Contents lists available at ScienceDirect



Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

### Pigments, binders, and ages of rock art at Viuda Quenzana, Santa Cruz, Patagonia (Argentina)



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#### ARTICLE INFO

Keywords: Dating Rock art Paintings Patagonia Animal fat Pigments Hematite Raman SEM EDS

#### ABSTRACT

The first direct AMS radiocarbon dating of two rock art motifs in separate rock shelters (VQ1 and VQ2) at the Viuda Quenzana (VQ) archaeological locality in Patagonia, has provided median probability ages of 3190 cal BP for two reddish dots, and 520 cal BP (1430 CE) for a pink negative hand. These ages are consistent with evidence of occupation of sites in the locality and in the nearby region during the later part of the Middle Holocene (8200-4200 cal BP) and Late Holocene (4200 cal BP to present), as indicated by ages for bones and charcoal from sediments in the VQ8 and VQ7 rockshelters, and the nearby La Martita 4 and La Gruta 1 and 3 rockshelters ranging from ca. 5470 to 305 cal BP (Rubinos Perez 2003; Franco et al. 2013; Brook et al. 2015). The pink hand is relatively recent, which supports the notion that such artwork continued through the Late Holocene despite changes in other artistic motifs. Characterization by Raman spectroscopy, powder x-ray diffraction, and highresolution scanning electron microscopy with energy dispersive spectroscopy shows that: 1) hematite is the main pigment in both the dot and hand motifs, 2) the reddish dot paint includes a specific type of hematite, microplaty hematite, and 3) animal fat appears to have been added as a binder to the reddish dot paint. Thus, rock art paint production at VQ involved two distinct processes. One, used to paint dots, entailed mixing a mineral coloring substance (hematite) with an organic binder (animal fat), which was then applied to the rock substrate with a painting tool and/or fingers. The second process, used to produce the hand motif, entailed using a mineral coloring substance (hematite) with no binder (or with a binder that left little chemical trace), which was then applied to the rock substrate by spraying, probably with the mouth.

#### 1. Introduction

The Southern Deseado Massif in central Patagonia is a volcanic landscape with evidence of hunter-gatherer presence from the Pleistocene-Holocene transition (Franco et al., 2010; Paunero, 2009; Paunero et al., 2007) to around  $290 \pm 20$  <sup>14</sup>C BP (1650 CE) (Brook et al., 2015; Franco et al., 2013). Because the environment has rock-shelters and caves, and water is available in streams and lagoons at least seasonally, this area was attractive to hunter-gatherers in the past (Brook et al., 2015; Franco et al., 2013; Panza and Marin, 1998). The current study focuses on art motifs in the abundant rock shelters of the Viuda Quenzana (VQ) area (Fig. 1) that are painted on ignimbrites belonging to the Chon Aike Formation of Jurassic age (Iglesias, pers. comm. 2013) (Panza and Marin, 1998).

Viuda Quenzana is a shallow 4 km long canyon oriented approximately northeast to southwest with a low-order ephemeral stream channel that joins the intermittent Seco River valley. The climate at nearby Gobernador Gregores, according to the Köppen climate classification, is a Cold Desert Climate (*BWk*), with an average annual precipitation of 185 mm and a mean annual temperature of 8.5 °C. The average number of precipitation days per year is 55. Exploration of the area has revealed 44 archaeological sites with rock art, adding information to the list of sites originally presented by Gradin and Aguerre (1983) and Molina (1972). The sites are principally shallow rockshelters located primarily in residual blocks of ignimbrite along the western interfluve of the canyon. The art of the area is dominated by painted motifs in various colors (red, reddish, black, white, yellow, orange and green) and, exceptionally, by engravings or a combination

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https://doi.org/10.1016/j.jasrep.2018.01.004

Received 7 September 2017; Received in revised form 23 December 2017; Accepted 4 January 2018 2352-409X/ © 2018 Elsevier Ltd. All rights reserved.



**Fig. 1.** Viuda Quenzana (blue triangle) and areas with major rock art localities mentioned in the text. Area 1 sites: La Gruta, La Martita, El Verano and La Maria. Area 2 sites: Cueva de las Manos, Alero Charcamata, Arroyo Feo, Alero Cárdenas. Area 3 sites: Cerro de los Indios. Red triangle and GG indicate the town of Gubernador Gregores. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of paintings and engravings (Fiore and Acevedo, 2016; Acevedo, 2017). The most frequent motifs are hand negatives (in different hues of red, black, white, yellow, orange and green), followed by red and black guanacos, simple geometric forms such as straight lines, curved lines, ovals and circles made with solid lines and dotted elements (in red hues, black and yellow), positive hands (in different hues of red), three-digits (i.e. bird tracks) in red, feline footprints in white and red, human foot negatives in red, and orthogonal geometric motifs like zig-zags, frets, rectangles and rhombuses in red and bichrome combinations.

The art motifs of the VQ area have been placed in stylistic groups (Gradin, 1988), but many motifs persisted over time and so are common to several groups; furthermore, these groups are poorly dated. There have been no direct ages determined for south-central Patagonian rock art, and very little is known about the nature of organic binders that hunter-gatherers may have used in preparing some paints. This paper is a first effort at correcting these shortcomings in our knowledge of south-central Patagonian rock art. Here, we examine the characteristics of the paints used to create two different common motifs, in particular looking for evidence of organic binders that might be dateable using AMS radiocarbon techniques. Recognizing how difficult it is to directly date paint used to create rock art, we also address the possibility that the surfaces on which the rock art is found can provide chronological information about the art itself. Because a major problem in dating paint on rock is obtaining samples that come only from the paint, we also dated a sample of unpainted substrate near the motif to determine how substrate material included in paint samples might affect the resulting ages.

Here we detail our efforts to characterize the nature of both the paints and associated substrates so that this research will provide maximum value to others addressing the complex task of dating rock art. Our materials characterization work encompasses a range of wellestablished techniques for identifying both organic and inorganic materials within archaeological contexts. Specifically, we use powder x-ray diffraction, micro-Raman spectroscopy, scanning electron microscopy, and energy dispersive spectroscopy techniques to provide detailed knowledge about the pigments and binders used to produce these rock art motifs, as well as identify deterioration products that have accumulated over time. Before we describe the analytical work, we present a brief background on some important aspects of south-central Patagonian rock art that are relevant to the research.

## 2. South-central Patagonian rock art: stylistic characteristics and organic binders in paint

#### 2.1. Stylistic sequence of rock art in South-central Patagonia

What is known about Patagonian rock art comes from a few archaeological localities where chronologies have been estimated on the basis of archaeological styles, superimposed paintings, ante quem and post quem dates of fallen slabs found in dated archaeological layers, dated archaeological layers covering rock art walls, or the relationship between motifs and cultural levels based on pigment composition studies (e.g. Duran 1983–1985; Gradin et al., 1979; Gradin and Aschero, 1983; Gradin, 1988; Aschero et al., 2005; Fiore and Hernández Llosas, 2007; Carden, 2009; Re et al., 2016). The Río Pinturas area is a central locality for Patagonian rock art because it was the place where most of the stylistic groups were defined and associated with occupation levels (Gradin et al., 1979). For this reason, the rock art sequence in this area has been, and is still, used as a basis for interpreting the sequences at other archaeological localities in Patagonia (ibidem). This sequence takes into account motif morphologies and superpositions at the Cueva de las Manos, Charcamata and Arroyo Feo sites (all in the Río Pinturas area, about 190 km northwest of VQ), as well as rock falloffs, which were used to establish minimum/maximum ages (Gradin et al., 1979).

The stylistic sequence includes *Stylistic Groups A, B, B1, C, D, and E* (e.g., Gradin, 1988). The earliest paintings in Patagonia (*Stylistic Group A*) date to ca. 10,450 cal BP (ca. 9300 <sup>14</sup>C BP) (Gradin et al., 1976, 1979; Aguerre, 1977) and show painted hunting scenes in which animals and humans interact (Gradin et al., 1979; Gradin, 1988). *Sty*-*listic Group B* dates from about 8050 cal BP (<sup>14</sup>C age of 7280  $\pm$  60 <sup>14</sup>C BP) and is dominated by hand negatives and guanaco groups; hunting scenes are no longer found. From 8050 to 3100 cal BP (ca. 3000 <sup>14</sup>C BP), *Stylistic Group B1* is characterized by more schematic images, which include painted static guanacos, groups of hand negatives, stylized and schematic zoomorphic figures, negatives of feet, including humans, birds (*Pterocnemia pennata*, a non-flying bird), guanacos (*Lama* 

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