructive techniques developed at the LANDIS laboratory (Laboratorio di Analisi Non Distruttive) of the INFN-CNR (Istituto Nazionale di Fisica Nucleare-Consiglio Nazionale delle Ricerche) in Catania (Italy), was applied for the characterisation of the surface paints of some archaeological fragments of Nasca pottery from the Ceremonial Centre of Cahuachi in Southern Peru.

Measurements were carried out on the black, white, red, orange and grey pigments; quantitative information on the chemical composition as well as on the mineralogical phases present on the paints were obtained.

Results allowed to make some considerations about the materials and the manufacturing technique used to realise such fired pigments.

It should be noted that during firing the precursor minerals composing the pigments undergo a phase transformation and their identification presents some difficulties.

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## 1. Introduction

The analysis of ancient mineral pigments provides information to archaeologists both on the technology and on the materials used in antiquity to realise artworks; moreover analytical results can be used to evidence the differences in the artistic and cultural evolution that occurred during the time at different geographical regions.

The polychrome Nasca pottery, realised at the Ica and Nasca valley in south coastal Peru from the 100 B.C. to A.D. 650, represents one of the most interesting cases in which different minerals and a well established technology were used to produce a large variety of colour shades [1,2].

The ceramic production of the Nasca, with particular reference to iconographical aspects and provenance analysis, has been largely investigated in the past [3–5]. However, only a few analyses, performed by using destructive methods, concern the chemical composition of the fired pigments [6].

A non-destructive approach and the use of portable instruments for determining both the chemical and the mineralogical composition of pigments, should be mandatory when a large number of samples

must be investigated or when the analysis refers with well preserved artworks that can not be moved, due to their artistic and historical value, to the laboratories.

In the last years at the LANDIS laboratory (Laboratorio di Analisi Non Distruttive) of the LNS-INFN (Laboratori Nazionali del Sud-Istituto Nazionale di Fisica Nucleare) and IBAM-CNR (Istituto per i Beni Archeologici e Monumentali-Consiglio Nazionale delle Ricerche) of Catania (Italy) many efforts have been dedicated in order to realise innovative portable PIXE-alpha (Particle Induced X-ray Emission) and XRD (X-ray Diffraction) systems for in situ applications in the cultural heritage field [7–9].

Recently, these systems have been combined for the quantitative investigation of ancient mineral pigments [10].

The PIXE-alpha technique, due to its analytical depth of a few microns, (about 15  $\mu\text{m}$  in a clay-based matrix as in the case of the Nasca pigments), is particularly suited for the elemental analysis of the painted surfaces. This way the investigation concerns mainly the pictorial layer and the substratum contribution is strongly reduced. In addition, the mineralogical nature of pigments can be investigated by the use of our portable XRD technique.

By combining results obtained by both non-destructive methods it is possible to quantitatively determine the paints composition.

In the present work the pigments present in some fragments of Nasca pottery from Cahuachi (Peru), have been analysed.

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The PIXE-alpha and XRD measurements focused on the chemical and mineralogical characterization of the different shades of white, black, red, orange and grey pigments.

The research has been performed within the scientific activities carried out by the ITACA mission (Italian mission of heritage Conservation and Archaeogeophysics) of IBAM-CNR in Peru. [11]

In view of a systematic *in situ* analysis of the polychrome Nasca artworks at Cahauchi, the present results allowed to evidence the potentiality and the limits of using the cited non-destructive techniques for the analysis of fired pigments.

## 2. Experimental: techniques and methods

The non-destructive analysis of ancient mineral pigments should be performed by using appropriate methods.

Fired pigments are painted on the pottery surface in a layer of about 20  $\mu\text{m}$  thickness or more, depending on the pottery typology [12,13]; however, variations down to a few microns can be observed even if they usually can be attributed to irregularities of the painted surface [14].

In order to minimise the substratum contribution in the experimental data, measurements must be performed by using techniques with a sharp analytical depth. Moreover, pigments are minerals and the use of elemental techniques can not suffice for a correct identification; the chemical characterization of the pigments should be combined with the mineralogical analysis.

Finally, the fired pigments (like in the case of the Nasca pottery) change their mineralogical phases during firing and the resulting minerals can not be the same as the original ones [13,15]. In this case data interpretation should be performed with particular attention in order to typify correctly the precursor materials.

Recently, many efforts have been made at the LANDIS laboratory, in order to develop complementary non-destructive methods for performing the quantitative analysis of ancient pigments. An analytical protocol based on the combined use of the portable PIXE-alpha and portable XRD systems was developed and used in some archaeometrical applications [10].

Such systems were used for the analysis of the Nasca pigments of the present paper.

The portable PIXE-alpha system [7] consists of a low activity  $^{210}\text{Po}$  radioactive source emitting alpha particles of 5 MeV energy coupled to a 20  $\text{mm}^2$  active area SDD detector with 138 eV energy resolution at the reference line of 5.9 keV. The spot size of the alpha beam on the irradiated sample is 7 mm diameter allowing the analysis of small dimension samples. Finally, the presence of an helium flux during the measurement allows to detect the low energy X-rays up to about 1 keV.

At the present time the polonium PIXE source is entirely developed and realised at the LAB-alpha facility of the LNS-INFN.

The portable PIXE-alpha system is particularly suited to perform the quantitative chemical analysis of the elements composing painted surfaces. As mentioned above, its analytical depth in a clay-based matrix is limited to about 15  $\mu\text{m}$  (such a value was estimated by means of SRIM calculation). Typical measurement time is about 30 min. The spectra detected by the portable PIXE-alpha system can be quantified by using the standard GUPIX code [16].

The portable XRD system was realised by installing on a commercial goniometric system a microfocus X-ray source equipped with modular X-ray optics and a Si-PIN detector, placed in a theta-theta geometry [8,9]. The  $2\theta$  angular range allowed to be investigated is  $24^\circ$ – $140^\circ$ .

The X-ray source consists of a Fe anode microfocus tube (produced by the German IFG) with a 50  $\mu\text{m}$  spot sizes; it is coupled to a polycapillary semi-lens that allows to obtain a parallel X-ray beam with high intensity and a reduced divergence of  $0.26^\circ$ . Such a X-ray source allows to operate the diffraction of the samples with an angular

resolution of  $0.12^\circ$  (that can be compared with the ones of laboratory XRD systems) and rapid measurement time (40–60 min) [9]. However, due to the low power of the compact X-ray microfocus source (only 10 W), such a system can be used mainly to determine the major phases of the sample under investigation, being the detection limit about 2–4% (it was estimated by using a reference standard composed of quartz and calcite).

The X-ray spot emitted by the modular polycapillary semilens is 6 mm diameter in the normal direction. However, the illuminated area at the smallest diffraction angles is significantly larger (about 2 cm) limiting the possibility of performing analysis of small dimension samples.

Recently a new modular slightly-focusing polycapillary optics was added to the portable XRD system; the spot size at the normal direction is limited 100  $\mu\text{m}$ . The new optics allows the analysis of small dimension samples (up to 5 mm) even if measurement time is longer (about 2 h).

The detection of the diffracted X-rays is performed by using a 25  $\text{mm}^2$  active area Si-Pin detector (190 eV energy resolution) equipped with a 1 mm wide slit.

The portable XRD has been successfully characterised to be used in the mineralogical investigation of the pigments most used in the antiquity [9]. Moreover, thanks to its goniometric geometry, the samples can be placed externally to the system and whole artworks (like frescoes or wall paintings) can be easily analysed *in situ*, without the necessity to perform destructive sampling from surfaces.

The analytical protocol used for the chemical and mineralogical characterization of the pigments is detailed in ref. [10]. It is briefly summarised in the following.

A preliminary PIXE-alpha measurement on a unknown sample allows to qualitatively identify its chemical elements (starting from Na).

Since the matrix composition (generally composed by the light elements not detectable by the PIXE-alpha system) is not known, the quantitative analysis is not allowed.

Then, a XRD measurement, in the same position of the previous PIXE-alpha one, is performed. The search/match of the obtained diffraction pattern is carried out by limiting the analysis to those phases containing the chemical elements already evidenced by PIXE-alpha. Such a filter allows to reduce the search only to a few phases, limiting the uncertainties during the identification of the minerals.

Finally, the XRD data are used to estimate the matrix composition of the pigments that, in turn, can be used to quantify the PIXE-alpha spectra.

The analytical protocol was tested by measuring a reference material constituted by 50% of  $\text{SiO}_2$  and 50% of  $\text{CaSO}_4$  [10]. Fig. 1 shows the PIXE-alpha and the XRD spectra.

The PIXE spectrum clearly evidences the presence of Si, S and Ca characterising quartz and gypsum. Oxygen is not detectable by PIXE. The subsequent XRD measurement allows to identify the mineralogical phases (quartz and gypsum as expected) and to establish the presence of light elements (oxygen) to be used, with the correct stoichiometry, in the quantification of the PIXE spectrum. The final GUPIX calculation of the PIXE measurement resulted  $50.9 \pm 3\%$  for  $\text{SiO}_2$  and  $48.3 \pm 4\%$  for  $\text{CaSO}_4$ .

## 3. Materials and analytical results

The different pigments of Nasca pottery fragments, analysed by combining the portable PIXE-alpha and XRD non destructive techniques, are shown in Fig. 2.

The elemental composition of the pigments was obtained by the PIXE-alpha measurements.

In all the samples the presence of major Al and Si, minor Mg as well as the presence of K, Ca and minor Ti was detected.

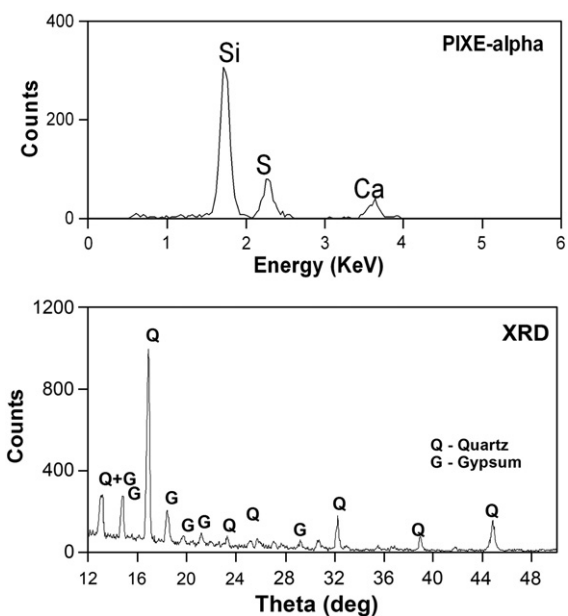


Fig. 1. The PIXE-alpha spectrum and the XRD pattern obtained by a quartz-gypsum reference material.

The presence of these elements, typically composing clay pastes, can be attributed to the manufacturing technique [1,2]. In fact, as already established by other authors, the Nasca introduced the thick slip paints technology made by mixing the finely ground mineral pigments to a fine suspension of clays; these slip were applied before firing in order to ensure their adherence with the pottery surface [1,2]. However, irregular thickness or in homogeneities on the painted layer can not be excluded especially for buried objects.

In all the samples, the white pigments are characterised by an high Ca content; the black ones by Fe and minor Mn; the red, orange and grey by an high Fe content.

Fig. 3 shows the PIXE-alpha spectrum of a white (M3) and of a red (M1) pigment.

The XRD patterns obtained in the subsequent measurements (performed on the same positions of the PIXE-alpha ones) were analysed using the PIXE-alpha qualitative data as chemical filter in the phases recognition. This approach allowed to significantly reduce the number of phases to be investigated in the search/match procedure, strongly reducing the possibility of erroneous attribution.

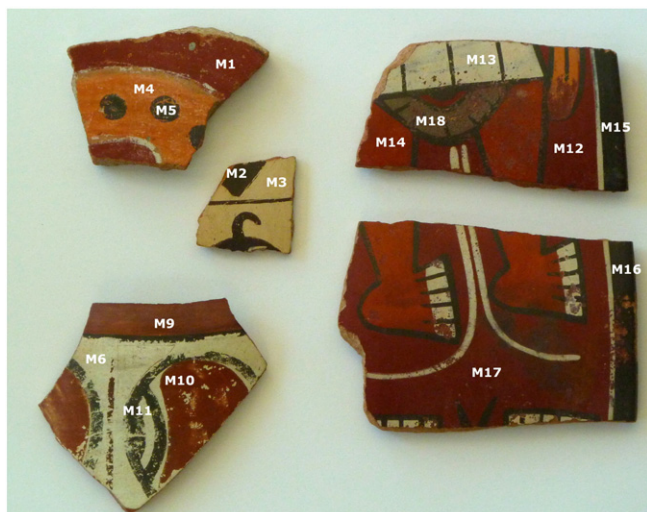


Fig. 2. The investigated pigments present on the Nasca fragment from Cahuachi (Peru). The position of the PIXE-alpha and XRD analyses is indicated.

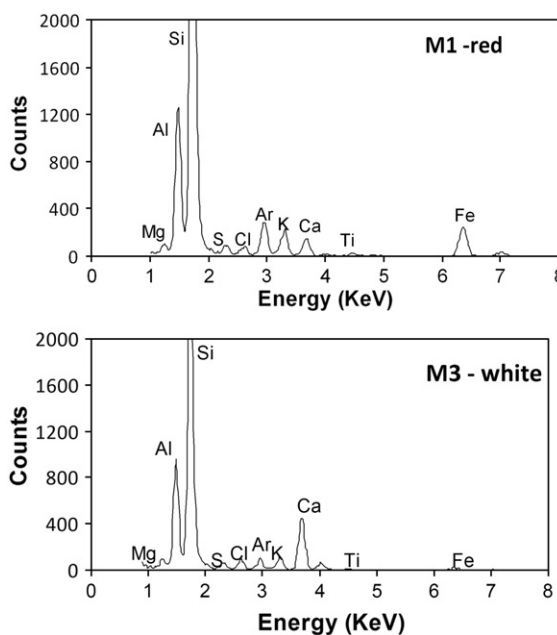


Fig. 3. The PIXE-alpha spectrum of a red and of a white pigment. The latter is characterised by an high calcium content; the red by the presence of iron.

Calcium was the main component characterising the white pigments. Gehlenite was systematically present in the XRD data; it forms completely at 850–900 °C by firing a mixture of calcite and clays [13,17]. A comparison of the diffraction pattern of M3, M6 and M13 samples is shown in Fig. 4.

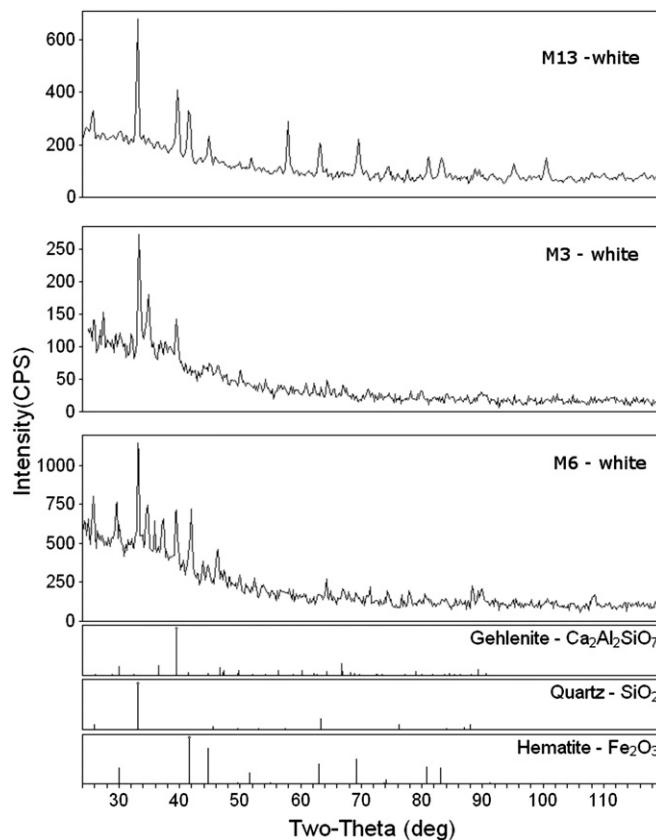


Fig. 4. Diffraction patterns of the white pigments. Gehlenite is present and suggests the use of calcite as precursor mineral. Hematite is present in the M13 sample.

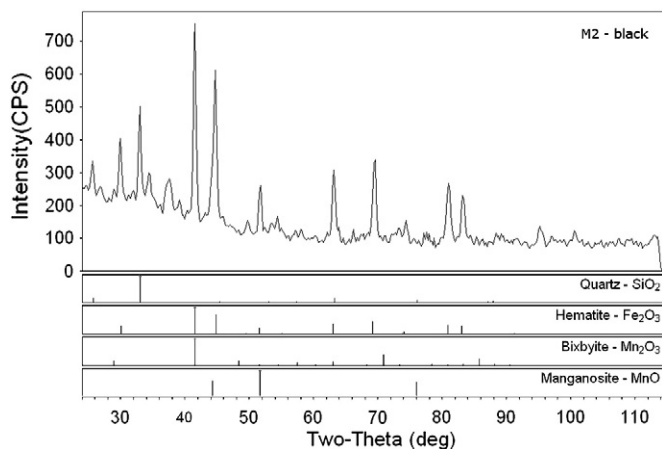


Fig. 5. Diffraction patterns of a black pigment. Hematite and Mn oxides are evidenced on the data.

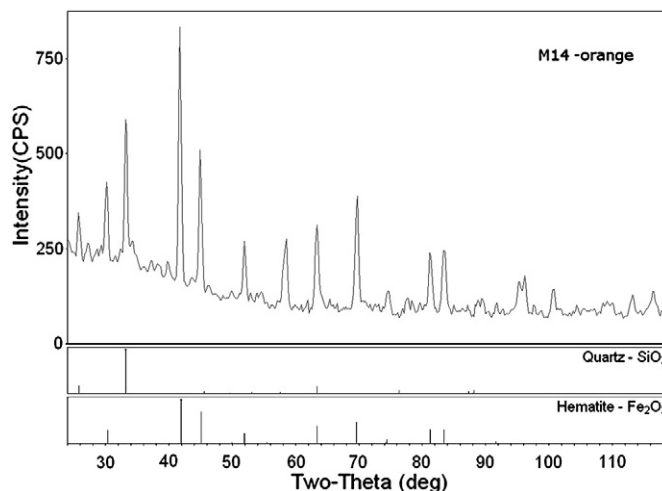


Fig. 7. Diffraction pattern of the orange pigment.

Such a mineral was observed in the analysis of similar fired white paints of pottery from the Aguada culture (Argentina) [13].

It should be evidenced that the above estimation of the firing temperature must be considered only qualitative in the case of our portable XRD. As mentioned in the previous section, our instrument is able to detect mainly the major phases; consequently the coexistence of gehlenite with minor phases of calcium minerals at lower temperature (like calcium oxides or carbonates) can not be detected. Also, higher firing temperature can not be a priori excluded.

Black pigments (M2, M1, M5, M15 and M16) characterised in the PIXE-alpha spectra by the presence of Fe and Mn, are composed of hematite and minor Mn oxides. The latter probably induce the dark

shade to the pigment. The diffraction pattern of a black (M2) is shown in Fig. 5; the overlap between some diffraction lines of the Mn oxides to the ones of quartz and hematite makes the mineralogical identification difficult.

Red paints (M1, M9, M10, M1 and M17) as well as orange pigments (M4 and M14) and grey pigment (M18) are clearly characterised by hematite. The diffraction patterns are shown in Figs. 6 and 7.

The extensive use of iron oxides for producing pigments was already established during the Nasca period [18].

However the identification of the original colouring minerals is difficult to be performed in the fired pigments. In fact, as clearly evidenced in ref. [15], most of the iron oxides used in antiquity for producing pigments change their mineralogical phase to hematite during firing.

Red paints were most probably realised by using a red ochre; orange pigment by the use of goethite or jarosite. In fact these latter oxides maintain a yellowish/red colour when they are fired mixed with clays below 900 °C [15].

Finally, the XRD analysis of the grey pigment (M18) showed the presence of both hematite and gehlenite. The experimental diffraction pattern is shown in Fig. 8. The use of the specular hematite (in this case mixed with calcite) have been already cited as the mineral used by the Nasca for producing their grey and light blue pigments in the slip paints [1,2].

The mineralogical phases identified by the XRD analysis were used to construct the matrix needed to perform the quantitative

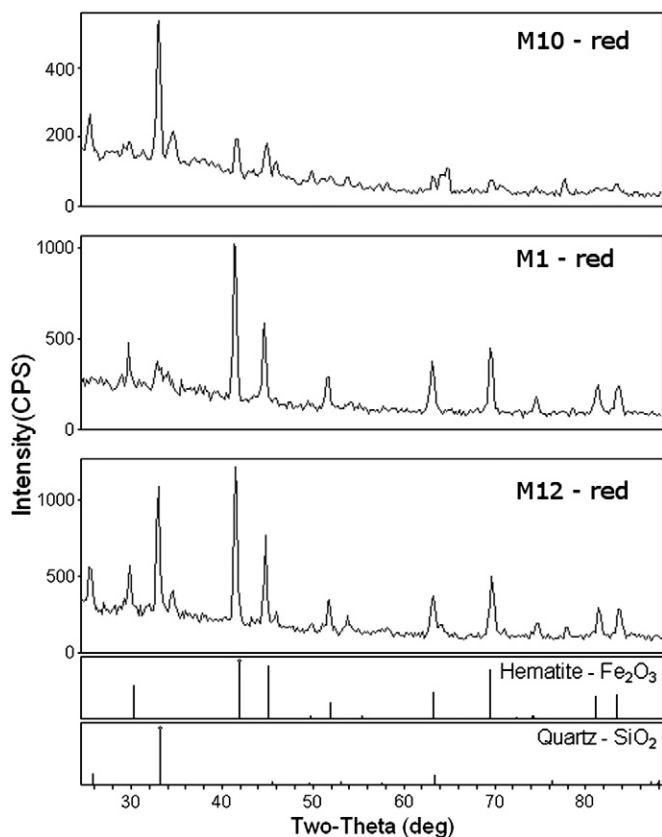


Fig. 6. Diffraction patterns of the red pigments.

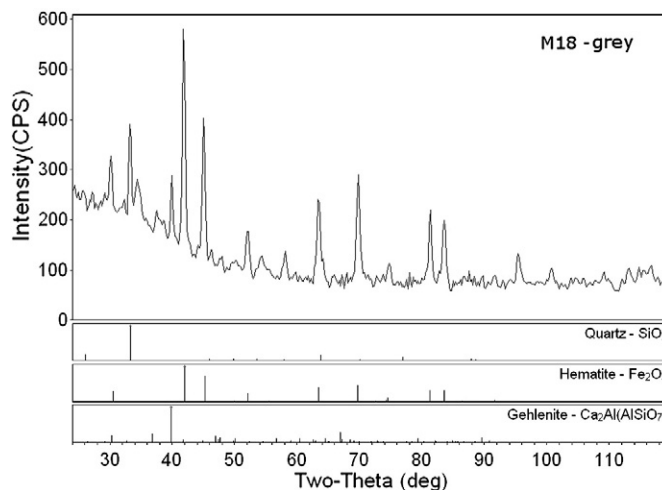


Fig. 8. The diffraction pattern of the grey pigment.

**Table 1**

Quantitative data of the analysed pigments. Errors are about 5–10%.

Sample	Pigment	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>
M2	Black	9.8	28.5	3.2	2.1	5.2		4.3	35.5
M5	Black	13.1	36.7	1.2	2.0	4.3	0.5	3.5	34.6
M11	Black	10.0	31.6	1.8	1.3	7.7	0.6	3.4	35.6
M15	Black	10.1	29.9	1.8	2.5	3.6	0.3	2.6	39.3
M16	Black	11.0	30.1	3.5	2.0	5.4	0.3	2.8	37.2
M18	Grey	13.4	35.7	2.7	1.9	7.2	0.4		28.3
M14	Orange	14.2	48.9	1.4	3.5	4.6	1.1		16.2
M1	Red	13.0	46.0	1.2	2.5	2.5	0.9		32
M9	Red	12.3	44.8	1.5	2.1	7.0	0.8		24.4
M10	Red	19.2	43.4	1.0	2.5	5.8	0.4		7.8
M12	Red	9.8	31.1	1.2	2.1	3.5	1.4		38.7
M17	Red	8.4	25.5	4.8	1.7	6.3	1.3		44.8
M3	White	16.6	51.0	1.7	2.6	17.6			5.1
M6	White	16.4	47.2	0.9	1.3	19.1	0.6		5.4
M13	White	14.5	44.6	1.3	2.0	9.6	0.7		6.0

analysis of the PIXE measurements. Calculation has been performed by using the GUPIX code [16]. Results are reported as oxides in Table 1; since the investigate samples are fired this hypothesis can be considered a working approximation. The errors on the concentrations are about 5–10% for the major elements. They are mainly due to the counting statistics and to the fitting procedure. Mg and Na were detected but, due to the large errors, were not reported in the table.

#### 4. Conclusions

The combined use of the non destructive and portable PIXE-alpha and XRD techniques of the LANDIS laboratory, was applied for the chemical and mineralogical investigation of the fired pigments present on the surface of some Nasca fragments from Chauachi (Peru).

Results allowed a chemical and mineralogical characterization of different pigments – white, red, black, orange and grey – present in the investigated fragments. Moreover, by combining PIXE and XRD results, a quantitative analysis of the paints was possible.

White pigments were characterised by gehlenite, that forms by firing calcite mixed with clays. A systematic analysis of the white produced during the Nasca period is necessary in order to assess the use of other white pigments (mainly kaolin as suggested in previous works); Black pigments were characterised by Mn and Fe minerals; red, orange and grey by iron oxides (they are present as hematite after the firing).

The analytical results evidenced the potentiality of using portable non destructive instruments for performing a systematic investigation in situ of the fired pigments in Nasca artworks. Limits (mainly due to the technology used to realise the fired pigments) have been also discussed in the text.

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