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Archaeological pottery from Nasca culture studied by Raman and Mössbauer spectroscopy combined with X-ray diffraction

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ABSTRACT

In the present paper, we report on a study of archaeological fragments from Nasca ceramics using Raman and Mössbauer spectroscopy combined with X-ray diffraction (XRD). By combining results obtained by these methods it is possible to quantitatively determine the paints composition, temperature and environment during the firing. The samples were collected from the Ceremonial Centre of Cahuachi in Southern coast of Peru. Raman spectroscopy allows us to determine the composition of the different pigments used in the preparation of Nasca ceramic. The results show that the composition of the white pigments is formed by rutile and anatase while the black and red pigments are formed by amorphous carbon and hematite, respectively. The Mössbauer spectra were measured at room temperature (RT) and show the presence of components associated with Fe^{3+} indicating an oxidizing environment during the manufacturing process of the ceramic. The analysis is complemented by data obtained by X-ray diffraction suggesting firing temperatures around 950 °C, in agreement with Raman measurements.

1. Introduction

Recently the Raman and Mössbauer spectroscopy has become a standard method for the characterization of archaeological materials. One of its main applications is in the study of ceramic sherds: the Raman spectroscopy can be determined of the composition of the pigments; the effect of firing on clay can be studied by following the transformations of the components in the Mössbauer spectra attributed to the different iron-containing phases. ^{57}Fe Mössbauer and Raman studies [1,2] combined with other techniques such as X-ray diffraction (XRD), mineralogical and chemical analysis, can help to gather a rather complete picture of the method of production of the pottery. This information, combined with the one classically provided by archaeologists, such as details of excavation, stratigraphic, stylistic and typological dating, among others, is very important to establish the technological level of the culture that produced the pottery. Here we report on a study of the Nasca ceramics. The Nasca Culture emerged during the Early Intermediate Period (100 B.C. to 650 A.D.) and was centered in the Ica and Nasca valleys of south coastal Peru. The Nasca people practiced intensive agriculture in a precarious area characterized by frequent droughts, earthquakes and flash flooding. The Nasca ceramic is distinguished by the use of polychrome slip paints applied to both effigy vessels as well as a broad range of utilitarian shapes [3]. The Nasca iconography is characterized by a wide variety of naturalistic as well as fantastic motifs, some of which are clearly recognizable as birds, fish, plants, and others portraying strange creatures exhibiting both human and animal characteristics [3]. These motifs were painted on a variety of different shapes: bowls, jars, cups, and bottles with double spouts connected by a flat handle. There are also modeled vessels in the form of humans, plants, animals, and the same mysterious creatures seen in the paint [4,3]. The firing of the ceramics Nasca was done in open air, and not in kilns. The aim of the Mössbauer study of ceramic materials is to obtain information on the firing conditions (temperature and environment). The Mössbauer spectra yield characteristic parameters, which make it possible to infer the oxidation state of the iron and the symmetry of its environment. All information one can draw from Mössbauer spectra of ceramics depends on the chemical variability of iron, which may occur as Fe^{2+} or Fe^{3+} in a variety of silicate and oxide phases, depending on the redox conditions during the firing [5,6]. Raman spectroscopy is used to study ceramic manufactures. Raman spectroscopy is a spectroscopic technique that allows non-destructive analysis, to obtain qualitative information about the investigated samples. It is used to study the composition of the colored pigments used in ceramics. Although the technique is widely known and used, investigation of ceramics with Raman spectroscopy is a challenge due to its weak effect and the heterogeneity of the ceramic ware. With complementary methods, such as X-ray diffraction, non-iron bearing minerals and oxides (e.g. hematite, magnetite and wüstite)

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Fig. 1. Representative samples (C1 and C2) collected from the Ceremonial Centre of Cahuachi.

present in ceramics can often be identified, which allows conclusions as to the raw materials used and may give further clues as to the firing conditions.

2. Materials and methods

The fragments of archaeological Nasca Ceramic were collected from the Ceremonial Centre of Cahuachi in Southern coast of Peru. Fig. 1 shows two representative fragments samples. The samples are analyzed by Raman and Mössbauer spectroscopy combined with X-ray diffraction. By combining results obtained by these methods it is possible to quantitatively determine the paints composition, firing temperature and environment during the firing.

The Raman spectroscopy is performed using a model LabRam HR800 spectrometer (Horiba Inc.) to obtain the Raman spectra, with objective lens of magnification 50× and 633 nm excitation line (He-Ne laser), and 15 mW power output. We performed 7 scans with 3 s of exposure for each measure in the range 80–1750 cm^{-1}. To prevent heating of the spot area has been selected optical density 0.6 filter for darker pigments. The spectra were collected by a CCD cooled to −70 °C (Peltier system). The Mössbauer spectra of the samples were recorded in transmission geometry at room temperature (RT) in a high velocity range (12 mm/s), using a 57 Co(Rh) source and a spectrometer with 512 channels. The drive velocity was calibrated with the same source and a metallic iron foil at RT. The average recording time was 12 h per sample. Mössbauer absorbers containing approximately 125 mg/cm^2 of the powdered ceramic material were used. Isomer shifts are given relative to α-Fe. The NORMOS code [7] was used for the spectrum analysis and fitting with appropriate superposition of Lorentzian lines grouped into quadrupole doublets and magnetic sextet.

The X-ray diffraction measurements were carried out on powder samples using a Bruker D8 Discover Advance diffractometer with Cu X-ray tube. The diffraction patterns were measured in steps of 0.05° with accounting time of 3 s for each step. The analysis of diffraction patterns is performed using the MAUD software [8] with a pseudo-Voigt function to describe the peaks and a Caglioti function to describe the full width at half maximum (FWHM), as a function of the angle.

3. Results and discussion

3.1. Raman spectroscopy

White pigment – Fig. 2 shows the spectrum collected from the white pigment of the sample C1 in one of the predominantly white areas. The most intense vibrational modes, 443 and 611 cm^{-1}, are associated with modes found in rutile ore (TiO_2, tetragonal). A sharp peak at 146 cm^{-1} is due to anatase (rutile polymorph) mode and 236 cm^{-1} band is associated with a non-ordinary Raman effect (second order scattering). Rutile is a mineral from which up to 70% of titanium oxide

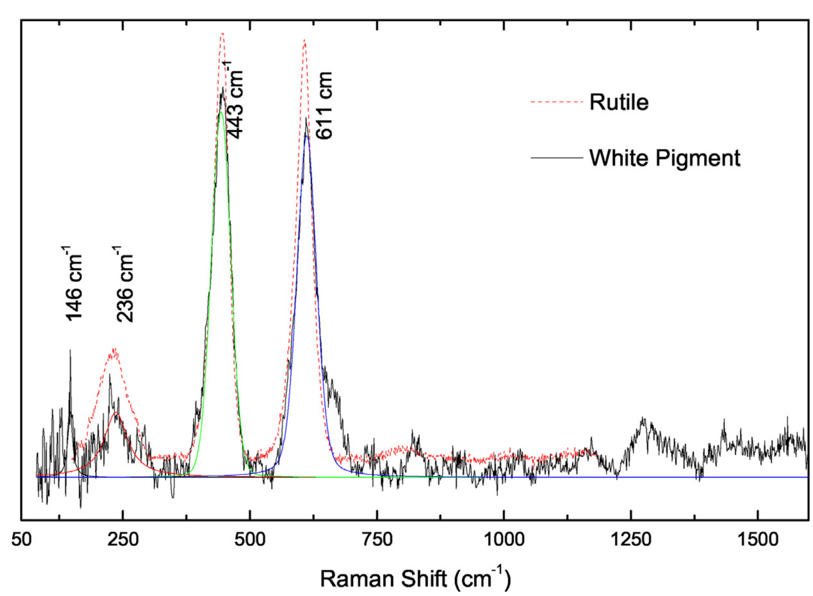

Fig. 2. Raman spectrum obtained on the ceramic painting with predominant white in section 1 of the selected area.