IN SITU PIGMENTS STUDY OF ROCK ART AT JAGUARIAÍVA 1 ARCHAELOGICAL SITE (PARANÁ, BRAZIL) BY PORTABLE ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF)

ESTUDO IN SITU DE PIGMENTOS DE ARTE RUPESTRE NO SÍTIO ARQUEOLÓGICO JAGUARIAIVA 1 (PARANÁ, BRAZIL) COM SISTEMA PORTÁTIL DE FLUORESCENCIA DE RAIOS X POR DISPERSÃO EM ENERGIA (EDXRF)

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Abstract

Jaguariaíva 1 rockshelter is located in the Jaguariaíva city region, Paraná State, Brazil (17x 21x5.20m size, E 632 454 e N 7 315 244 UTM coordinates and 887m high). It is a sandstone shelter with paintings from, at least, two different periods. The oldest one is around 7.000 years BP. Rock art in the Jaguariaíva 1 shelter is on part of two walls and ceiling, from 0.5m until 1.90m high at west side, and from 1.80m to 3.60m at north side. The main documented panel of the rock shelter has paintings of animals and lattice motifs. The oldest ones are deer figures infilled with red. The more recent are reddish brown outline figures filled by straight lines. Rock art regions were analyzed by two portable EDXRF systems, one employing an X-ray tube with Ag filter and target and another one with an X-ray tube with W target and Ag filter, both with Si PIN diode detectors and a special designed mechanical system for the detector and X-ray tube positioning, that enables angular and XYZ movements of the excitation-detection system respect to the measurement area. Elements from Si to Pb were measured. X-Ray Fluorescence spectra were analyzed using the AXIL-WinQXAS software.

Keywords: Rock Art, PXRF, Pigment, In Situ.

Resumo: *O abrigo Jaguariaiva 1 está localizado nas proximidades da cidade de Jaguariaiva, Estado do Paraná, Brasil (dimensões 17x 21x5.20m, coordenadas UTM E 632 454 e N 7 315 244 e altitude 887m). É um abrigo de arenito com pinturas de pelo menos dois períodos diferentes. O mais antigo é de aproximadamente 7000 anos BP. A arte rupestre no abrigo Jaguariava 1 está sobre duas paredes e teto, no lado oeste de 0,5m até 1,90m de altura e no lado norte de 1,80m a 3,60m. O principal painel documentado do abrigo rochoso tem pinturas de animais e motivos reticulados. As mais antigas são figuras de cervídeos em vermelho chapado. As mais recentes são figuras esboçadas em castanho avermelhado preenchidas por linhas. As regiões com pinturas rupestres foram analisadas com dois sistemas portáteis de EDXRF, um empregando um tubo de raios X com alvo e filtro de Ag e outro com um tubo de raios X com alvo de W e filtro de Ag, ambos com detectores de diodo de Si PIN, acondicionados em um mecanismo projetado especialmente para o posicionamento do detector e do tubo, permitindo movimentos angulares e translações nos eixos XYZ do sistema de excitação detecção em relação à área de medida. Foram medidos elementos do Si ao Pb. Os espectros de Fluorescência de Raios X foram analisados usando o software AXIL-WinQXAS.*

Palabras Chave: *Fluorescência de Raios X; Portátil; Arte rupestre*

INTRODUCTION

Prehistoric art, as Pessis (2003) wrote, is the expression and the result of thematic choices, of technical achievements and imaginary staging performed by given ethnical groups. Rock art is a general term related to human symbolical marks on rock surfaces, and in this paper it will be discussed the rock paintings of Jaguariaíva I shelter, placed on Paraná State, south of Brazil, in a sandstone region with natural fields called "Campos Gerais", where the majority of Paraná shelters occured. Many other archeological sites were characterized near this rockshelter, specially of hunters and gatherers people and Jê indians ancestors, some with rock paintings related to different periods of human occupations in this region, of sandstones called Furnas Formation and Itararé Geological Group (Parellada, 2006). In Paraná State there are known about 100 rockshelters with paintings, the majority is on sandstones, discussed by Laming & Emperaire (1956), Laming-Emperaire (1962, 1968), Blasi (1970, 1972), Chmyz (1976), Maranhão & Parellada (1991), Blasi et al. (1991, 2002), Parellada & Gottardi Neto (1991), Parellada (1993a,b, 1997, 2003, 2006), Gottardi Neto (1995), Lima & Justo (2002), Arnt (2002), Cavalheiro (2003), Naumes & Spoladore (2005), Silva, Melo & Parellada (2005) e Silva, Parellada & Melo (2007), and a recent synthesis by Parellada (2009). The pigments that have been added to the rock surface, and possible binders, could be a variety of organic and inorganic materials, the most commonly and easier to identify are the mineral pigments like hematite, manganese, malachite, gypsum, limonite, clays and various oxides (Lage, 1997). Other materials, like wooden resins, blood and beeswax could also be applied to the rock. The rock art in Paraná could be associated with different groups: at least, the oldest ones are related to "Umbu" hunters and gatherers populations, and the more recent to the Itararé-Taquara ceramist group, of Jê linguistic family. In this case its is very interesting to test other pigments possibilities than the usual inorganics ones, such as the organic pigments usually employed by these indigenous groups and already know in the literature, like the bark of araucaria pine tree, charcoal, some kind of lianas, honey and others (Fernandes, 1941; Parellada, 2008). However, the majority of the rock art in Paraná are over rocks, which usually does not show this behavior, and our knowledge about Jaguariaíva Rock Art pigments is still poor. The investigation of pigments is very important because it can be useful to stylistic analysis and introduces new aspects in the research on the raw material used in these paintings. Three main issues are: pigments and technology operational chain, the steps in the implementation of existing paintings and the possible existence of connections between different paintings. Knowledge of pigments is very important also to know how the paintings interact with the local environment and can thus determine the best strategies for managing and conserving these sites (Ford et al., 1994). In situ sampling is done only in very special situations. So, non-destructive in situ examinations, as performed by PXRF, are very suitable for the conservation and management of rock art sites. The identification of pigments can be done with fragments of the rock with paintings which, in the past, had come off the wall and were recuperated in archaeological digs. That is not as frequent as desirable. There are many non-destructive methods for the analysis of rock art paintings (Zoppia et al., 2002), but, until now, in Brazil, the analyses of the rock paintings pigments are made taking samples to the laboratory both for destructive or non-destructive methodologies. Here it is presented one test-program of the potentialities of a "home made" portable EDXRF for the paintings in situ characterization, performed at Jaguariaíva 1 rockshelter.

Analytical approach

Measurements were performed *in situ* and non-destructively employing a portable EDXRF system (Appoloni et al., 2007) with an X-ray tube (Ag filter and target), a Si-PIN photodiode detector (5mm^2, 680μm, 0.5 mil Be Window, 149eV FWHM for the 5.9keV line of ^{55}Fe), standard X-ray spectrometry electronic chain and a special designed mechanical system for the detector and X-ray tube positioning, that enables angular and XYZ movements of the excitation-detection system respect to the measurement area. A portable stabilized electric generator sustained the whole system. Excitation-detection time was 300 s for each measurement. The diameter of each region measured by this PXRF system was approximately 3 to 5mm. All the elements were analyzed by it's Kα line intensities, except Pb, which Lα line was employed. Only net areas greater than three sigmas above mean

background level were accepted for the analysis. X-Ray Fluorescence spectra were acquired with PMCA software. Spectra analysis was performed with the WinQ-XAS software (International Atomic Energy Agency, 2002).

JAGUARIAÍVA 1 ROCKSHELTER

Jaguariaíva 1 rockshelter is located in the Jaguariaíva city region (Figures 1 and 2), Paraná State, Brazil (17x 21x5.20m size, E 632 454 e N 7 315 244 UTM coordinates, SAD 69, 22 Zone, and 887m high). The studies started in 2002 by Paranaense Museum team, in a Archaeological Rescue Program for the implantation of 230kV Transmission Lines between Bateias and Jaguariaíva, sponsored at that time by the Energy Company of Paraná/ COPEL (Parellada, 2006). The shelter is 250m far of 293 energy tower, 300m of Guatelar channel related to Jaguariaíva river, part of Itararé Hydrographic Basin. Nowadays this shelter is in a reforestation of pine trees (*Pinus* sp), in the future could be inside a new State Park (since 2007 the government was studying the creation of Butiá Park). Since 2002 till 2005, many archaeological sites were studied in this area, and in Jaguariaiva I shelter was done topographic maps, documented rock paintings and excavated the shelter floor on twelve days, with two 1x1m close squares, one till 1,27m depth and another till 0,92m, in front of the main panel. The stratigraphic analysis showed six different levels of human occupations. The more recent has glasses and iron pieces, and a coin of the end of XIX century. There are tree subsequent occupations of ceramists and farmers Itararé-Taquara people, related to south Jê linguistic family, and the two oldest are related to hunters and gatherers that could be related to Umbu Archaeological Tradition. The rock paintings of Jaguariaíva I sandstone shelter are related to, at least, two different periods. The oldest one is around 7.000 years BP, the next moment of paintings could be around 2.000 years BP, as another dated and related Paraná rockshelter called Janela suggests (Parellada, 2009). Rock art in the Jaguariaíva 1 shelter is on part of the walls and ceilings of two sides: the majority is on the west positioned from 0.5m until 1.90m high, and at north side some geometric signs and barred lines that were placed from 1.80m to 3.60m at north. The main documented panel of the shelter, on west side, has a superimposition of paintings of animals and lattice motifs placed over deer figures infilled with red, possibly related to hunters and gatherers. The more recent are reddish brown outline figures filled by straight lines, which could be related to Jê people. On north side there are many barred lines in red (six or seven lines), and emblematic figures with many dots in yellow and brown, those seem to be related to the second period of painters, the Jê people. In Jaguariaíva 1 rockshelter there are some paintings with geometric forms that could be humans or animals figures, as a hypothesis. Also different styles of paintings can be observed. The colours of the paintings are yellow, red, brown and black. The majority are animal figures, like deer, and a big variety of reds, light to dark, that could also represent different pigments or variations of conservation and age of each painting. Figure 1 shows the location of Jaguariaíva city region. Figure 2 presents the Jaguariaíva 1 rockshelter. Figure 3 shows some rock paintings of the shelter. Figure 4 shows a painting area and the PXRF system positioned for measurement.

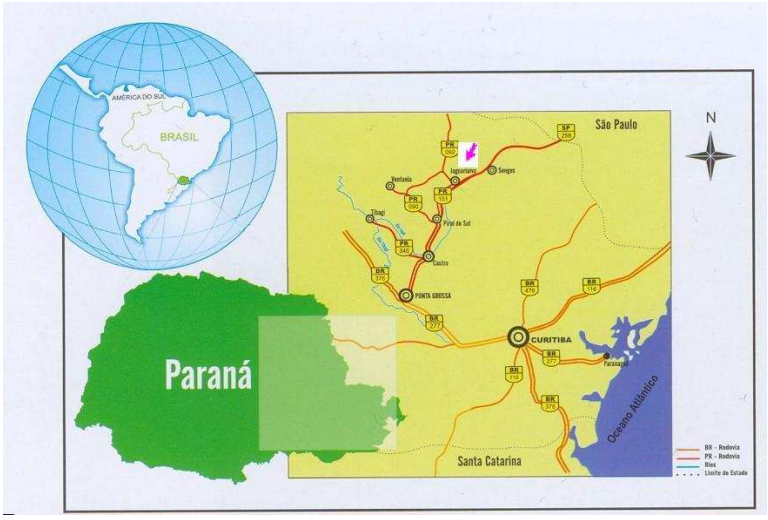

FIGURE 1. Location of Jaguariaíva city region.

FIGURE 2. Jaguariaíva 1 rockshelter (left) and details of the entrance at the west side (right).

FIGURE 3. Three rock paintings of Jaguariaíva I shelter.

FIGURE 4. A rock painting area and the PXRF system positioned for measurement.

RESULTS

Nineteen regions of the west side wall were analyzed, with measures in different paintings, and in some of them, like one infilled deer (measures 1 to 4) in many parts of it: head, neck and two points of the body. Other paintings of Jaguariaíva shelter were also measured: animals with other characteristics, barred lines, lattice motifs, and little circles that form figures. White sandstone regions without pigment and paintings with red and yellow pigments were measured. Elements from Si to Pb were identified. The last one could be due to atmospheric pollution of the nearby road. Ni and Cu are contaminants of the system. Both red and yellow pigments have Fe as

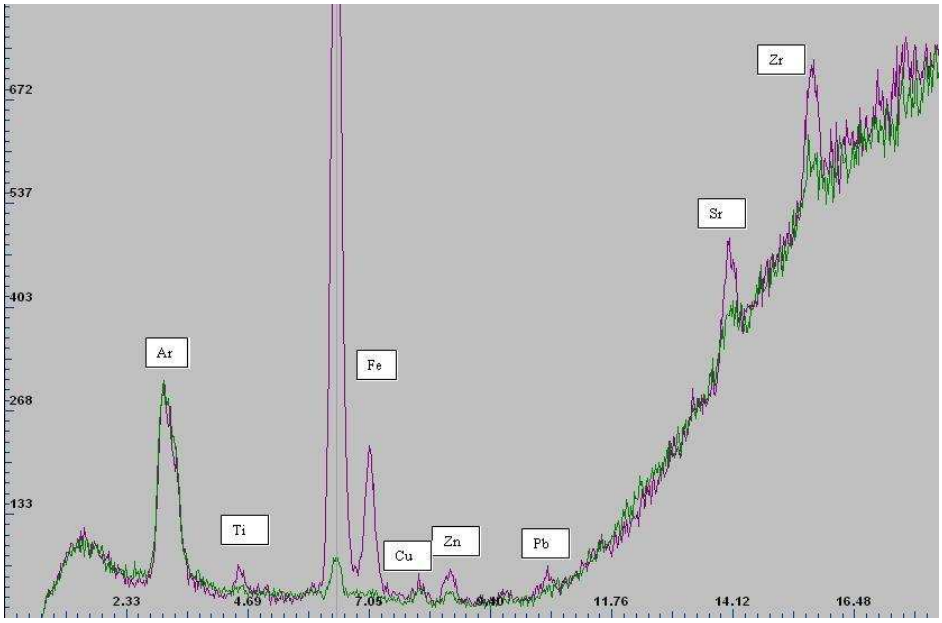

FIGURE 5. Energy spectrum (counts versus energy keV) of the rock (green line) and of a near red colored rock painting (lilac line).

strong key element, clearly indicating use of raw materials with iron oxides of these colors. Sandstone regions presented Ca, Ti, Mn, Fe, Cu, Zn, Sr and Zr. Figure 5 shows the energy spectrum (counts x energy keV) of the rock (green line) and of a near red colored picthograph region (lilac line). Table 1 presents the elements peak areas of the spectra at Figure 5.

Pigment key element is Fe, so, it is an iron oxide based pigment, which raw material also includes other elements currently found in soil as Ti, Mn and Sr. Figure 6 shows the energy spectra (counts versus energy keV) of the white rock (green line spectrum), the near yellow painting of a deer figure (lilac line spectrum) and a red line (blue line spectrum). The yellow painting is well characterized by Fe, so the pigment must be made of iron oxide. Table 2 presents the elements peak areas of the spectra at Figure 6. The Fe ratio between the white rock and the yellow area is 2.1. As the red line was very thin, its composition resulted similar to the rock one. Ca and Ti are clearly present In the white rock.

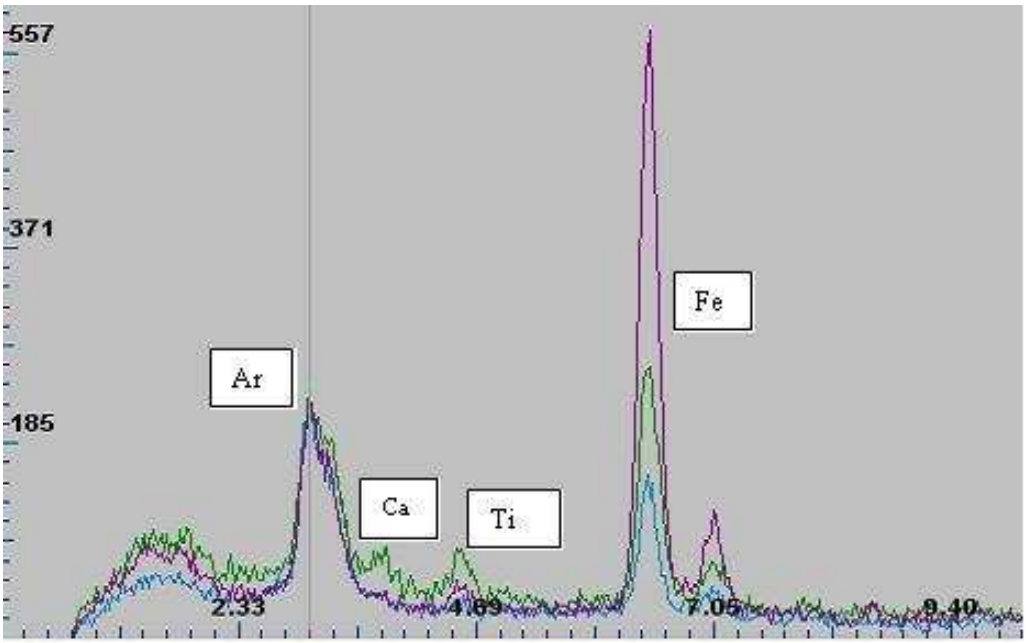

FIGURE 6. Energy spectrum (counts versus energy keV) of the white rock (green line spectrum), the near yellow painting of a deer figure (lilac line spectrum) and a red line (blue line spectrum).

Element	Rock area			Red figure area		
	Counts	error	background	Counts	error	background
Ar	3221	99	1197	3213	89	1063
Ti	-	-	-	325	39	783
Mn	158	35	714	-	-	-
Fe	**890**	**94**	**710**	**15327**	**129**	**583**
Ni	-	-	643	146	30	611
Cu	264	45	627	239	32	614
Zn	223	40	666	462	35	633
Sr	1116	177	12467	1867	123	675
Zr	1207	519	19119	1662	367	11917
Pb	-	-	-	126	34	967

TABLE 1. Elements peak areas of the same spectra presented at Figure 5. Fe results are highlighted.

TABLE 2. Elements peak areas of the same spectra presented at Figure 6.

	White rock		Yellow area		Red area	
Element	Counts	Error	Counts	Error	Counts	Error
Ar	2019	82	2308	76	2267	84
Ca	406	52				
Ti	490	45	198	34		
Fe	3163	69	6756	91	1630	53
Sr	1353	121	1021	172	811	156
Zr	1559	216	3513	786	2366	520

CONCLUSIONS

The obtained results indicate that the possibility of an organic pigment, as mentioned before, due to the Itararé-Taquara groups tradition knowledge, can be discarded. Results strongly indicate that the portable EDXRF equipment used offer a viable alternative for *in situ* rock art analysis. This is an encouraging result employing portable equipment and an *in situ* non-destructive analysis, which is a very cheap, easy and fast method compared to the others currently employed in this area. Due to the difficult of access to the rock paintings, in six hours of work, with a team trained in the use of the equipment, nineteen spectra were measured. The knowledge about the pigments of Jaguariaíva I shelter will help the understanding of techniques and process to paint over the rock were used, the changes that occurred through the time, and some aspects that also will aid the selection of strategies of heritage management and conservation. Other rockshelters in Paraná State with paintings and petroglyphs that have special interest of the Archaeology Departament of Paranaense Museum will be studied with this methodology. In these further studies it is planned to work also with a Raman portable system, together with the PXRF equipment, in order to provide information about the chemical composition of the compounds, in special the organic ones.

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