

Archaeometric characterization of prehistoric rock paintings, natural mineral pigments and saline efflorescences from archaeological sites

Luis Carlos Duarte Cavalcante

cavalcanteufpi@yahoo.com.br

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The present experimental work was devoted to the chemical and mineralogical characterization of prehistoric rock paintings, of mineral pigments and of saline efflorescences from archaeological sites located in the states of Piauí, Bahia and Ceará, in Brazil, and in the Perito Moreno National Park, in Argentina. Samples were investigated in the laboratory by several analytical techniques, including (i) ^{57}Fe transmission and conversion electron Mössbauer spectroscopy; (ii) grazing incidence X-ray diffraction; (iii) energy dispersive spectroscopy; (iv) scanning electronic microscopy; (v) powder X-ray diffraction; (vi) energy dispersive X-ray fluorescence and (vii) Fourier-transform infrared spectroscopy. Results revealed that the red paintings were basically prepared with hematite ($\alpha\text{-Fe}_2\text{O}_3$)-rich materials; the yellow paintings contained goethite ($\alpha\text{-FeOOH}$); the black paintings were essentially composed by carbon, presumably from charcoal (except the sample PCI-03, which was found to contain carbon together with hematite), and the gray painting was prepared with a mixture of carbon and aluminosilicate minerals. The iron oxides and oxyhydroxides appear as being of small particle sizes, high isomorphic substitution of different cations for iron and low crystallinity. Results related to saline efflorescence samples revealed the occurrence of chabazite ($\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24}\cdot 12\text{H}_2\text{O}$); partheite ($\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{15}(\text{OH})_2\cdot 4\text{H}_2\text{O}$); taranakite ($\text{H}_3\text{K}_3\text{Al}_5(\text{PO}_4)_8\cdot 18\text{H}_2\text{O}$); newberyite ($\text{MgHPO}_4\cdot 3\text{H}_2\text{O}$); kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$); brushite ($\text{CaPO}_3(\text{OH})\cdot 2\text{H}_2\text{O}$); gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$); $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$; potassium aluminum sulfate ($\text{KAl}(\text{SO}_4)_2$); $\text{K}_2\text{SO}_4\cdot 7\text{KHSO}_4\cdot \text{H}_2\text{O}$ and $5\text{ZnO}\cdot \text{Al}_2\text{O}_3\cdot \text{ZnSO}_4\cdot 15\text{H}_2\text{O}$. The red pigments contained predominantly hematite, together with quartz, kaolinite, illite and $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, whereas the yellow pigment contained goethite, quartz and kaolinite. The white pigment was composed mainly by illite and quartz.