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Micro-Raman spectral identification of manganese oxides black pigments in an archaeological context in Northern Chile

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Abstract:
The micro-Raman spectroscopy was used to identify manganese oxides, pyrolusite, manganite and cryptomelane in archaeological sites in northern Atacama Desert, Chile. The present micro-Raman data allow us to compare and expand the origins of raw materials used by archaic groups of the Atacama Desert. In the Andean highlands, pyrolusite and manganite were identified while in the coastal lowlands manganite and cryptomelane were found. The present results complement the data obtained from the lithic materials and rock art painting analyses pointing to a better understanding of the daily life of ancient populations and minerals use in this region.

Keywords: Black pigment, Manganese oxides, Micro-Raman spectroscopy, Archaeological contexts, Atacama Desert

Background

Manganese (Mn) is one of the most abundant elements in nature–tenth within the Earth's crust [1]. Geochemically, Mn is part of minerals formed in the early stages of magmatic crystallization. According to Ossa [2], the genesis of manganese deposits in northern Chile was traced to the deposition by circumvolcanic hot springs during the Pleistocene, deposits of manganese occurring at modern erosion levels are due to secondary mobilization. Significant quantities of Mn persist, however, it melts and can be plentiful in late-stage deposits such as pegmatites; near the Earth's surface, Mn is easily oxidized, giving rise to several oxide-hydroxide minerals [1]. Its sedimentary origin can be found in simple oxides such as Mn_xO_y, or as mixed oxides such as $A_xMn_yO_z$, where A is K or Ba [1, 3, 4]. The most common mineral is pyrolusite (MnO_2), which is black in colour [5]. Manganese is also found in other minerals [6], such as rhodochrosite ($MnCO_3$), rhodonite ($MnSiO_3$), manganite ($MnO(OH)$), alabandite (MnS), cryptomelane ($K_x(Mn^{4+},Mn^{3+})_8O_{16}$), and hollandite ($Ba(Mn_6^{4+}Mn_2^{3+})O_{16}$) [7, 8].

The use of manganese pigment has a long cultural history, since prehistoric time in Upper Palaeolithic [3]. Different manganese oxides in various archaeological contexts were identified by using Raman spectroscopy [9]. This technique is a recognized power tool for the analysis of archaeological objects [10–21]. It is a non-invasive and non-destructive technique, displaying high specificity, sensitivity and reproducibility [12, 22]. Raman microscopy was used in a micro-analysis of red and black colours of Palaeolithic paintings in the three limestone caves of Les Fieux, Les Merveilles and Pergouset of the Quercy District, France [20]. Results indicated the presence of hematite in the red micro-samples from each cave, goethite in a red–orange phase, amorphous carbon in some black micro-samples and Mn oxide/hydroxide in some black micro-samples. Black manganese oxides, romanechite and pyrolusite were used as pigments by prehistoric artists in the cave of Rouffignac-Saint-Cernin in Dordogne, France, from the upper Magdalenian Palaeolithic period (13,500–12,000 BP) [17].

The Atacama Desert in northern Chile is rich in different kinds of minerals that have been used to obtain pigments and produce paintings since pre-Hispanic times.

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The study of manganese oxides resulted interesting since the most significant sources of manganese in northern Chile are specifically located in Andean highlands over 4800 m altitude [2, 3, 23].

The use of manganese oxide black pigments was identified in different archaeological contexts of northern Chile from Archaic period, between 10,500 and 3700 BP (Fig. 1) [3, 24–27]. In the coastal tradition, black pigment was restricted to funerary contexts for Chinchorro hunter-gatherers and used as part of mummified bodies or as offerings, since 7000 BP [24] (Fig. 2). This colour was also described as applied to vegetable fibre and used for plant matting [3]. The minerals identified in this area were cryptomelane and hollandite [2]. In the highlands, the manganese oxide in paintings was registered only in rock art representations [28–30], mainly camelids found at different sites, more probably since the late archaic period, around 6000 BP (Fig. 2). Recently, it has been suggested that Los Pumas Mine, where the presence of cryptomelane was identified, was probably a provisioning mineral source used by the coastal tradition of Chinchorro during the archaic period. The presence of manganite was identify through micro-XRD [3, 25]. The elementary analysis performed in some of the paintings from the highlands indicated the use of two different types of manganese compounds detected by scanning electron microscopy (SEM) and X-Ray scattering [30]. The observed difference was attributed to the presence or absence of Ba.

In this work, we perform a comparative molecular analysis of black pigments found in three archaeological sites from northern Chile. Two of them are from the highlands: Tangani (Ta-1 and Ta-14), Pampa El Muerto 3 (PM-3-aA) and one from the coast, Maderas Enco-Cuerpo 1 (Ari-26 and Ari-27). We also analyse samples from the Los Pumas Mine 5000 m above sea level, in the Andean mountains (LPM-1, LPM-2 and LPM-3). The purpose of this comparative analysis is to give some insights about the use of manganese oxide minerals by archaic hunter-gatherers from northern Chile. The mineral characterization is mainly performed using micro-Raman Renishaw InVia Reflex apparatus. It is the intention that the present results will contribute with solid arguments to the discussion about the possible interactions between the early traditions of hunter-gatherers from the coast and the highlands in northern Chile.

Fig. 1 Map of northern Chile. *Map* showing the archaeological area of archaic hunter-gatherers in Northern Chile

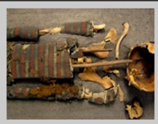
Code	Location	Image
Ta-1	Tangani (highland)	
Ta-14	Tangani (highland)	
Ari-26 and Ari-27	Maderas Enco (Coastal)	
PM-3-A	Pampa el Muerto (highland)	

Fig. 2 Codes, localization and images of samples

Methods

Samples collection

Samples were collected in situ for rock art paintings from Tangani and Pampa El Muerto. Samples from the mummy of Maderas Enco-Cuerpo 1 were taken at the Archaeological Museum of Universidad de Tarapacá in San Miguel de Azapa (Fig. 2). In order to determine possible differences between samples, various areas of Los Pumas Mine were examined. Samples were extracted using a scalpel with a blade that was changed after each extraction. Black pigments were carefully scraped with the tip of the scalpel; grains size was in the range 2–100 mm^2. Materials were gathered into a clean and sterile receptacle, preferably small glass tube, kept inside and unused.

Samples description

Ta-1. Anthropomorphic figure represented by simple black linear traces from Tangani 1. Ta-14. Anthropomorphic figure represented by simple black linear traces from Tangani 14.

PM-3-A. Black-coloured camelid figure in naturalistic style found in Pampa El Muerto 3. Ari-26 and Ari-27 are samples from the thorax of an adult individual from the Maderas Enco-Cuerpo 1 site in Arica. This mummy corresponds to one of the so-called "black mummies". The body was modelled in clay with a black surface covering it; particular alternating horizontal red and yellow stripes are observed in the trunk. Samples collected in the laboratory were classified as Ari-26 and Ari-27 [25]. This mummy is preserved at Museo Universidad de Tarapacá, San Miguel de Azapa, Arica, Chile.

LPM-1, LMP-2 and LPM-3. Samples corresponding to mineral fragments collected at the surface of different areas of Los Pumas Mine.

Micro-Raman measurements

Micro-Raman spectra of samples were recorded with a Raman Renishaw InVia Reflex apparatus, equipped with the 532, 633, and 785 nm laser lines, a Leica microscope and an electrically cooled CCD detector. The instrument was calibrated using the 520 cm^{-1} line of a Si wafer and a 50× objective. Its resolution was set to 4 cm^{-1} and 1–20 scans of 10–30 s each were averaged. Spectra were recorded in the 150-1800 cm^{-1} region. The laser power was set between 10 to 100 mW. Spectral scanning conditions were chosen to avoid sample degradation and photodecomposition. Data was collected and plotted using the programs WIRE 3.4 and GRAMS 8.0.

Results and discussion

Micro-Raman spectra of black pigments

Micro-Raman spectra were recorded on different black zones for each sample (Figs. 3, 4). Micro-Raman spectra were assigned following published data in the RRUFF database online [8] and from Gao et al. [31]. Spectral scanning was performed in the sample areas where black

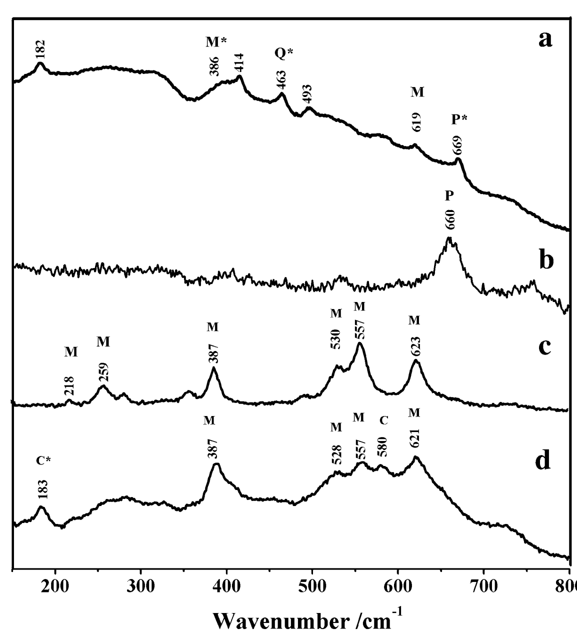


Fig. 3 Micro-Raman spectra. Raman spectra of different manganese oxides *a* Ta-1 (pyrolusite + manganite), *b* Ta-14 (pyrolusite), *c* Ari-26 (manganite) and *d* Ari-27 (manganite + cryptomelane). *P** pyrolusite, *M* manganite, *C* cryptomelane, *Q* quartz

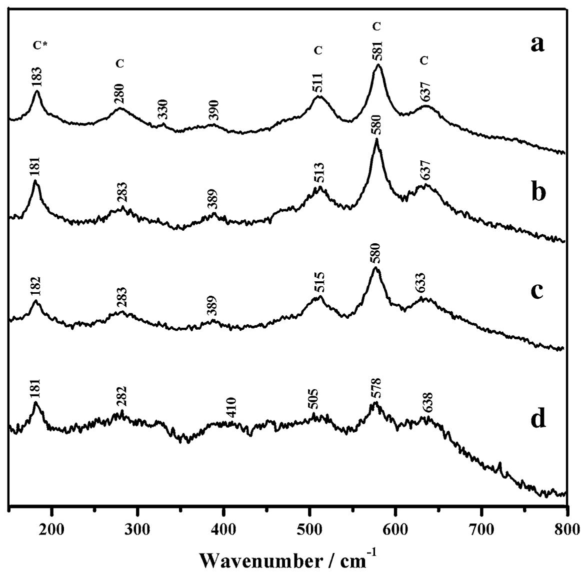


Fig. 4 Micro-Raman spectra. Raman spectrum of cryptomelane in *a* PM-3-A, *b* LPM-1, *c* LPM-2 and *d* LPM-3. *C** cryptomelane

tonality was clearly identified. The spectra displayed the characteristic bands ascribed to the manganese oxide family [8, 31, 32]. The spectrum of the site Ta-1 sample (Fig. 3a), is not easy to interpret. However, some bands were identified and assigned as a combination of manganese compounds; this is the case for the band at 669 cm^{-1}, which was attributed to a Mn–O stretching mode (νMn–O) of pyrolusite. The 386 and 619 cm^{-1} bands were ascribed to manganite. The band at 463 cm^{-1} was attributed to quartz.

The micro-Raman spectrum of the sample Ta-14 (Fig. 3b) displays a spectral profile similar to pyrolusite [8] with a unique band at 660 cm^{-1} ascribed to νMn–O.

In the case of the sample Ari-26 (Fig. 3c), the spectrum displays the characteristic bands of manganite 218, 259, 387, 530, 557 and 621 cm^{-1} [8, 32, 33]. The Raman spectrum of two types of manganese oxyhydroxides, groutite and manganite, was recorded by Bernard [33]. In both cases, three bands at 388, 555 and 620 cm^{-1}, were observed. The present spectrum is not different with the exception of the relative intensity of the last band.

The Raman bands in the spectrum of the sample Ari-27 (Fig. 3d) 387, 557 and 621 cm^{-1} were attributed to manganite; the bands at 183 and 580 cm^{-1} are ascribed to cryptomelane.

Spectra in Fig. 4a–d, corresponding to samples from Pampa El Muerto (PM-3-A) and Los Pumas mine (LPM-1, LPM-2 and LPM-3), show a spectral profile corresponding to cryptomelane [31]. Bands located around 183, 513, 580 and 637 cm^{-1} were attributed to different vibrational modes of the Mn–O moiety. The two sharp bands at 574 and 634 cm^{-1} would indicate a well-developed tetragonal structure with an interstitial space consisting of (2 × 2) tunnels [31]. In the present case, these bands were observed near 586 and 637 cm^{-1}. The band at 183 cm^{-1} was assigned to an external vibration ascribed to a translational motion of the MnO_6 octahedral, following Gao [31]. The band at 386 cm^{-1} was ascribed to a Mn–O bending vibration [31]. Finally, the possibility is not excluded that hollandite was also present in the analysed samples; this is based on the strong relative intensity of the band observed at 580 cm^{-1} [8, 34].

The molecular analysis allowed the characterization of the black pigments used by archaic communities in the lowlands and the highlands of northern Chile. From this point of view and focusing on the manganese oxides analyses, the results suggested that the sample from Ta-1 contains different manganese minerals, particularly pyrolusite and manganite. Pyrolusite was also identified in Ta-14. In Ari-26 was identified only manganite. Manganite and cryptomelane were used in Ari-27, thus confirming previous results obtained from micro-X ray-diffraction [25]. Cryptomelane was also identified in the samples of PM-3-A, LPM-1, LPM-2 and LPM-3. The cryptomelane used in Pampa El Muerto as well as in Maderas Enco-Cuerpo 1 could come from high-altitude sources in the region. Coastal groups could have obtained it directly from these sources, but they also could have exchanged with highland hunter-gatherers. In the case of the manganite and pyrolusite, the mineral's origin source remains unknown, but they could come from the same source, as it is common that manganite transforms itself in pyrolusite [35, 36]. Thus, according to these results, it is possible to infer that archaic groups used various types of raw natural manganese minerals, such as natural or intentional mixture. So it is possible to propose that inhabitants from the coastal and the highland used similar but also different minerals.

Conclusions

Manganese black minerals pyrolusite, manganite and cryptomelane in an archaeological context have been identified by micro-Raman spectroscopy. Cryptomelane was probably extracted from Los Pumas mine area. The present micro-Raman data allows comparing and expanding the origins of the raw materials used by archaic hunter-gatherers groups from the Atacama Desert. We need to identify more possible raw mineral sources. We also need to precise possible mineral modification under different conditions of preservation to understand the relation between the manganite and pyrolusite in the same samples. Finally, the present results complement the data obtained from lithic materials and rock art paintings, pointing to a better understanding of mineral and raw material, in general, used by ancient populations in the northern Atacama Desert.

Authors' contributions

MS: drafted the manuscript from the archaeological point of view. SG: participated in reviewing and editing of the manuscript. MCV: participated in the Raman analysis and revising of the manuscript. VGS and BTA: participated in revising the manuscript. JJCV: carried out the Raman analysis, drafted the manuscript and participated in reviewing and editing. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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