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In-situ ^{57}Fe Mössbauer characterization of iron oxides in pigments of a rupestrian painting from the Serra da Capivara National Park, in Brazil, with the backscattering Mössbauer spectrometer MIMOS II

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Abstract It is reported the use of the miniaturized portable ^{57}Fe Mössbauer backscattering spectrometer MIMOS II to perform *in situ* measurements in the archaeological site known as Toca do Boqueirão do Sítio da Pedra Furada (BPF), in Serra da Capivara National Park, in order to specifically examine shades of dark red pigments and compare their differences relatively to the light red part of the same painting. The hyperfine Mössbauer parameters reveal that the dark red area of the rupestrian painting is composed of three populations of hematite and of a small proportion of maghemite, whereas the light red are of the same painting contain hematite mixed with a small proportion of maghemite and a (super)paramagnetic Fe^{3+}. The Fe content in the dark red area from the rupestrian painting is of approximately twice the amount in the light red of the same prehistoric graphism. The corresponding analysis of red ochre sample collected in the excavation of these archaeological site exhibited two populations of hematite and also a small proportion of maghemite.

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1 Introduction

The archaeological site known as Toca do Boqueirão do Sítio da Pedra Furada (BPF), located in the Serra da Capivara National Park (Southeast Piauí, Brazil; Fig. 1), is a sandstone shelter decorated with an exceptional collection of prehistoric rupestrian paintings (Fig. 2). Systematic excavations, by Niéde Guidon and her colleagues of the FUMDHAM (acronym for the name in Portuguese: "Fundação Museu do Homem Americano", literally meaning "Foundation Museum of the American Man") since 1973, evidenced in this archaeological site several well-structured hearths associated with abundant lithic industry (tools) in different levels, dated as being from at least 100,000 years before present (BP) [1–4].

The rupestrian paintings of the Serra da Capivara National Park were reportedly dated with a combination of different techniques used on samples of several archaeological sites and the data available up to now suggest that some paintings date to around 30,000 years BP [4–7].

The archaeometry has been used as an important tool for the analysis of several types of ancient materials of archaeological sites from Piauí [8–15].

Detailed stratigraphic and mineralogical descriptions of samples of pigment layers from prehistoric paintings of the Serra da Capivara National Park were first reported on basis of chemical and mineralogical data obtained by various methods, including X-ray fluorescence spectroscopy, infrared spectroscopy, X-ray diffraction and scanning electron microscopy [15]. From those previous analyzes, we know that the red pigments are mainly composed of hematite (α-Fe_2O_3); the yellow does contain mainly goethite (α-FeOOH); the white, gypsum ($CaSO_4.2H_2O$) or kaolinite ($Al_2Si_2O_5(OH)_4$); the grey is a mixture of kaolinite and hematite, and the black is derived from charcoal more likely from burnt plants or parts of animal carcasses.

In this work, we used the miniaturized portable ^{57}Fe Mössbauer backscattering spectrometer MIMOS II [16] to perform *in situ* measurements in a rupestrian painting of the Toca do Boqueirão do Sítio da Pedra Furada site, in order to specifically examine shades of dark red pigments and compare their differences relatively to the light red part of the same painting. It was also analyzed a red ochre sample (dated from 8000 years BP) collected in an excavation in this archaeological site.

2 Materials and methods

The Mössbauer spectra were collected *in situ* at room temperature (∼298 K) with a miniaturized portable ^{57}Fe Mössbauer backscattering spectrometer MIMOS II in constant acceleration setup and a ^{57}Co/Rh gamma-ray source with nominal activity of about 35 mCi, and Doppler velocities ranging between approximately ±11.66 mm s^{-1}. Mössbauer isomer shifts are quoted relatively to an α-Fe foil at room temperature. The experimental data were fitted with Lorentzian functions by least-square fitting with NORMOS™ − 90 and winNORMOS for IGOR Pro version 6.1 computer programs.

In situ measurements of X-ray fluorescence of the dark red and light red areas of the rupestrian painting were made with an energy dispersive X-ray fluorescence spectrometer,

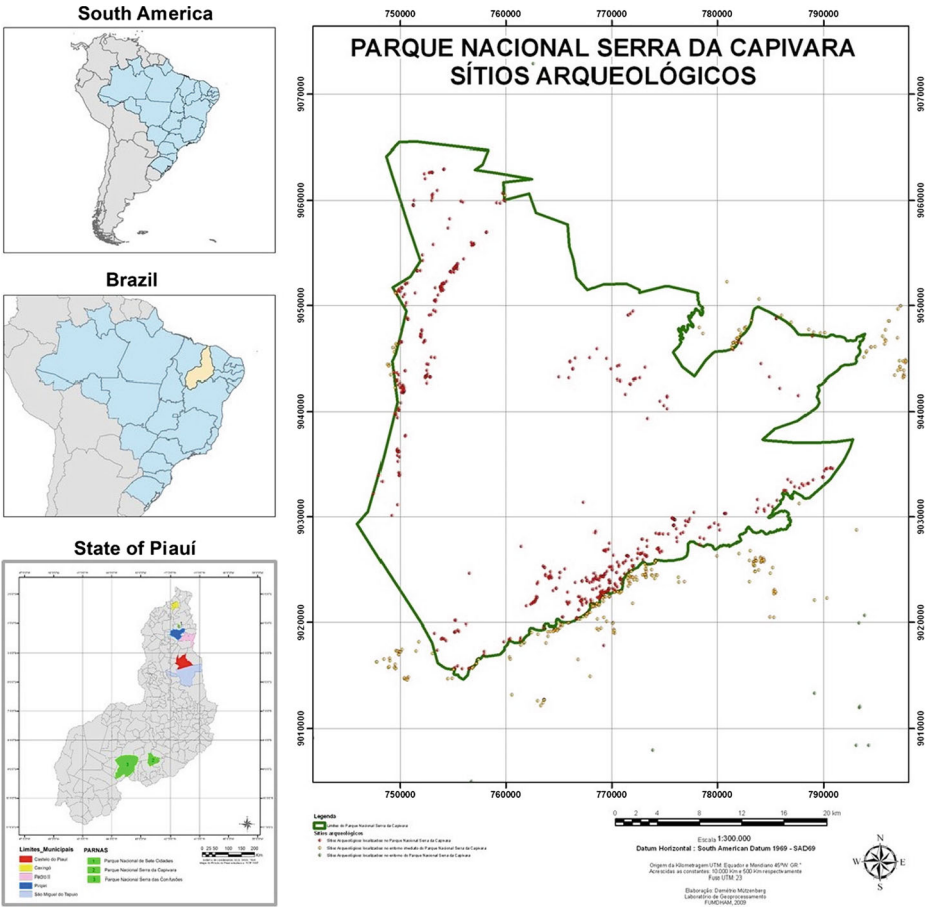

Fig. 1 Map of the Serra da Capivara National Park

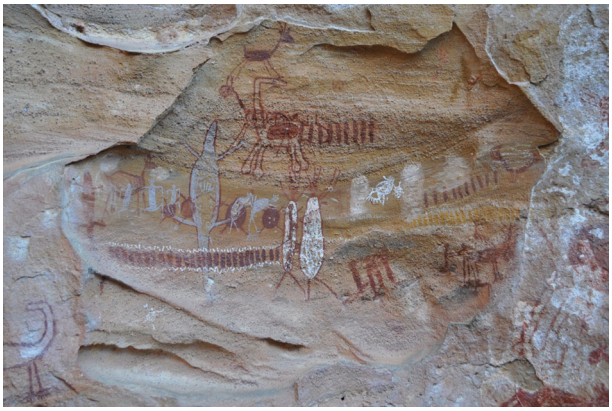

Fig. 2 Detail of polychromatic rupestrian paintings in a niche at Toca do Boqueirão do Sítio da Pedra Furada, showing anthropomorphic and zoomorphic figures, including crocodiles, a puma, deer and llamas

Table 1 Chemical composition of the dark red and light red areas of the rupestrian painting as determined with portable X-ray fluorescence spectroscopy

	Oxides content/mass %	
	Dark red	Light red
Fe_2O_3	41.2(1)	19.5(1)
SiO_2	33.1(1)	37.8(1)
Al_2O_3	19.3(5)	28.4(2)
K_2O	3.35(1)	9.3(1)
CaO	2.08(1)	4.06(1)
TiO_2	0.49(1)	0.50(1)
MnO	0.25(1)	0.25(1)
SnO_2	0.12(1)	
SrO	0.11(1)	0.11(1)

The number in parentheses are uncertainties over the last significant digit, as provided by the spectrometer

Oxford X-MET5100, with 45 kV X-ray tube and Silicon Drift Detector (SDD). Data were collected without vacuum.

The X-ray fluorescence analysis of the red ochre sample was made with an energy dispersive X-ray fluorescence spectrometer, Shimadzu EDX-720, with rhodium tube and silicon-lithium detector. Data were collected under vacuum of 40 Pa with collimator of 10 mm.

3 Results and discussion

The results of the elemental chemical composition determined by EDXRF showed that the Fe contents (as Fe_2O_3) in the rupestrian painting are of approximately 41.2(1) mass % (dark red area) and of 19.5(1) mass % (light red area; Table 1). The Fe content in the red ochre sample is of 52.26(1) mass % (Table 2).

Mössbauer spectra (Fig. 3) and corresponding hyperfine parameters (Table 3) indicate that the dark red area on the rupestrian painting is composed of three populations of hematite (α-Fe_2O_3), with different mean particle sizes, reflecting fractions of particles undergoing different degrees of collective magnetic excitation [17], and of a small proportion of maghemite (γ-Fe_2O_3) (a previous distribution of magnetic hyperfine field indicated the existence of these three main populations of hematite and of the maghemite supported the final fitting model of the experimental data). A remarkable point is that the hematite with magnetic hyperfine field, B_{hf}, of 51.9(2) tesla and quadrupole shift, ε, of -0.22(5) mm s^{-1} correspond to a presumably well-crystalline structure [11, 18]. The lighter red area of the same painting, on the other hand, contains hematite mixed with a small proportion of maghemite and a (super)paramagnetic Fe^{3+}, probably also hematite in very small particles or paramagnetic iron in the structure of silicates.

The distribution of particle sizes may indeed impart some change in the purple color of hematite, as it was reportedly found by Marshall et al. [19] for ochre samples. This effect may be also, at least in part, an interpretation for the observed differences in color of the painting. Moreover, it should be additionally mentioned that the corresponding analysis of

Table 2 Chemical composition of the red ochre as determined with X-ray fluorescence spectroscopy

	Oxides content/mass %
Fe_2O_3	52.26(1)
SiO_2	29.0(1)
Al_2O_3	15.3(1)
P_2O_5	0.97(2)
TiO_2	0.74(1)
K_2O	0.64(1)
SO_3	0.55(1)
BaO	0.32(2)
Cr_2O_3	0.09(1)
MnO	0.07(1)
CaO	0.02(1)
CuO	0.02(1)
ZrO_2	0.01(1)
SrO	0.01(1)

The number in parentheses are uncertainties over the last significant digit, as provided by the spectrometer

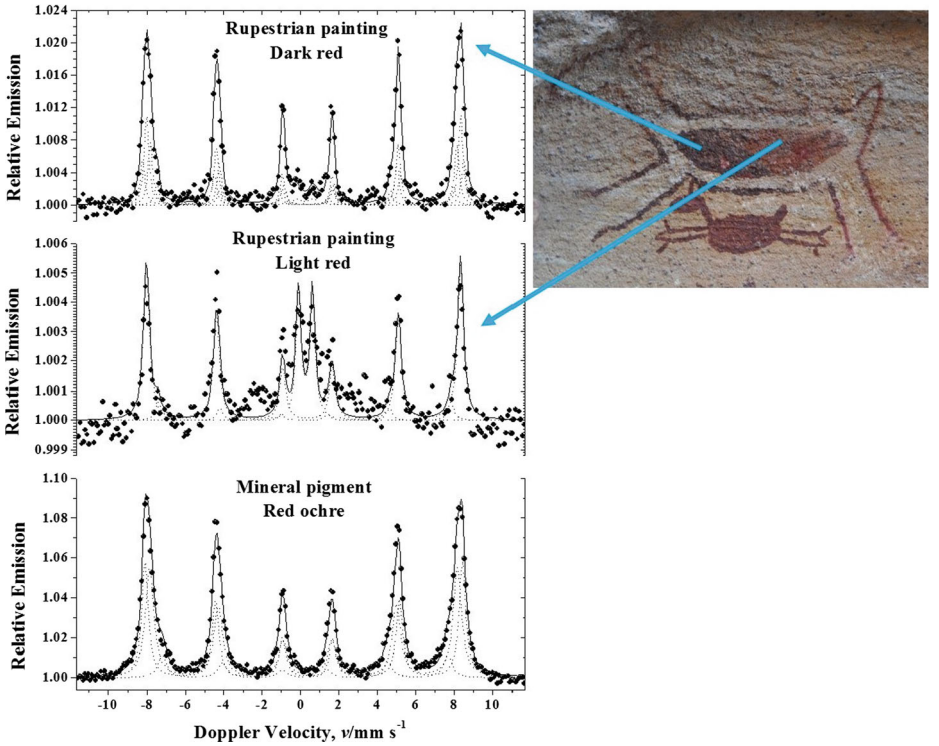

Fig. 3 ^{57}Fe Mössbauer spectra for the dark red and light red areas of the rupestrian painting and for the red ochre sample

Table 3 Values of 298 K-Mössbauer fitted parameters for the dark red and light red areas of the rupestrian painting and for the red ochre sample

Sample	Fe site	δ/mm s^{-1}	ε, Δ/mm s^{-1}	Γ/mm s^{-1}	B_{hf}/T	RA/%
Dark red	Hematite	0.391(4)	−0.237(9)	0.27(1)	49.58(8)	26(1)
	Hematite	0.371(4)	−0.196(7)	0.27(1)[b]	50.78(7)	39(1)
	Hematite	0.36(3)	−0.22(5)	0.27(1)[b]	51.9(2)	20(1)
	Maghemite	0.34(2)	0*	0.27(1)[b]	47.90(8)	9(1)
	Fe^{3+} doublet	0.34(5)	0.85(8)	0.6(1)		6(1)
Light red	Hematite	0.369(5)	−0.20(1)	0.37(2)[b]	50.78(4)	68(2)
	Maghemite	0.33(5)	0[a]	0.37(2)[b]	47.3(4)	8(1)
	Fe^{3+} doublet	0.373(8)	0.72(1)	0.31[a]		24(1)
Red ochre	Hematite	0.364(3)	−0.204(7)	0.53(1)[b]	49.76(7)	49(4)
	Hematite	0.373(3)	−0.197(6)	0.41(2)	51.31(5)	40(4)
	Maghemite	0.34(1)	0[a]	0.53(1)[b]	46.2(1)	11(1)

δ = isomer shift relative to αFe; ε = quadrupole shift; Δ = quadrupole splitting; Γ = line width; B_{hf} = magnetic hyperfine field; RA = relative subspectral area. The number in parentheses are uncertainties over the last significant digit, as it was estimated from the least-squares fitting algorithm

[a]Fixed parameter during least-squares fitting convergence

[b]Linked parameter during least-squares fitting convergence

the collected red ochre (the piece that was assumed to has been used to paint the archaeological panel) exhibited also two populations of hematite and also revealed a small proportion of maghemite as in the painting pigment.

4 Conclusions

The hyperfine Mössbauer parameters reveal that the dark red area of the rupestrian painting from the Toca do Boqueirão do Sítio da Pedra Furada is composed of three populations of hematite and of a small proportion of maghemite, whereas the light red are of the same painting contain hematite mixed with a small proportion of maghemite and a (super)paramagnetic Fe^{3+}. The Fe content in the dark red area from the rupestrian painting is approximately twice the amount in the light red of the same prehistoric graphism.

The corresponding analysis of the collected red ochre exhibited two populations of hematite and also a small proportion of maghemite. The painting pigment and the iron oxide-enriched clayey precursor (ochre) do contain the weak ferromagnetic (at room temperature) hematite and the ferrimagnetic maghemite, both ferric iron oxides.

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