

Iron-bearing minerals of a rupestrian painting from the Manantial Solís site, Cardiel Lake, Patagonia, Argentina

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Abstract The archaeological site *Manantial Solís* is located on shores of the Cardiel Lake, Santa Cruz Province, Patagonia, Argentina. The main characteristic of this site is the occurrence of 251 rupestrian paintings, namely abstract figures, anthropomorphic and zoomorphic motifs, painted in different hues of red, but also in yellow, orange, pink, violet and white; these paintings are often formed by overlapping pictorial motifs. The basaltic rock-wall supporting these graphisms has been naturally degraded and, as a consequence, covered with saline efflorescence. The chemical and mineralogical analyses of a micro-sample from a red rupestrian painting were made in the laboratory by (i) energy dispersive X-ray fluorescence; (ii) CHN elemental analysis and (iii) ⁵⁷Fe transmission Mössbauer spectroscopy at 298 K and 110 K, in an effort to identify the main iron-bearing minerals composing the painting pigments. The stratigraphy of the paint layer was investigated on a polished cross-section. From the Mössbauer spectra of this red painting, two sextets assignable to hematite ($\alpha\text{Fe}_2\text{O}_3$) were identified. The Fe^{3+} central doublet is assumed to

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be due to superparamagnetic phases, more likely as iron (oxyhydr)oxides (likely including some goethite, αFeOOH) in very small particles and paramagnetic iron in the crystalline structure of aluminosilicates. The Fe^{2+} doublet was interpreted as being due to the basalt rock support of this prehistoric painting.

Keywords Prehistoric pigment · Hematite · Mössbauer spectroscopy · Archaeometry

1 Introduction

The archaeological site *Manantial Solís* (picture of the site area, Fig. 1) is located on shores of the Cardiel Lake, Santa Cruz Province, Patagonia, Argentina [1]. The main characteristic of this site is the occurrence of 251 rupestrian paintings (Fig. 2), namely abstract figures, anthropomorphic and zoomorphic motifs, painted in different hues of red, but also in yellow, orange, pink, violet and white; these paintings are often formed by overlapped pictorial motifs [1]. The basaltic rock-wall supporting these graphics has been naturally and continuously degraded and, as consequence, covered with saline efflorescence. The ancient inscriptions are distributed for about 1 km in length. Dating of an archaeological level of the *Manantial Solís* site provided a radiocarbon age for the human occupation of the area as being of $1,140 \pm 40$ years before present (BP) [2, 3].

Results of the archaeometric analysis of a microsample of red rupestrian painting from the archaeological site *Manantial Solís*, with the main purpose of contributing to a better understanding of the main physical, chemical and mineralogical characteristics of the prehistoric paint layer is reported. The ^{57}Fe Mössbauer spectroscopy is used as a non-destructive central analytical technique on the identification and quantification of iron-bearing species in materials from the archaeological cultural heritage.

2 Materials and methods

The X-ray fluorescence measurement of the sample was made by using an energy dispersive X-ray fluorescence spectrometer Shimadzu EDX-720 with a rhodium tube and silicon-lithium detector. Data were collected under vacuum, at 40 Pa, with a collimator of 3 mm.

The carbon, hydrogen and nitrogen contents were determined with a PerkinElmer 2400 Series II CHNS/O elemental analyzer.

The Mössbauer spectra were collected at room temperature (~ 298 K) and 110 K with a conventional transmission ^{57}Fe Mössbauer spectrometer setup in the constant acceleration mode and a $^{57}\text{Co}/\text{Rh}$ gamma-ray source with nominal activity of about 20 mCi. Data were stored in a 512-channel MCS memory unit, with Doppler velocities ranging between approximately ± 10.4 mm s^{-1} . Mössbauer isomer shifts are quoted relatively to an αFe foil at room temperature. The experimental data were fitted with Lorentzian functions by least-square fitting with WinNormosTM for Igor ProTM software version 6.1. The stratigraphy of the paint layer was investigated on a polished cross-section.

3 Results and discussion

Data about the stratigraphy, as drawn from a selected polished cross-section from this rupestrian painting, revealed that the thickness of the thin red layer range from ~ 3 to ~ 8 μm



Fig. 1 A view of the archaeological site *Manantial Solís*



Fig. 2 Details of the rupestrian paintings of the archaeological site *Manantial Solís*

(Fig. 3). The thickness of the red paint layer is relatively uniform and in some areas overlap to saline efflorescence.

Results of the elemental chemical composition (Table 1), as determined by X-ray fluorescence, show that the iron content (expressed as Fe_2O_3) in the sample of red rupestrian painting is 12.71(2) mass%. The high contents of calcium, potassium, sulfur and phosphorus suggest that these chemical elements can be due to the saline efflorescence, as it has been reported for some Brazilian archaeological sites [4, 5].

The carbon, hydrogen and nitrogen contents, as determined by elemental analysis of CHN, for the sample are 0.86(1), 0.09(1) and 0.51(1) mass%, respectively.



Fig. 3 Cross-section for the sample of rupestrian painting investigated evidencing the thickness of the thin red paint layer

Table 1 Chemical composition for the sample of red rupestrian painting, as determined by X-ray fluorescence spectroscopy

	Oxides content/mass%		Oxides content/mass%	
SiO ₂	42.97(1)	P ₂ O ₅	1.96(3)	
Al ₂ O ₃	18.75(2)	MnO	0.167(3)	
Fe ₂ O ₃	12.71(2)	SrO	0.092(1)	
CaO	12.14(2)	ZrO ₂	0.030(1)	
MgO	4.1(2)	Cr ₂ O ₃	0.028(2)	
TiO ₂	2.75(1)	NiO	0.016(1)	
K ₂ O	2.19(1)	NbO	0.004(1)	
SO ₃	2.11(2)			

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

From Mössbauer spectra (Fig. 4; corresponding hyperfine spectral parameters are presented in Table 2) for this red painting, two sextets assignable to hematite ($\alpha\text{Fe}_2\text{O}_3$; from the 110 K spectrum, the corresponding relative subspectral area, *RA*, totals 34.8%) were identified [5–8]. The corresponding fitted value of the quadrupole shift for one of two hematite subspectra appears to be indeed low. This low value might be due to the numerical fitting conditions. Experimental points are rather scattered. As usual for such archaeological samples, due to the small amount of the available sample, the resonant absorption lines are not intense enough to favor a better fitting. The Fe^{3+} doublet is assumed to be due to a superparamagnetic fraction, very likely either as iron (oxyhydr)oxides (including some goethite, αFeOOH) in very small particles or paramagnetic iron in the crystalline structure of aluminosilicates. If superparamagnetic the relaxation is not blocked down to 110 K. As no further

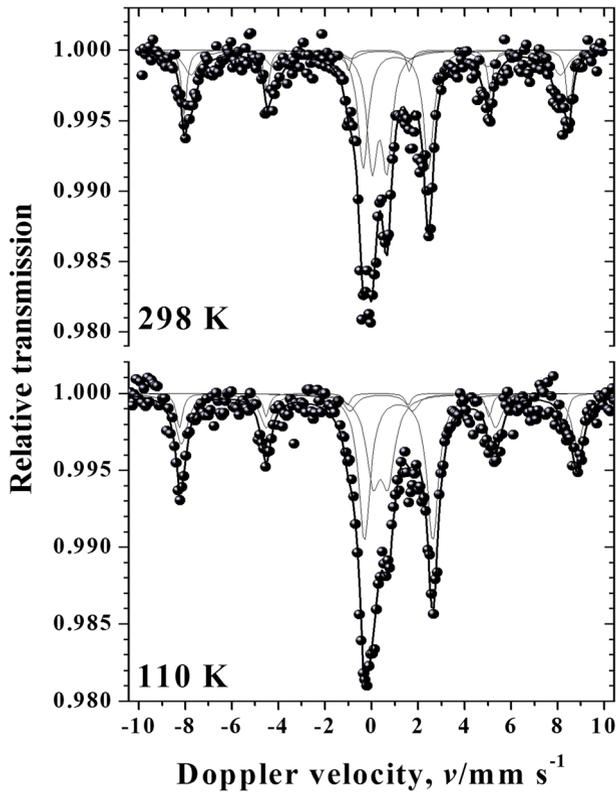


Fig. 4 ⁵⁷Fe Mössbauer spectra at 298 K and 110 K for the sample of *red* rupestrian painting

Table 2 Fitted Mössbauer spectral parameters for the sample of red rupestrian painting

Fe site	Temperature/K	$\delta/\text{mm s}^{-1}$	$2\epsilon, \Delta/\text{mm s}^{-1}$	B_{hf}/T	RA/%
Hematite	298	0.39(2)	-0.21(5)	49.2(3)	28.9(4)
Hematite		0.37(1)	-0.08(3)	51.3(1)	9.9(2)
Fe ²⁺		1.141(6)	2.81(1)		31.0(1)
Fe ³⁺		0.438(7)	0.64(1)		30.2(1)
Hematite	110	0.51(3)	-0.06(3)	52.8(2)	29.6(3)
Hematite		0.27(5)	-0.24(7)	51.3(3)	5.2(2)
Fe ²⁺		1.290(7)	2.94(1)		37.9(1)
Fe ³⁺		0.51(1)	0.64(2)		27.3(1)

δ = isomer shift relative to αFe ; 2ϵ = quadrupole shift; Δ = quadrupole splitting; B_{hf} = magnetic hyperfine field; RA = relative subspectral area. The numbers in parentheses are uncertainties over the last significant digit, as it was estimated from the least-squares fitting algorithm

attempt was made to collect spectra at lower temperatures than 110 K, the occurrence of such superparamagnetic phase could not be fully confirmed, at this stage of the work. The Fe²⁺ doublet (RA = 37.9%, from the spectrum at 110 K) is interpreted as being due to the basalt rock support of this prehistoric painting.

4 Conclusions

The archaeometric analysis of a sample of red rupestrian painting from the archaeological site *Manantial Solís* revealed that the hematite is the main iron oxide in the pigment imparting the red color to this archaeological painting on the basaltic rock wall. However, other iron-bearing species do occur, certainly as iron (oxyhydr)oxides in very fine particles and silicate minerals of the basaltic rock support.

The ^{57}Fe Mössbauer spectroscopy was used as a non-destructive nuclear technique and a decisively fundamental analytical tool on the identification and quantification of iron-bearing species in the archaeological sample here investigated.

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