# IRON COMPOUNDS IN BRAZILIAN PRE-COLUMBIAN PIGMENTS IDENTIFIED BY $^{57}$Fe MÖSSBAUER SPECTROSCOPY AND X-RAY POWDER DIFFRACTION

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## ABSTRACT

Mössbauer spectroscopy and X-ray powder diffraction have been used to identify iron compounds in pre-Columbian pigments, probably used for art decorating,collected from the oldest archaeological site of Early Man presently known in America at São Raimundo Nonato, in Northeastern Brazil. The iron compounds were idenfied as beeing alpha-Fe2O3 (haematite) with full Morin transition supressed and small particles of alpha-FeOOH (goethite).

## 1. INTRODUCTION

São Raimundo Nonato, Piauí, in the Northeast of Brazil, is famous due to the richness of pre-Columbian rupestral art, decorating its numerous rockshelters. Measurements of Carbon-14 data from charcoal have stablished a continuous chronology indicating human occupation of the site from 6,160 ± 130 years to 32,160±160

years B.P.[1].

In the site known as Boqueirão da Pedra Furada, one of 200 human painted rockshelters, a series of powders of different colours has been found in a way that may suggest their use as a raw material for the numerous drawings found on the walls of the rockshelters. They were found side by side in a probable human made arrangement besides the walls.

## 2. RESULTS AND DISCUSSION

Three samples have been selected to perform the Mössbauer and X-ray studies: a red powder, a light-red powder, and a yellowish powder. The spectra of sample # 1, red powder, recorded at room temperature, 200K, 80K, and 4.2K are dispayed in figure 1. The room temperature Mössbauer data with least-squares fitting, give $\delta$= .38mm/s, relative to metallic iron at room temperature, $\Delta q$ = -.22mm/s and a hiperfine field of 508kG. The sample has been identified as being haematite with full Morin transition suppressed, since at room temperature its quadrupole splitting should be around + .20mm/s.
The spectra of samples # 2 (light-red powder) and # 3 (yellowish powder), also obtained at room temperature, 200K, 80K and 4.2K are shown in figures 2 and 3. It is visible from figs. 2 and 3, that for both samples there exists a slight superparamagnetic relaxation. Through the fitted Mössbauer parameters we have identified the iron compounds in samples # 2 and # 3 as being haematite and small particles of goethite. Mössbauer parameters of magnetic components at 4.2K are listed in table I. The change in quadrupole splitting of haematite from -.21mm/s to -.16mm/s must correspond to a change in $\langle\theta\rangle$, since for the least-squares fitting we have assumed $\theta$=0. The X-ray powder diffraction patterns fully confirmed the Mössbauer results.

| INK | δ(mm/s)* | Δq(mm/s) | (H(KG) | ÁREA (%) |
|---|---|---|---|---|
| red | .49 | -.16 | 534 | 100 |
| light-red | .49 | -.16 | 534 | 54 |
| | .49 | -.26 | 502 | 46 |
| yellowish | .49 | -.16 | 534 | 26 |
| | .49 | -.26 | 503 | 74 |

TABLE I - Brazilian pre-Columbian ink Mössbauer parameters of magnetic components at 4.2K

*relative to metallic iron at room temperature

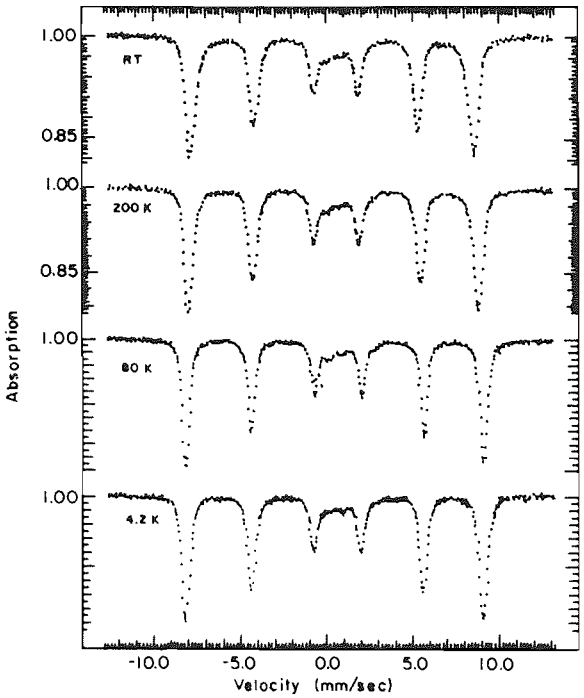


Figure 1 - Prehistoric Ink (Red Powder)

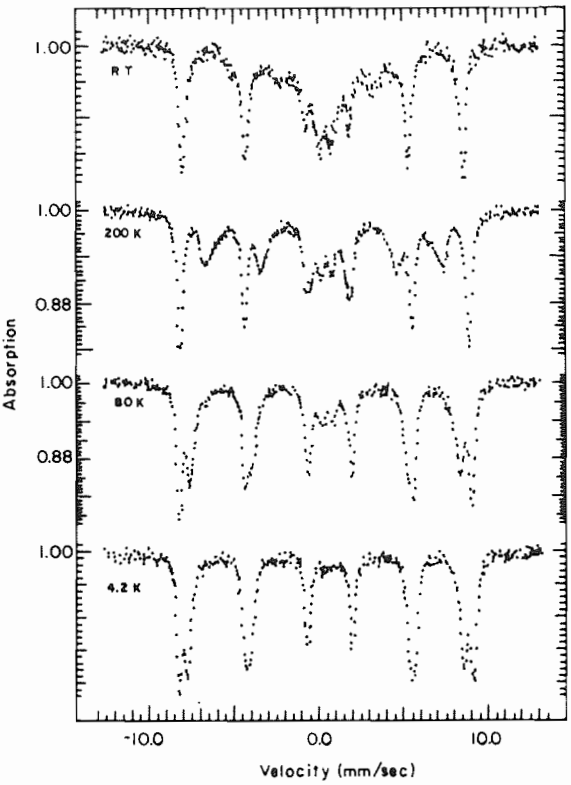


Figure 2 - Prehistoric Ink (Light Red Powder)

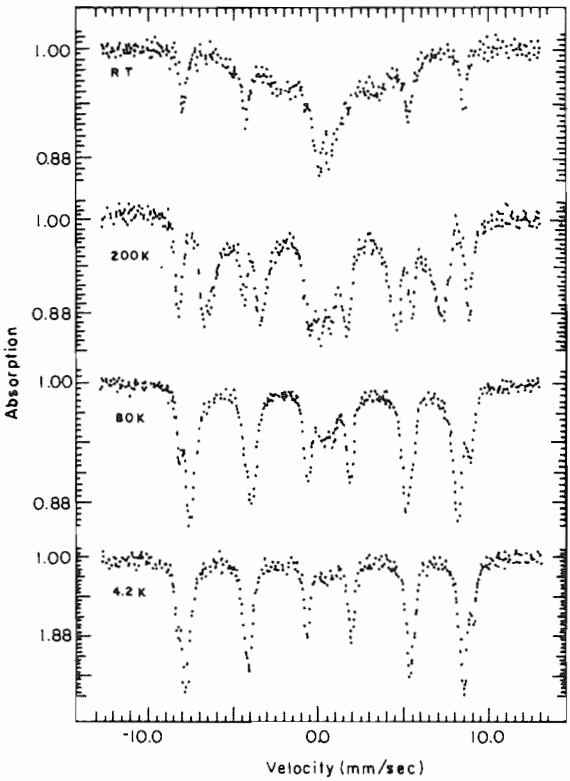


Figure 3 - Prehistoric Ink (Yellowish Powder)

REFERENCES

(1) N. Guidon and G.Delibrias, Nature 321, 769 (1986).