RAMAN SPECTROSCOPY AND X-RAY FLUORESCENCE IN MOLECULAR ANALYSIS OF YELLOW BLOCKS FROM THE ARCHEOLOGICAL SITE PLAYA MILLER 7 (NORTHERN CHILE)

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ABSTRACT

Yellow blocks from the archaeological site Playa Miller 7 (PLM7), on the coast of Atacama Desert in northern Chile, were analyzed by Raman spectroscopy and X-ray fluorescence (XRF) portable. Our results identify for the first time the use of K-jarosite and natrojarosite in prehispanic times (approx. 2500 year BP). In search of a possible source of supply for this mineral hydrothermal origin, our surveys were focused on Andean geothermal areas with identification, so far, from a single source in the region of Arica and Parinacota: Jurasi (JU), located at 4000 mamsl. Comparison of the Raman spectra between samples archaeological and Jurasi, allow us to infer that this hydrothermal source could be used as obtaining source of yellow pigment by prehispanic inhabitant of Formative period (3700-1500 years B.P.).

Keywords: Pigments, X-ray fluorescence, Raman spectroscopy, Jarosite, northern Chile.

1. INTRODUCTION

The use of Raman spectroscopy and X-ray fluorescence has proved to be a powerful combination of techniques for the analysis of archaeological objects[1-4]. Raman spectroscopy allows obtaining structural information of various molecular systems. This technique is part of vibrational spectroscopy, allowing information of the normal modes of vibration of different molecular groups. The greatest potential of Raman relates to their specificity, sensitivity, reproducibility, applicability *in-situ*, spatial and spectral resolution[5], besides being a non-invasive and non-destructive technique. These advantages, coupled with recent developments in Raman instrumentation, have made it possible to extend the use of this technique to the conservation and archaeology[5-11]. Among others, the use of Raman allowed characterizing pigments and dyes used in the preparation of manuscripts, paintings, ceramics and textiles[12-17].

Moreover, X-ray fluorescence (XRF) is, undoubtedly, one of the most commonly applied techniques in conservation and archaeology[18]. The development of portable equipment has contributed over the last 40 years to increase its application because of its non-destructive and non-invasive characteristics, besides allowing, in many cases, *in-situ* analysis without sample preparation. To these characteristics adds the ability to identify the presence of elements in major and minor amounts. Finally, this technique is appreciated for its relatively low cost and short analysis[19].

From the archaeological point of view, the particular conditions of the Atacama Chilean desert favour the conservation of a wide variety of archaeological materials, some of them, attributed to the different periods of the prehispanic's chronological sequence (10500- 450 years B.P.) and post-Spanish contact (posterior to the fifteenth century). From the time of the first settlements in the region, pigment is registered on fibber mats in funerary contexts along the coast or as fragments found in the stratigraphy of some occupations in eaves located about 4000 mamsl[20]. During the Archaic period (10500- 3500 years B.P.), the presence of color is found in other supports such as wood, leather, filling and coating of mummified bodies and rocky walls [20-21]. In each of these, pigment is prepared and applied as painting, ie, as a mixture containing at least one pigment and a binder. The pigment consist in manganese oxide for black color[20], iron oxide for red[22], copper oxides for green[23], different sorts of clay for white or grey[24]. In hunter-fishermen Chinchorro from Archaic period (7000- 3500 years B.P.)[25-26], these pigments are mixed to white or grey clay[27-28] to be incorporated in the stuffing bodies or applied as a surface coating. In the rock art of andean hunter gatherers the use of iron and manganese is recognised too, but with different morphologies and sizes, aluminosilicates and possibly mixed with water as binder[21].

Until now in South America, yellow pigments have received little attention. Moreover yellow pigment such as natrojarosite, has only been reported in the cave paintings of Inca Cave 4 site in the region of Jujuy, Argentina[29] and other various sites in Patagonia Argentina[30]. The use of jarosites in South America joins other known cases as in, for example, the old world and the Egyptian Old Kingdom (2300 - 2600 year BC)[31] or in the murals of Beroe fortress, Romania (4th-6th century)[32]. Jarosites are a large family of minerals that have a general formula of the type $M_n(Fe^{3+})_6(SO_4)_4(OH)_{12}$, where M can be K^+, $(NH_4)^+$, Na^+, Ag^+ or Pb^{2+} and where $n = 2$ for monovalent cations and 1 for the divalent cations[33]. The mineralogical characteristics and chemical properties of this family of compounds have been widely studied[33-37].

In this paper, we present the results obtained from the analysis by Raman spectroscopy and XRF of samples of yellow pigment blocks from the PLM7 Site, located on the coast of northern Chile (fig. 1). This colour is very rarely found in contexts archaic hunter-gatherer groups. Until now, yellow paint has only been identified on coating of a mummy of the Macarena Chinchorro site[38] and in rock art paintings of Andean foothills but without analyses. Samples analyzed here have a very clear yellow colour and very bright, which may acquire an ocher tonality. Thus the aim of this paper is to account for the first time of using minerals jarosites family in Chile, in ancient times (3700-1500 years BP). Moreover, this work represents the first application of these techniques to the analysis of archaeological remains in Chile.

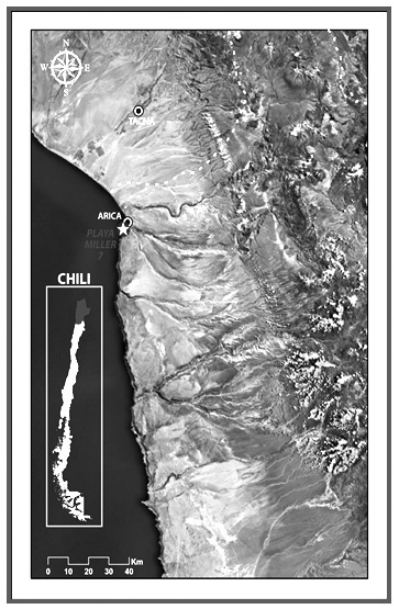

Figure 1: Map of Playa Miller 7 on the coast of northern Chile.

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2. Experimental

2.1. *Samples*

PLM7 samples were taken in the laboratories of the University of Tarapacá Museum of San Miguel de Azapa. These blocks come from yellow ovoid block, with compact to semi-compact structure (Table 1 and fig. 2). Many of them have linear fingerprint extraction, so that these blocks can be intentionally manufactured as a product, probably to store the pigment for his use at different times as needed. Blocks consist mainly of finely ground pigment that adheres very easily. In some cases blocks have a more heterogeneous composition visible to the naked eye, given the presence of finely ground elongated structures and incorporated in the mixture, identified as algae[39]. For sampling, we privileged unarmed blocks, detached fragments or powder (fig. 2). Each sample was stored in a plastic container to be moved and then analyzed.

Table 1: Results obtained by magnifying glass and XRF from samples taken from PLM7 and Jurasi.

CODE	TEXTURE	ELEMENT BY XRF
PLM7-14	Ovoidal homogeneous block with a very fine granulometry (powder)	S, Cl, K, Ca, Ti, Cr, Fe
PLM7-15	Ovoidal homogeneous block with a very fine granulometry (powder)	S, Cl, K, Ca, Ti, Cr, Fe
JU-17	Powder	S, Cl, K, Cr, Fe
JU-18	Powder	S, Cl, K, Ti, Fe

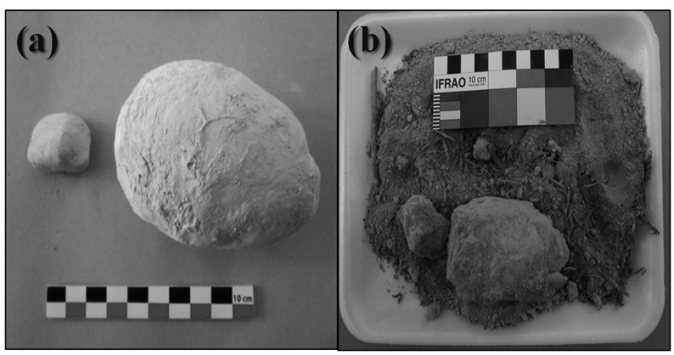

Figure 2: Type samples analyzed by yellow blocks, (a) ovoidal and (b) powder

Additionally, surveys were conducted in different areas of the region, which could be places of supply´s pigments in ancient times. Recent mining uses difficult to find evidence related to the extraction of pigment in the past. So far, only the area known as Los Pumas evidence remains linked to a mining prehispanic[20]. Regarding yellow sources analyzed in this study, only JU area showed reservoir similar to the colour identified in PLM7. This search was conducted in order to reproduce the conditions of exploration occurred in the past.

2.2. *Analytical measurement*

Raman spectra of the yellow blocks extracted from Playa Miller 7 and Jurasi were recorded on a Raman Renishaw Microscope System RM1000 apparatus, equipped with 514, 633, and 785 nm laser lines for excitation, a Leica microscope and an electrically cooled charge-coupled device detector. The instrument was calibrated using the 520 cm^{-1} line of a Si wafer and a 50× objective. The resolution was set to 4 cm^{-1}, and 5–20 scans of 10 s each were averaged; spectra were recorded in the 1800–200 cm^{-1} region to observe the Raman spectra. The spectral scanning conditions were chosen to avoid sample degradation and photodecomposition. Data were collected and plotted using the programs WIRE 2.0 and GRAMS 8.0.

XRF spectra were recorded with a XRF Bruker Tracer III-SD portable equipment with a detector fitted 10 mm^2 XFlash® SDD, Peltier cooled; typical resolution 145 eV at 100000 cps and equipped with a X-ray tube Rh target; max. voltage 40 keV, using 15 keV of energy and an acquisition time of 120 s. Data were collected and plotted using the program Tracer software S1PXRF 3.8.3.

3. RESULTS

A total of seven samples from the archaeological of PLM7 site and 3 extracted from the JU hydrothermal site were analysed. Raman spectra were recorded on different zones for each sample. Each spectrum obtained was compared with data published in RRUFF online databases[40]. In most of the yellow blocks of heterogeneous composition, containing algae, it was not possible to obtain the Raman spectrum due to fluorescence. Only in two cases it was possible to analyse the spectrum. The spectral scanning was performed in sample areas where yellow tonality was clearly distinguished. Furthermore, two of the three yellow blocks from the hydrothermal JU, display an analysable spectrum. All registered Raman spectra of yellow zones, showed characteristic bands ascribed to the jarosite family (fig. 3).

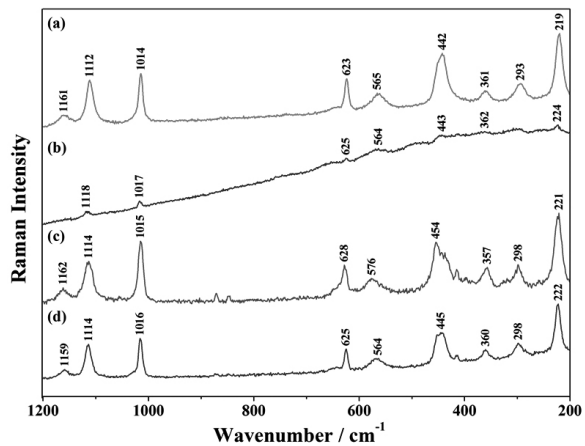

Figure 3: Raman spectrum of natrojarosite extracted from the (a) Playa Miller 7 Archaeological Site (PLM7-14), (b) Playa Miller 7 Archaeological Site (PLM7-15), (c) Jurasi hydrothermal site (JU-17) and (c) Jurasi hydrothermal site (JU-18).

Different jarosite synthetic compounds were identified by Sasaki et al.[37] by using Raman, infrared and X ray data. They assigned different vibrational modes for the SO_4^{2-} molecular fragment (ν_1, ν_2, ν_3 y ν_4). ν_1 and ν_3 correspond to symmetric (ν_s) and antisymmetric (ν_{as}) stretching, respectively. The ν_2 and ν_4 modes correspond to bending (δ) vibrations. Other features observed in the vibration spectra of jarosites are associated with the FeO fragment. The spectral assignment in Table 2 is proposed on the basis of works by Sasaki et al.[37] and Frost et al.[36] and general spectral data[41]. In our Raman spectra (fig. 3), the $\nu_s SO_4^{2-}$ mode is observed in the 1014-1017 cm^{-1} range. A $\nu_{as} SO_4^{2-}$ mode is ascribed in all spectra to signals in the 1112–1118 cm^{-1} region. Another $\nu_{as} SO_4^{2-}$ vibrational mode is observed near 1160 cm^{-1}. A δSO_4^{2-} mode appears in all spectra in the 623–628 cm^{-1} range. Another δSO_4^{2-} vibrational mode is assigned to the band located in the region 442–454 cm^{-1}, following Frost et al.[36]. The single band observed at 565 cm^{-1} in the spectrum of the PLM7-14 samples is assigned to FeOH deformation modes. The strong band in all spectra in the 219–224 cm^{-1} range is assigned to one of the vibration modes of the Fe-O bond. Two bands in the 280-370 cm^{-1} spectral range are assigned to FeO vibrations.

Table 2. Wavenumbers and the most probable assignment for the Raman bands of jarosites from PLM7 and JU.

PLM7–14	PLM7–15	JU-17	JU-18	Assignment
1161w		1162w	1159w	$\nu_{as}(SO_4^{2-})$
1112m	1118 m	1114m	1114m	$\nu_{as}(SO_4^{2-})$
1014ms	1017ms	1015ms	1016ms	$\nu_s(SO_4^{2-})$
623m	625m	628m	625m	$\delta(SO_4^{2-})$
565mw	564mw	576mw	564mw	γFeOH
442ms	443ms	454ms	445ms	$\delta(SO_4^{2-})$
36m	362m	357m	360m	O–Fe
293m		298m	298m	O–Fe
219vs	224vs	221vs	222vs	O–Fe
Band description: vw, very weak; w, weak; mw, medium weak; m, medium ; ms, medium strong; sh, shoulder; s, strong.				

To distinguish different types of jarosites in natural samples is difficult due to their heterogeneity. Therefore, we decided to realise complementary XRF analysis.

XRF analysis of yellow blocks from PLM7 and JU showed significant amounts of S and Fe (fig. 4), which is consistent with the presence of compounds of the jarosites family. Furthermore, the significant amount of K, suggests that K-jarosite is present in samples. Under the conditions of XRF measurement, it was not possible to detect the presence of Na (Table 1). However, in our previous work by SEM-EDX and X-ray diffraction[39], we detected the presence of this element in PLM7´s samples. Finally, the absence of vibration modes associated with the molecular N-H fragment in Raman spectra, as well as the absence of the metals Ag and Pb in the XRF analysis, suggest in PLM7 and JU the presence of K-jarosite and Na-jarosite.

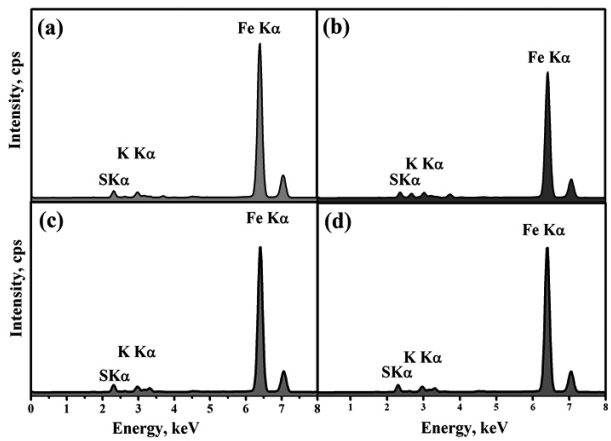

Figure 4: X-Ray spectrum of natrojarosita extracted from the (a) Playa Miller 7 Archaeological Site (PLM7-14), (b) Playa Miller 7 Archaeological Site (PLM7-15), (c) Jurasi hydrothermal site (JU-17) and (c) Jurasi hydrothermal site (JU-18).

4. CONCLUSIONS

Results obtained by Raman spectroscopy indicate that several of the observed vibrational signals correspond to vibration normal modes associated with jarosite type compounds. Slight differences in wavenumbers are not enough to differentiate the type of jarosite. However, from our XRF results, and previous results obtained by SEM-EDX and XRD[40], we conclude that in the yellow blocks accruing from archaeological site PLM7 and font hidrotermal JU, predominant yellow pigments are Natrojarosite and K-jarosite.

Alongside K-jarosite and Natrojarosite used as base and principal material in the yellow blocks, it is possible to find other elements such as algae and quartz[39]. While, Sepulveda et. al. were able to determine the presence of Natrojarosite by SEM-EDX and XRD in these same yellow blocks, it was not until this work that identify more specifically jarosites mixtures used by the prehispanic inhabitant of the coastal Atacama desert.

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