A first approach to chemical and mineralogical study of pigments from Lajeado Complex in Tocatins, Brazil

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Summary

In recent years chemical analysis has been established as a significant contributor to science-based archaeology. The present work is a first approach to the study of chemical and mineralogical composition of pigments used in archaeological rupestrian arts of Vão Grande site, included in Lajeado Complex in Tocatins State, Brazil. Representative pigments micro-samples were removed from rock paintings and substrate rock. The characterization of the pigments was carried out by micro X-ray diffraction (μ-XRD) and Fourier transform infrared micro-spectroscopy (μ-FTIR).

Riassunto

Questo lavoro è un primo approccio allo studio della composizione chimica e mineralogica dei pigmenti utilizzati nel sito archeologico di arte rupestre di Vão Grande, facente parte del complesso di Lajeado nello Stato di Tocatins, Brasile. Micro-campioni dei pigmenti sono stati rilevanti dalle pitture rupestri e dal substrato di roccia. La caratterizzazione dei pigmenti è stata condotta con microdiffrazione dei raggi-X (μ-XRD) e microspettroscopia a infrarossi a trasformata di Fourier (μ-FTIR).

Introduction

Lajeado Complex is located between the cities of Palmas and Lajeado, on Tocatins state (TO), on the right bank of Tocantins River, between Planalto Residual do Tocantins, Serra do Lajeado and Depressão do Tocantins. This area is known by brazilian archaeologists since the late eighties, due to the environmental review (EIA-RIMA) done before the construction of the city Palmas (De Blasis 1989), capital of Tocantins state. Since then, archaeological research has been going on in the region due to large enterprises, but only in 2012 with the project: *Projeto Tecnologia e Território: dispersão e diversificação no povoamento do Planalto Central Brasileiro*, coordinated by Dr. Lucas Bueno and funded by the National Council for Scientific and Technological Development (CNPQ), academic projects started. The present work resulted from data collected within this project, and is also part of the doctoral thesis: *Paisagens e técnicas distintas, motivos semelhantes. A dispersão da Arte-Rupestre no Rio Tocantins, o caso de Palmas e Lajeado – TO, Brasil*, of Ariana Braga, supported by *Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES)*.
As a result of the archaeological work referred, they are now known in the area of Lajeado Complex a total of 30 archaeological sites with a significant variety of styles and technics. For the collections of samples the site Vão Grande was select not only due to the stylistic variety but also because in the rock paintings of the site are present all colours used in rock art of this region. We try to sample all shade of each colour and also of stylistic variations, so that in a near future it is possible to relate techniques, colours and pigments to establish consistent interpretation parameters.
Vão Grande site is a large sandstone shelter, probably the largest in the region, (Berra, 2003). The dating from two archaeological samples found in the site indicates an occupation of 180 years, between 480 and 660 before present (Berra 2003; Morales 2005). The paintings are divided into 21 panels, very different on repertoire, technique and morphology of support. Both crayons and paint techniques are used. The colours are varied also, black, white, yellow and different shades of red, like purple-red and orange-red. The bichromias are rare, occasionally with a red-yellow or a red-white one (Braga in press) (Fig. 1).

Materials and methods

Only 7 of the 21 panels of Vão Grande site were sampled. A micro-sampling of pigment of each different colour and of each style in each panel was performed (Table 1). For a blank a sample of support of each panel was also collect. Data collection was done using an inox scalpel blade to scrape a small area of the painted surface, in order to achieve the greatest amount of pigment with the lower damage of the paintings and before each collecting all materials were sterilized and the gloves changed to minimize, as much as possible, any contamination. The pigment was directly collected in an eppendorf which was below the scraping area (Fig. 2).
Each sample was given a code number referring to the panel and painted motives collected.

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Panel	Sample	Figure	Colour
4	P4-S1	support	
	P4-S2	anthropomorphic	red
5	P5-S1	support	
	P5-S2	anthropomorphic	red
6	P6-S1	geometric circular	dark red
	P6-S2	zoomorphic	white
	P6-S3	geometric	orange red
	P6-S4	support	
10	P10-S1	support	
	P10-S2	anthropomorphic	dark red crayon
14	P14-S1	support	
	P14-S2	zoomorphic	brown
	P14-S3	zoomorphic	red
	P14-S4	phytomorphic	red
	P14-S5	geometric	white
	P14-S6	anthropomorphic	black
	P14-S7	anthropomorphic	Light yellow
	P14-S8	crayon zoomorphic	red
	P14-S9	zoomorphic	yellow
18	P18-S1	support	
	P18-S2	zoomorphic	red
19	P19-S1	support	
	P19-S2	anthropomorphic	yellow

Table 1 – Description of the samples collected in Vão Grande site

Micro x-ray diffraction was performed using a commercial Bruker AXS D8 Discovery diffractometer, with a Cu K*a* radiation source and a LYNXEYE linear detector. The diffraction image was converted to a conventional diffractogram by integration of the diffraction rings and simulating an interval 3–75° 2θ and step of 0.05°/s.
The FTIR spectra were recorded with a micro-FTIR spectrophotometer, TENSOR 27 FOCAL PLANE ARRAY, in the range of 400–4000 cm−1, with an IR source, KBr beam splitter. Thin sections were obtained by squeezing each sample between two diamond cells. For each sample, 256 scans were recorded with a resolution of 4 cm−1. The FTIR experiments were performed in order to permit the assignment of characteristic absorption bands of functional groups, allowing the identification of some pigments.

Results and Discussion

Micro-XRD results reveal that quartz is present in all samples, pigments and rock supports, what may mean that there was no pretreatment of the sample (separation) or that quartz was used to facilitate grinding (Fig. 3).
Hematite was identified in all pigments of red based colour, and goetite, an iron hydrate mineral with a brownish colour, was found in brown pigment, but is difficult to say if it was used on purpose or result from hematite decomposition. Halotrichite, a mineral that form white hair-like crystals was identified in the white pigment. Other mineral that was only found in a white pigment is gibbsite, an aluminium compound that is formed from rocks rich in feldspar in warm and wet climate (Cavalcante 2014).
Other minerals were identified, but we are not yet sure if they were part of the initial composition of the pigment or are the result of a process of decomposition that may have occurred. For example, the mineral taranakite was identified in samples P10-A1 and P10-A2, but it is a mineral that can be formed from the action on the rock of solutions contaminated with bat and bird guano and, in fact, this panel is in an area with presence of guano; resulting also from guano action is archerite that was identified in sample P4-A.2 (Gross 2004; Frost 2012). The mineral glushinskite was identified in samples P18-A2 and P18-A3, it may be related to the lichens occurring on the panel 18, since it may result from the reaction of minerals rich in magnesium with oxalic acid resulting from the excretion of lichen encrusted (Chen 2000; Wilson 1980; Kiros 2013).
The micro-FTIR experiments were performed in order to permit the assignment of characteristic absorption bands of functional groups allowing a more precise identification of pigments. But as it is a work in progress, at the moment we just can said that in some samples from panel 14 were observed some bands that correspond to organic matter, but more experiments have to be done before it is possible to confirm its origin.

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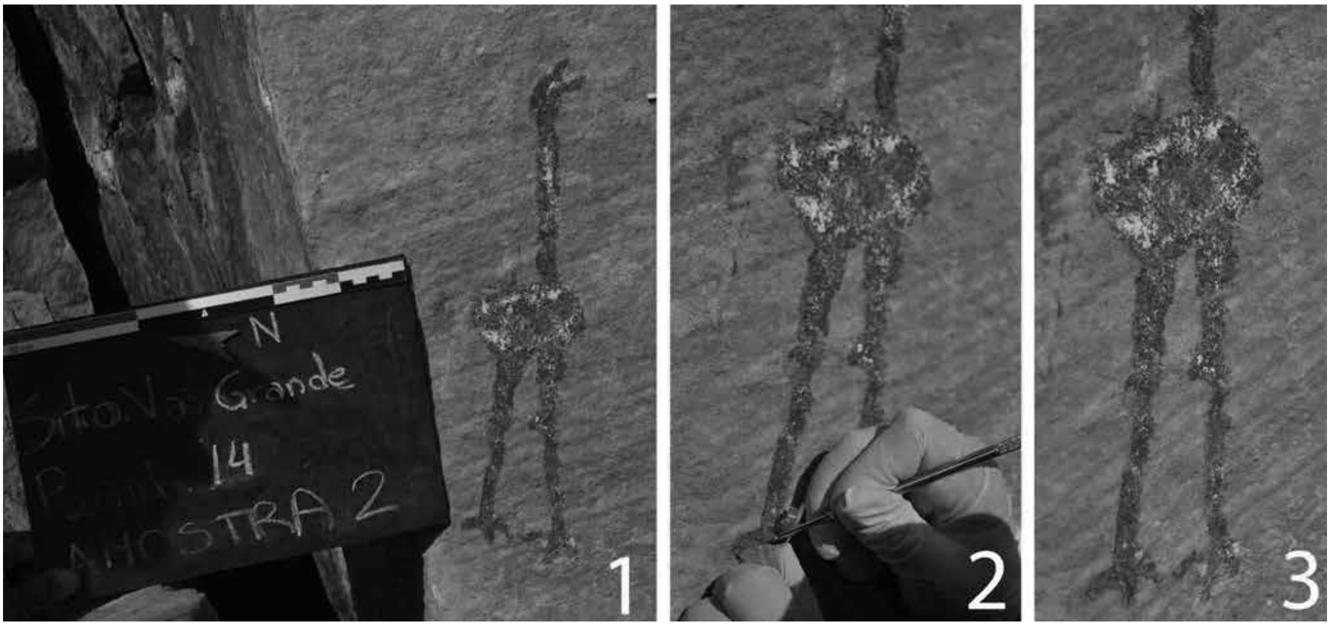
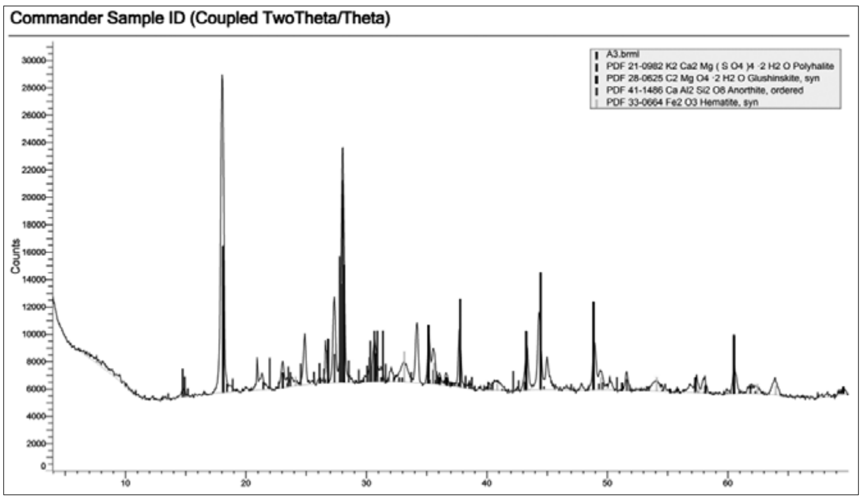
Fig. 1 - Panel 14 (Braga in press, 1, p. 299).





▲Fig. 2 - Detail of collection of sample 2 panel 14. 1-before, 2-during, 3-after (Braga in press, 1, p. 115).

◄Fig. 3 - Example of a micro-XRD spectra (sample P18-A3)