KEYWORDS: ***Rock painting – Granite – Mineral pigment – Painting colour***

CHARACTERISATION OF MATERIALS AND TECHNIQUES USED IN MEXICAN ROCK PAINTINGS

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Abstract. The aim of this investigation was to determine the physicochemical characteristics, the microstructure and texture of the polychrome paintings found on rocks encountered in the mountainous, arid zones of Baja California, Mexico. Tiny painting samples were collected and analysed by SEM, EDS and FTIR techniques. The painters used four main colours: red, black, yellow and white. The paint raw materials are mostly mineral pigments: kaolin, calcite and gypsum for white; hematite for red; ochre or limonite for yellow; and charcoal from burnt wood or calcined bones for black. These are all encountered in the painters' habitat, and water was used as a diluent and/or binder. The dry paint, of 100% solids, has been converted into a dense, hard layer, embedded into the grainy, rough, porous granite rock surface. The analysis of the paint composition permits inferences about the techniques used by the ancient painters, which can be now applied for restoration and preservation of this important cultural heritage.

Introduction

The ancient paintings of Baja California constitute an important contribution to the national, historic and cultural patrimony of Mexico (Bendimez 1989; Crosby 1997; Gutierrez 1994, 2003; Serrano 2003). The first stage of the work described here was devoted to the examination and recording of the rock paintings of the archaeological site El Vallecito in the village La Rumorosa, located in a narrow fluvial valley featuring large granite rocks emerging from the sandy soil (Bendimez 1999).

The minerals were collected, ground and sometimes heated to change their tone. This explains the presence of yellow traces made with limonite obtained after hydration of haematite. This reaction is easily reversed by heating, producing the orange or orange-reddish colours observed in the paintings at the Cueva del Indio. By mixing with water, a spreadable paste or thick slurry was produced, which was applied with the fingers for lines, or with a piece of animal skin for figures, respectively. Pre-Historic man utilised rock-shelters to produce the coloured mural paintings, using wet-ground mineral pigments (Anon. 1996). Two 'fantastical' rock paintings depicting 'humans' are presented in Figures 1 and 2.

Materials and methods

The paintings of El Vallecito as well as many other rock paintings in the peninsula of Baja California were done on the surface of granitic rock; an igneous, hard rock with a coarse or medium-grained texture, rich in quartz and feldspar (Chalmin et al. 2003; Pappalardo 1999). The ancient painters took advantage of the natural, exfoliated, rough surface, with minute cracks, voids and hollows for the mechanical anchorage of their mineral-based paint applied as a paste or slurry.

Painting samples coloured red, orange-red, black and white, with an area of approximately 10 mm^2, were collected from several sites in El Vallecito and analysed. The samples detached from the painted rock walls contain granitic material on their back, due to the adherence of the paint to the rough surface. They were covered with a glass plate on the painted area and two other plates were used to fix the sides. After that, the bottom of the samples was polished in a grinding machine to obtain a flat surface, which facilitates their placing in the instruments during the scanning electron microscopy (SEM) and energy disperse x-ray spectroscopy (EDS) analyses. SEM analyses were performed on the samples to identify the materials' morphology. In parallel, EDS analysis were carried out

Figure 1. *Rock painting at El Vallecito, Baja California, called 'El diablito'.*

Figure 2. *Rock painting at El Vallecito, Baja California, called 'El hombre enraizado'.*

to obtain information about the chemical composition (Zoppi 2002). To detect the presence of organic components in the paint, Fourier transform infrared spectroscopy (FTIR) technique with an attenuated total reflectance (ATR) device was used to analyse the solid surface directly and as powder.

A simulation of the painting technique was done at the Materials and Corrosion Laboratory by collecting mineral pigments in the field, preparing the paint as thick, soft paste or semi-liquid slurry and applying it on a granitic rock, brought from the desert nearby.

Results and discussion

SEM and EDS analyses of painting samples indicate the presence of mineral pigments composed of inorganic oxides and salts (Table 1) and the absence of organic matter residues. White minerals (calcite, gypsum and kaolin) were used as support, or as colour diluents for the coloured pigments (Table 1).

SEM and EDS analyses of a red painting sample from El Vallecito shows the use of a mixture of iron oxide pigment, gypsum and calcite (Fig. 3). The presence of three characteristic peaks can be observed at 6.4, 7.05 and 0.7 KeV, corresponding to Kα, Kβ and Lα x-ray emitted by iron atoms in the haematite pigment, during the EDS analysis. The presence of calcite

PIGMENT COLOUR	MINERALOGICAL NAME AND FORMULA
Black	*Carbon*: C
White	*Calcite*: $CaCO_3$ *Gypsum*: $CaSO_4 \cdot 2H_2O$ *Kaolin*: $Al_2Si_2O_5(OH)$
Red	*Haematite*: Fe_2O_3 *Gypsum*: $CaSO_4 \cdot 2H_2O$
Orange	*Haematite* + *Limonite*: $Fe_2O_3 + FeO(OH) \cdot 2H_2O$
Yellow	*Limonite*: $FeO(OH) \cdot 2H_2O$

Table 1. *Mineral pigments in rock paintings of El Vallecito.*

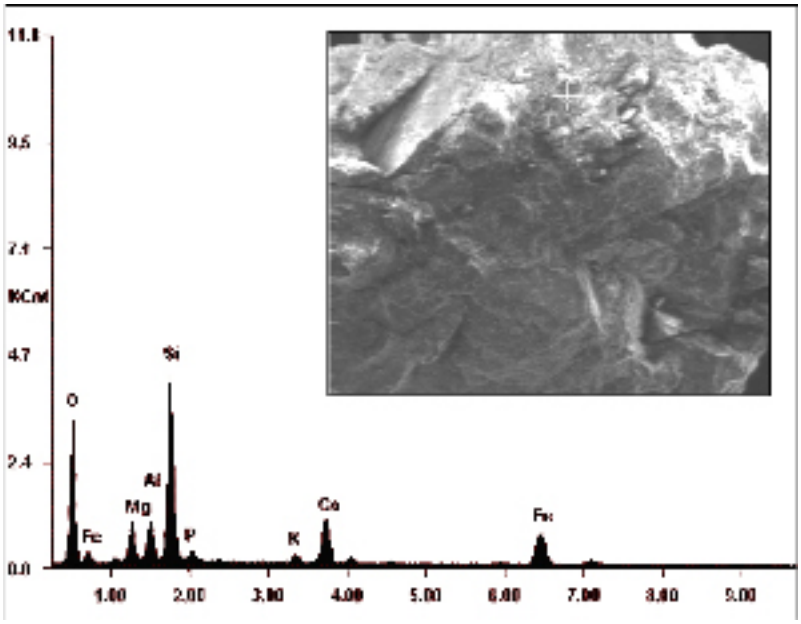

Figure 3. *SEM and EDS analyses of a red painting sample from El Vallecito.*

($CaCO_3$) in the white pigment was confirmed by FTIR analysis (Fig. 4). The bands appear at 1408 cm^{-1} (γ_3), 873 cm^{-1} (γ_2) and 712 cm^{-1} (γ_4), corresponding to vibration frequencies for CO_3^{2-} of the calcium carbonate. The chemical composition of both minerals, rock substrate and pigments, promotes the formation of microcrystalline bonds through a hardening process (Edwards et al. 1998).

Figure 5 shows the distribution of the chemical elements of three painting samples: black, white and red; every paint with its main characteristic chemical element — carbon for black, Ca for white and Fe for red. The additional elements, common to these three paintings, O, C, Ca, Si and Al, are present in similar amounts.

The similar mineral and chemical composition of both the rock substrate and the mineral pigments promotes the formation of microcrystalline, ionic bonds through a hardening process. This silicification process is facilitated by a slightly alkaline pH, of around 8, of the carbonate and the potassium magnesium aluminosilicates mixture in the paste or the slurry. The amorphous silicates in the paint occur dominantly as colloidal particles, which bind electrostatically to the rock surface. This generates a strong cohesion of mineral nature between the paint particles and improves the adhesion to the rock substrate, forming insoluble products. The adhesion is then favoured by both the chemical bonding and the mechanical anchoring in the rough and cracked surface of the granitic rock.

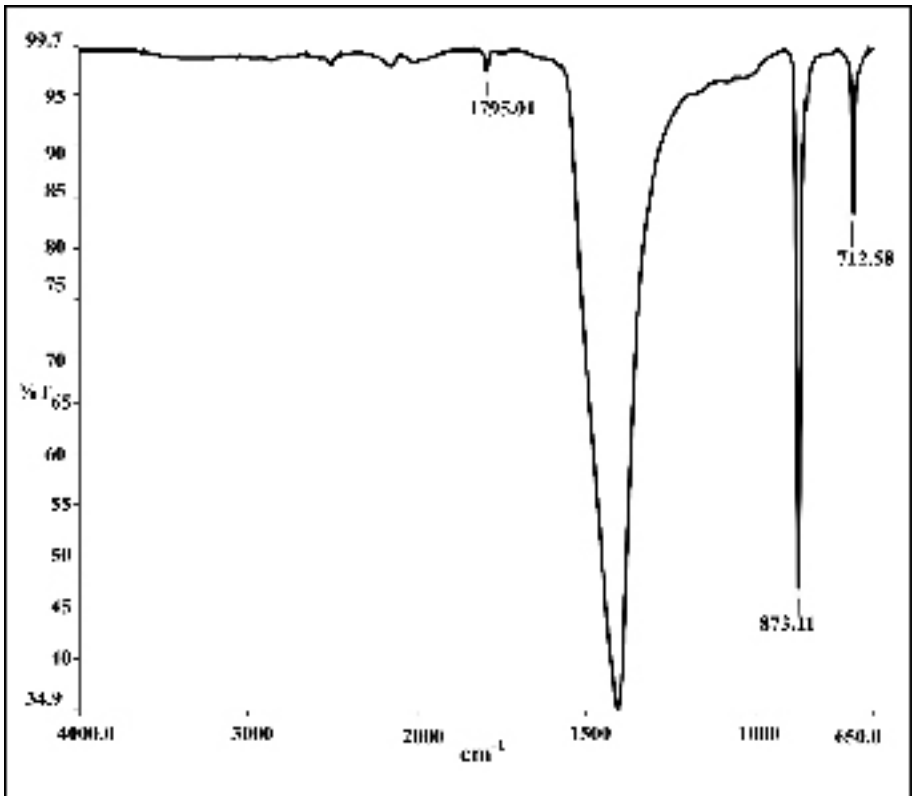

Figure 4. *FTIR analyses of a white pigment used at El Vallecito.*

Paint preparation and application

The painter, as a creative artist, cares about his materials and tools, needs to understand their properties and behaviour, and manipulates them for the preparation of his paint.

By drying, heating or calcination, the mineral colour may be altered, for instance yellow limonite or orange-reddish goethite can be converted into red haematite. The colour depends also on the average particle size, the presence of other trace

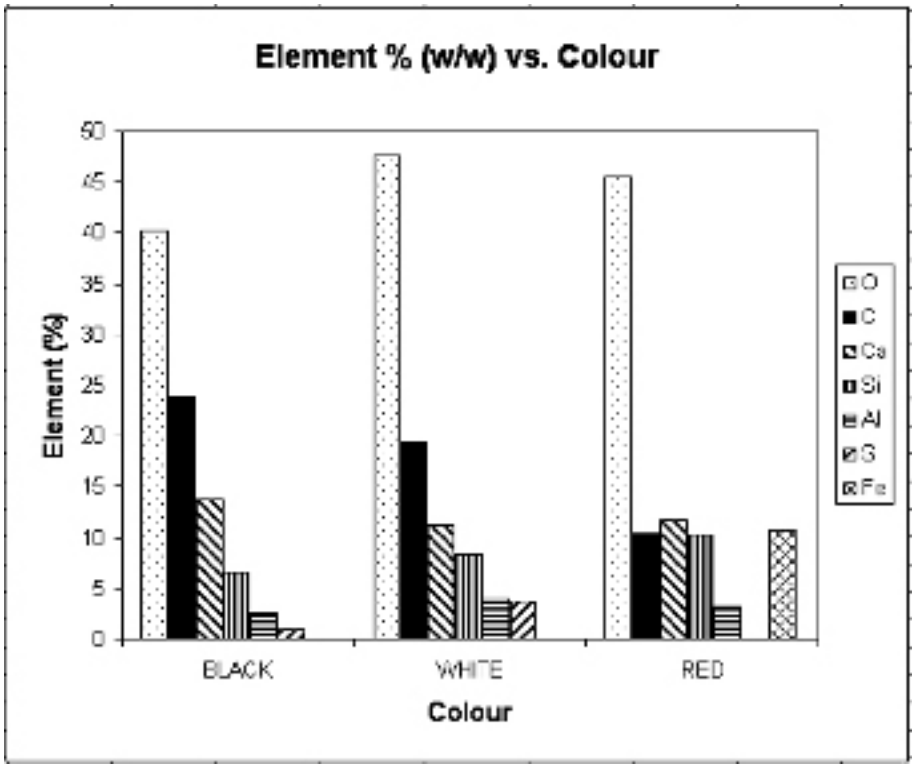

Figure 5. *Distribution of chemical elements in paintings of El Vallecito.*

Figure 6. *Mortars and pestle stone used for the grinding of pigments at La Tinaja Partida.*

metallic elements, and whether water is chemically bonded to the crystalline structure. If the paint was applied as a soft, thick paste only a small amount of water was required for wet grinding of the mineral pigment. The paint raw materials, white minerals, other pigments and water are all encountered in the painters' habitat. The minerals were ground in man-made, round bedrock bowls similar to the *molcajetes* (ancient Nahuatl language) created by several cultures in Mesoamerica, carved in the stone floor using lithic tools, and then mixed with water. The mortars and pestle stone used for the pigment grinding are shown in Figure 6. The application technique of the wet paint depends on its rheological properties such as density, viscosity, fluidity, agglutination, temperature etc.

The cave La Pintada, the site of a large mural, has a dozen such bowls, some with remains of paints of different colours indicating that the paints were prepared, mixed and applied in situ by the painter and his assistants. This special activity and the painting was surely part of a tribal, magic or ritual ceremony. The form and size of the rock painting components, in particular those of geometric line design, circles or semicircles, concentric lines, required fast, harmonic movements; lines of 5 to 10 mm width suggest that the paint was applied as a paste with the different fingers of the hand, according to the width of the paint lines. Another possibility is the use of a small, narrow brush prepared from a cactus leaf formed of strong thick fibres. The thick paint was applied within incised contours or white and black outlines, that were scratched on the rock rough surface with a piece of chalk or charcoal. Taking into account the area of a human or animal figure, and the dry paint layer with a thickness of 1 mm, such a figure should require about 5 kg of dry paint.

At the end, in the arid area with summer temperatures reaching 40–50°C, there remains on the rock the residue of a 100% solids-content, multi-phase, thixotropic paint containing finely ground minerals strongly embedded in the rough rock surface. This is the reason that these paintings are well preserved and no mechanical disintegration or chemical decomposition, deterioration or detachment has been observed during the last centuries, even if they are exposed to weathering, rainfall and water infiltration, and erosion by wind-borne dust and affected by indirect or direct intense solar radiation. The applied paint returns to its original, dry natural state as mineral oxide and/or silicate, and is now an integral adhering and cohesive layer, clinging to the rock surface.

Conclusions

The physical and chemical characteristics of the ancient rock painting samples of El Vallecito archaeological site in Baja California, Mexico, have been determined by SEM, EDX and FTIR techniques. The paints consisted of a mixture of ground white minerals (mainly $CaCO_3$ and $CaSO_4{\cdot}2H_2O$), coloured mineral pigments and water. The paints were applied as a thick paste or concentrated slurry on the natural surface of rough granite rocks. This paint of 100% solids might be called 'stone on stone', which explains its permanence, without deterioration, for centuries. Knowing the paint composition and application techniques will be useful in the conservation and restoration of the Stone Age rock paintings of Baja California.

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REFERENCES

Anonymous 1996. The great murals: conserving the rock art of Baja California. *The Getty Conservation Institute Newsletter* 11(2): 4–9.

Bendimez Patterson, J. 1989. Antecedentes históricos de los indígenas de Baja California. *Revista de Estudios Fronterizos, Instituto de Investigaciones Sociales UABC* 14: 11–46.

Bendimez Patterson, J. 1999. El arte rupestre en el norte de Baja California. *Antología de la Arqueología de Baja California*, pp. 32–40. Instituto Nacional de Antropología e Historia INAH, Mexicali.

Chalmin, E., M. Menu and C. Vignaud 2003. Analysis of rock art painting and technology of Paleolithic painters. *Measurement Science and Technology* 14: 1590–1597.

Crosby, W. H. 1997. *The cave painting of Baja California*. Sunbelt Publications, INAH.

Edwards, H., L. Drummond and J. Russ 1998. Fourier-transform raman spectroscopic study of pigments in Native American Indian rock art: Seminole Canyon. *Spectrochimica Acta* Part A, 54: 1849–1856.

Gutierrez Martinez, M. de la Luz 1994. *Guia arte rupestre de Baja California sur*. INAH-SALVAT, Mexico.

Gutierrez Martinez M. de la Luz 2003. El estilo gran mural en la Sierra de Guadalupe, B.C.S. *Arqueología*, INAH, 11(62): 44–45.

Pappalardo, L. 1999. A portable PIXE system for in situ characterization of black and red pigments in Neolithic, Copper Age and Bronze Age pottery. *Nuclear Instruments and Methods in Physics Research* B, 150: 576–580.

Serrano Gonzalez, J. 2003. El Vallecito, Baja California. *Arqueología*, INAH, 11: 62, 54.

Zoppi, A. 2002. Characterization of painting materials from Eritrea rock art sites with non-destructive spectroscopic techniques. *Journal of Cultural Heritage* 3: 299–308.

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