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

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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 high-resolution 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 ± 20 ^{14}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 rock-shelters 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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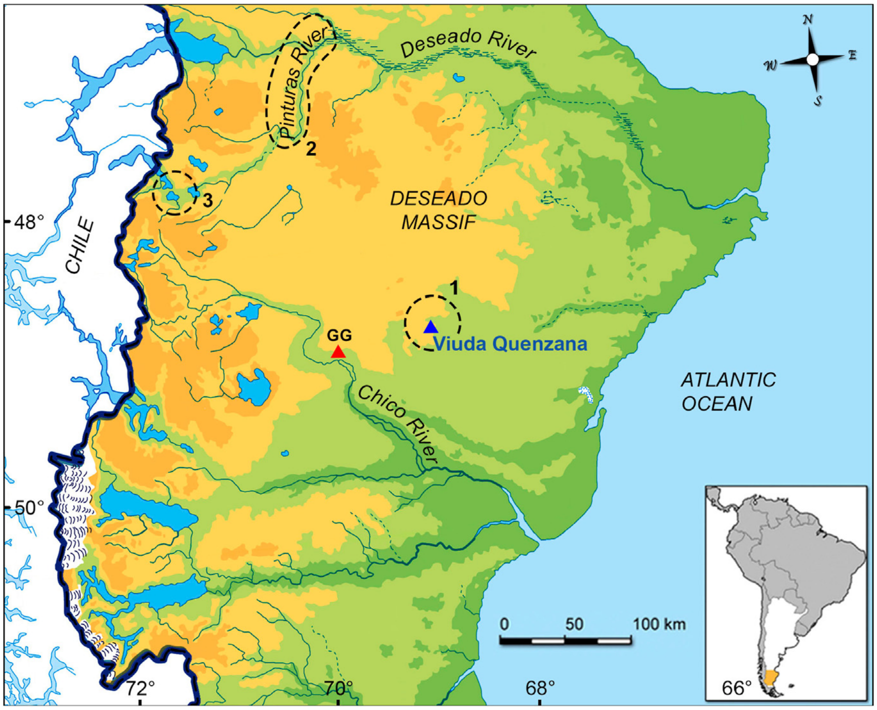


Fig. 1. Viuda Quenzana (blue triangle) and areas with major rock art localities mentioned in the text. Area 1 sites: La Gruta, La Martita, El Verano and La Maria. Area 2 sites: Cueva de las Manos, Alero Charcamata, Arroyo Feo, Alero Cárdenas. Area 3 sites: Cerro de los Indios. Red triangle and GG indicate 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 well-established 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 ^{14}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). ***Stylistic Group B*** dates from about 8050 cal BP (^{14}C age of 7280 ± 60 ^{14}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 ^{14}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* guanicoe) and puma (*Puma concolor*), anthropomorphic figures, and geometric motifs made with solid and dotted elements (Gradin et al., 1979; Gradin, 1988). ***Stylistic Group C*** dates to the period ca. 5700–1900 cal BP (ca. 5000–2000 ^{14}C BP) and includes painted simple geometric motifs of solid and dotted elements, three-digits, and meanders (idem). The sequence continues with ***Stylistic Group D***, which dates from ca. 2550–900 cal BP (2500–1000 ^{14}C yr BP). This group includes engraved animal footprints (of birds, guanacos and puma), anthropomorphic figures, human hands, guanaco and lizard outlines, and simple geometric motifs (both curvilinear and rectilinear) (Gradin et al., 1979; Gradin, 1988). The final stage of the sequence is ***Stylistic Group E***, from ca. 1120–450 cal BP (1250 ± 80 to 430 ± 50 ^{14}C BP), consisting of complex geometric motifs of orthogonal design, including frets, ladders, and crosses (idem). This sequence of rock art continues until just before the Spanish conquest (Gradin et al., 1976), although rider representations have been found to the north of Patagonia (Gradin, 2001).

2.2. Stylistic groups in the Deseado Massif

Based on stylistic similarities, Gradin and Aguerre (1983) included motifs at VQ within the main rock art sequence proposed for central-south Patagonia, particularly *Stylistic Group B1* (Gradin et al., 1979; Gradin, 1988). *Stylistic Group D* is also represented by a few engraved curvilinear motifs (Gradin and Aguerre, 1983; Acevedo, 2017). Following excavations at La Martita Cueva 4 (ca. 25 km to the north of VQ), Gradin and Aguerre (1983) linked *Stylistic Group B1* and *Stylistic Group D* motifs in the area to human occupations dated to ca. 4500 ^{14}C BP (5100 cal BP) and around 1700 ^{14}C BP (1560 cal BP; 390 CE), respectively. Gradin and Aguerre (1983) also examined whether motifs of different color at 12 sites in the VQ area were of different relative age by studying superimpositions, but found that the order between red and black motifs varied. Therefore, they concluded that it was not possible to use tonal series for relative dating. More recently, Acevedo (2017) studied 463 superimpositions at 22 sites in the VQ area, which involved a total of 535 motifs: results show a complex sequence of tonal series, confirming that tonal series do not currently provide accurate relative dates for reddish paintings.

At El Verano, there are 14 sites with rock art within ca. 12 km of VQ. Durán (1983–85) attributed dotted motifs in this area to *Stylistic Group B1* and assigned an age of ca. 4500 ^{14}C BP (5100 cal BP) to them, following Gradin and Aguerre (1983); in a similar fashion, he assigned an age of ca. 1300 ^{14}C BP (1180 cal BP) to motifs of *Stylistic Group E*, based on dates from Río Pinturas (Gradin, 1988). Furthermore, Paunero et al. (2005) suggest that dotted motifs at La María, 30 km from VQ, based on superimposition, can be related to dated Early and Middle Holocene human occupations of the area.

Hand negatives, which are one of the motif types dated here, have been related to several stylistic groups in Patagonian rock art: they have been considered as one of the main motif types in *Stylistic Groups A, B,* and *B1,* and have been identified as motif types (less common) associated with *Stylistic Groups C and D* (Menghin, 1957; Gradin et al., 1979; Gradin, 1988, 2001). Additionally, using relative dates, Gradin has noted that hand negatives were produced from the ninth to the third millennium BP, after which they "continued until more recent times" (Gradin, 2001: 844–845).

These findings indicate that two of the more common art motifs, dot patterns and negative hands, may have been produced at VQ and in nearby areas for a long time and so provide limited information on their ages or the ages of sites where they are located. Clearly, other methods of dating rock art are needed. One possibility is direct AMS radiocarbon dating. However, rock paintings are typically difficult to date by this method because most prehistoric pigments are inorganic minerals. Radiocarbon dating becomes viable only in two cases: (1) when the pigment itself is composed of carbon, e.g., charcoal (carbon black), burnt bone (bone black), or (2) when an organic component was incorporated into a paint mixture, either intentionally, as in the case of binding agents, or inadvertently during the painting process. These cases are accompanied by important caveats. One major consideration is the presence of carbon-containing components that are not contemporaneous with paint production and the creation of the rock art, including and not limited to issues with calcium carbonate (possibly millions of years old or much younger), byproducts of lichen activity (e.g., oxalate compounds), microorganic accumulations (algae, fungi, bacteria), soil components (e.g., humic acids), soot, insect deposits, and weathering accretions bonded at different times to the rock and/or painted surfaces. For instance, charcoal may be considerably older than the rock art in which it is found, or it may be younger if added after the art was created (e.g., soot from cooking or brush fires). Since the first radiocarbon dates on charcoal pigments from pictographs were published in 1987 (Hedges et al., 1987; Van der Merwe et al., 1987), there have been numerous case studies highlighting these complications (e.g., Hedges et al., 1998; Steelman et al., 2002; Pettitt and Pike, 2007; Rowe, 2009; Aubert, 2012; David et al., 2013).

2.3. Organic binding agents in paints

Organic binding agents are usually contemporaneous with paint production, although these materials often degrade over time and become difficult to characterize. Known and proposed organic binding agents in rock art include plant juices or oils, urine, animal fat, bone marrow, blood, eggs (yolk and/or albumen), and human saliva (Watchman, 1993; Watchman and Cole, 1993; Dobrez, 2014). Possible organic contaminants can derive from painting tools, such as brushes made from animal hair or feathers, small sticks, or pieces of bone, and also from pads of lichen or moss used to cover larger areas with paint. Negative hand stencils may have been painted on rock faces by a spraying technique: the liquid paint being held in the mouth and then sprayed through the lips or through a narrow tube onto a hand held against the rock surface. Because the liquid is circulated in the mouth, the paint may contain traces of saliva (e.g., Dobrez, 2014).

In all cases, we echo the caution articulated by Watchman (1993) and more recently by Armitage (Livingston et al., 2009; Li et al., 2012) that dating unidentified organic matter is treacherous because this information could include contributions of ^{14}C from unknown sources. For this reason, it is important to thoroughly characterize materials in order to correctly interpret AMS dating results; that is, it is imperative to understand the nature of the carbon being dated.

In prior studies at Cueva de Las Manos and Cerro de los Indios in Patagonia, to the northwest of our study area, no evidence of organic binder agents was found in paintings there, but proteinaceous components, likely part of a binding medium, were identified in red paint on a rock fragment uncovered by the archaeological excavations (Wainwright, Helwig, Rolandi, Gradin et al., 2002). However, so far no direct dates have been obtained for paintings in Argentine Patagonia. Recently, Amalia Nuevo Delaunay (pers. comm. to Franco, 2017) has obtained direct ages from black motifs in Chilean Patagonia.

3. Methods

3.1. Sample collection

The ignimbrite walls of the caves and rock shelters at VQ are unstable because thin layers of rock (rock flakes) are constantly being released from them. Some of these rock flakes have art motifs, which end up on the rock shelter floor. In this study we examined two samples of rock art on such layers of rock that were about to fall from the disintegrating walls of two rock shelters about 80 m apart. These sites were recorded initially by Gradin and Aguerre (1983), who named them Site 1 and Site 2 of VQ; therefore we will refer to the sites as VQ1 and VQ2, respectively. VQ1 is a cave 17 m wide, 7 m deep and 6 m high, oriented to the north-northwest (Gradin and Aguerre, 1983; Acevedo, 2017)

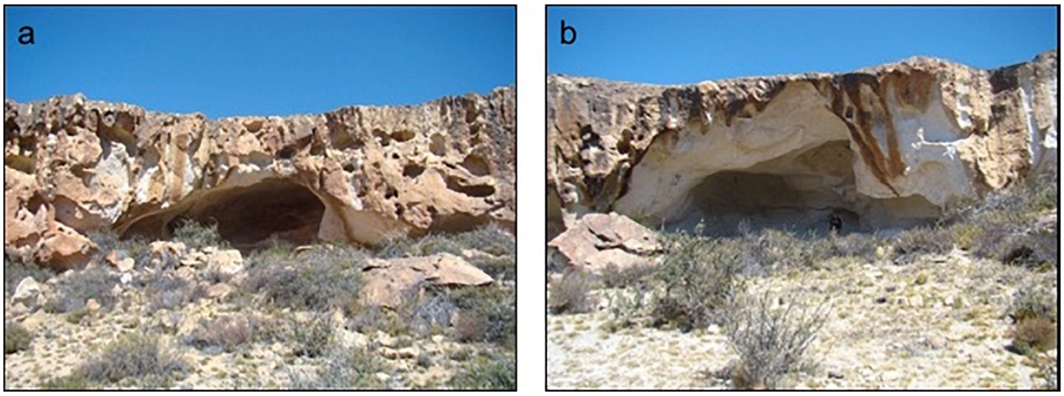


Fig. 2. Rockshelters VQ1 (a) and VQ2 (b) showing iron staining on the exposed bedrock but not inside the shelters themselves.

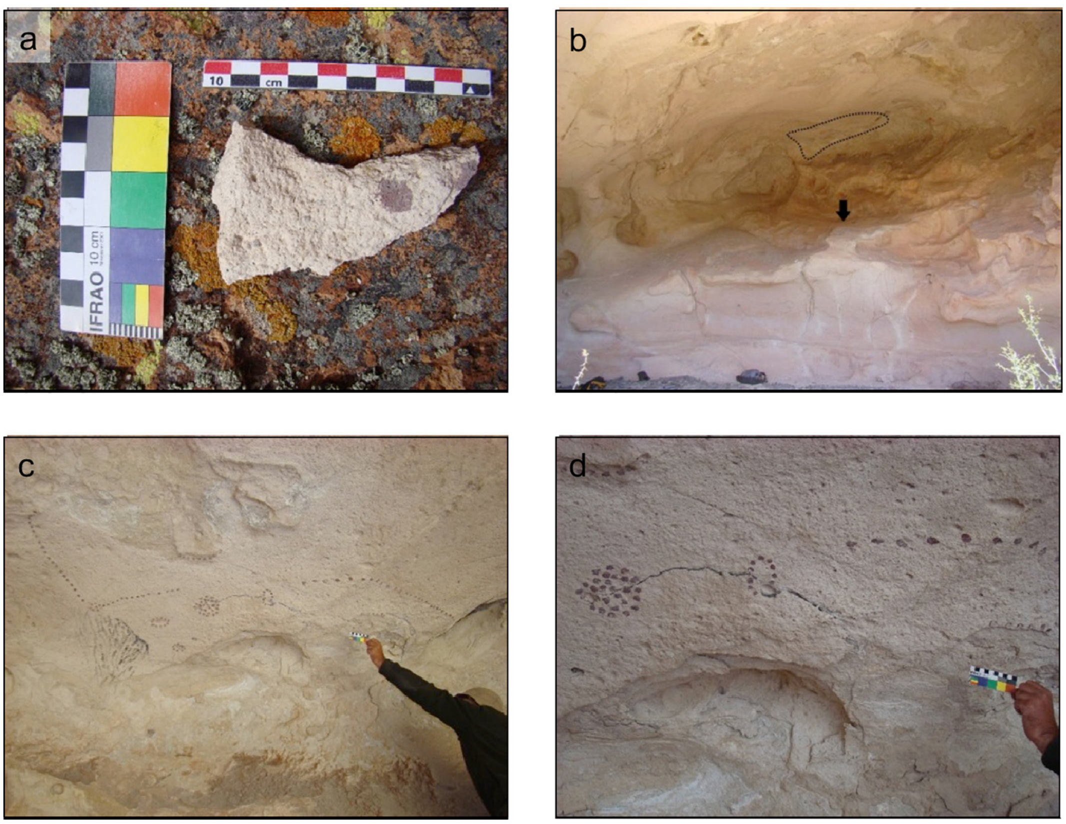


Fig. 3. Sample VQ1-1 and the poor state of preservation of some areas of rock art at VQ1. (a) Spalled fragment of rock (VQ1-1) from the shelter wall with one complete and one partial reddish dot at right. Note the lichens on the boulder, where the fragment was placed in sunlight for photography, in contrast to the complete absence of lichens on the walls and ceilings of the rock shelters, which are typically in shade (see Fig. 2). In image (b) the arrow points to the location where the rock fragment was found, and the dotted line indicates the probable origin of the sample within the panel. Image (c) shows the full panel with reddish dots grouped to form straight lines, curved lines and circular geometrical designs. Image (d) highlights the poor state of preservation of these paintings and substrate.

(Fig. 2a). Inside the cave there are 16 panels with rock art paintings, including: red negative hands of different tones, reddish dots grouped to form straight lines, curved lines and circular geometric designs, black schematic guanacos, and a set of black irregular lines (possibly produced by dragging fingers with paint over the rock surface) grouped as a triangular figure. The second site, VQ2, is also a cave; it is 22 m wide, 10 m deep and 7 m high, oriented to the northwest (Gradin and Aguerre, 1983; Acevedo, 2017) (Fig. 2b). In this case 6 panels were recorded, with a few red negative hands, painted vestiges and one motif consisting of the head and neck of a guanaco. There is no macroscopic evidence of recent lichen growth or smoke residue from human-made fires on the ceilings or walls of these two shelters (see Figs. 2–4).

Rock art sample VQ1-1, from VQ1, consists of two reddish (Munsell color 10R/2.5/1; reddish black) dots on a thin rock fragment (Fig. 3a). One has a diameter of 1.5 cm and is complete; the other is partial, having been damaged by the weathering of the fragment. The rock fragment with the painted dots was found resting on a rock shelf and apparently had fallen from a panel of art on the back wall/ceiling of the shelter. The art making up the panel is mainly composed of nine motifs: three circumferences, three curved lines, one circle, one circle combined with curved lines all in the same reddish hue and designed with dotted elements, plus one triangular figure composed by black irregular lines (Acevedo, 2017) (Fig. 3c, d). It was not possible to locate the original position of the rock fragment within the panel in the shelter.

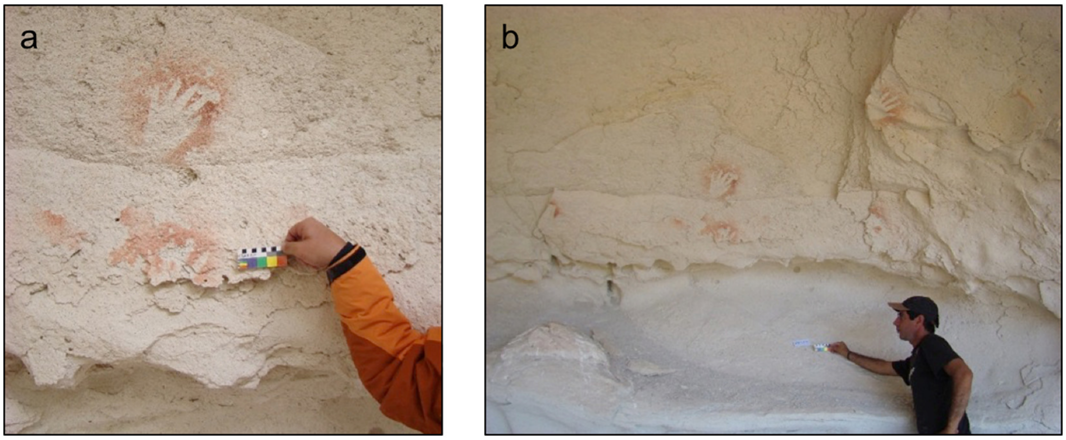


Fig. 4. Negative hand prints at VQ2. Sample VQ2-2 was obtained from the broken hand negative shown in image (a); note the poor preservation of the motif. The full rock art panel containing three pink negative hands is shown in image (b). Note the complete absence of any vegetal cover (e.g., lichens, mosses) or staining due to soil humic acids on the rockshelter walls. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

However, the fact that it was found beneath a panel where the art consists of dotted motifs of the same hue suggests that it was dislodged from the panel and fell to the shelf below (Fig. 3b–d).

Sample VQ2-2, from VQ2, comes from a panel of art with seven pink motifs, including three negative hands, one negative of an unidentified object, and three stains of undefined morphology due to the panel's deterioration (Acevedo, 2017). VQ2-2 is a 2 × 2 cm rock fragment with red pigment (Munsell color 2.5YR/8/4; pink), which formed part of a broken pink negative hand that is in an advanced state of deterioration (Fig. 4a and b). In this case, the sample was removed gently from the wall with the help of a stainless steel cutting instrument following the natural fissures already present around the rock flake. The extraction process was performed on a marginal sector of the motif to affect its morphological integrity as little as possible. Both the motif and the entire extraction process were photographed before, during and after taking the sample.

At no time during the collection and storage process was the art or the rock surface touched by hand so as to avoid contamination. After photography, the pieces of rock art were stored in clean plastic bags and wrapped in bubble wrap to prevent damage between site and laboratory. The rock art was kept in the dark and at a low temperature to limit any organic activity on the painted rock surfaces.

3.2. Powder X-ray diffraction

X-ray diffraction patterns of the substrate associated with the rock art were obtained on powdered samples using a Bruker D8-Advance diffractometer (Co-Kα radiation source) operated at 40 mA and 40 kV. Data were collected from 3 to 80 2θ at a rate of 0.1 s per step.

3.3. Raman spectroscopy

Prior to sampling for radiocarbon dating, the rock art samples were analyzed by Raman spectroscopy to determine the nature of the pigments and to search for and identify any organic materials present. Microsamples for Raman analysis were removed from the painted rock flakes using a tungsten-tipped needle tool. Raman measurements also were conducted on polished cross sections of the samples.

Spectra were acquired using two Raman instruments. The first was a Renishaw InVia Raman Microscope System. The excitation used in this study was 785 nm. Typical resolution was approximately 2 cm^{-1}. The spectrometer was calibrated with an internal Si reference (521 cm^{-1}). Magnifications of 50 to 200× were used. The second instrument was a home-built, probe-head design apparatus with Kaiser Spectrophotometer and Coherent Verdi-V5 Laser operating at 532 nm. A standard acquisition time of 20 s was used, along with a laser power between 0.1 and 0.5 W. This setup did not include a microscope system, thus the spot size was on the order of millimeters in diameter. The resolution was estimated to be 2 cm^{-1}. In all cases, spectra were baseline-corrected in OriginPro 8.5; cosmic ray spikes were removed using this software.

3.4. Scanning electron microscopy and energy dispersive spectroscopy

Samples were prepared by embedding in epoxy, polishing with successively finer grits, and then coating with carbon. Scanning electron microscopy (SEM) imaging was conducted with an FEI Teneo FE-SEM at 10 kV with a spot size of 10. Energy dispersive spectroscopy (EDS) was conducted with an integrated 150 mm Oxford Instruments X-MAX^N detector operated at 20 keV.

3.5. AMS radiocarbon dating and stable carbon isotope analysis

Because the technique of plasma chemical extraction of organic carbon (e.g., Russ et al., 1991; Rowe, 2009) is not available at the University of Georgia's Radiocarbon Dating Laboratory (in the Center for Applied Isotope Studies), we adopted a traditional acid treatment to remove calcium carbonate and calcium oxalates from our pigment samples. After thorough testing involving Fourier Transform infrared spectroscopy analysis, Bonneau et al. (2011 and 2016) found that hydrochloric acid was totally effective in removing both calcium carbonate and calcium oxalate from pigment samples and used this pretreatment protocol to date black pigments in San rock art (see also Rowe, 2001).

Our approach to dating the VQ rock art was to obtain samples for analysis by scraping the paint from the rock surfaces using a rotary tool (Dremel) with a diamond point bit. This technique unavoidably results in a powder composed of both the paint and contributions from the topmost layer of the underlying substrate. We also obtained samples from unpainted substrate surfaces adjacent to the art. The purpose of these reference samples was to determine whether our paint sampling protocol included carbon contaminants that might influence the dating results (e.g., see discussion in Brook et al., 2010).

The residues obtained by this sampling procedure were treated with 1 N HCl at 80 °C for 1 h to remove carbonate and oxalate materials. The pretreated samples were then combusted at 900 °C in sealed evacuated quartz ampoules in the presence of CuO. The yield of carbon was quite low: 31 μg and 42 μg for the reddish dot (VQ1-1) and pink hand (VQ2-2) samples, respectively. The resulting carbon dioxide was cryogenically purified from the other reaction products and catalytically converted to graphite using the method developed by Cherkinsky et al.

(2010). Such small samples were measured with standards and backgrounds of similar size to unknown samples to decrease dependency between the beam current and sample size (Cherkinsky et al., 2013). Graphite $^{14}C/^{13}C$ ratios were measured using the 0.5 MeV accelerator mass spectrometer at the Center for Applied Isotope Studies, University of Georgia. The sample ratios were compared to the ratio measured from the Oxalic Acid I (NBS SRM 4990) standard. Sample $^{14}C/^{13}C$ ratios were measured separately using a stable isotope ratio mass spectrometer and expressed as $\delta^{13}C$ with respect to PDB, with an error of less than 0.1%. Uncalibrated ages are in radiocarbon years BP or years before 1950 CE, and were calculated using a ^{14}C half-life of 5568 years. Errors are one standard deviation and reflect both statistical and experimental errors. Ages were corrected for isotopic fractionation to a $\delta^{13}C$ value of −25‰. Radiocarbon ages in ^{14}C years BP (^{14}C BP) were calibrated using CALIB 7.0 (Stuiver and Reimer, 1993) and the Southern Hemisphere (SHcal13) atmospheric calibration curve of Hogg et al. (2013). Calibrated ages at the 2σ level are given in calendar years BP (cal BP) or calendar years CE (CE). Calibrated ages are sometimes reported as a range (e.g., 4500–4750 cal BP) but in many cases for simplicity only a single, Median Probability Age (MPA) is reported (e.g., 4625 cal BP).

4. Results

4.1. Substrate characteristics

From the very start of this research project, we were aware that the nature of the substrate might influence our attempt to date the rock art at VQ. Thus, we have taken care to characterize its material components carefully. The substrate at VQ1 and VQ2 is a fine-grained, porous, white- to cream-colored ignimbrite, with visible black platelets that cleave easily. Powder XRD and micro-Raman analyses (Fig. 5) of fresh substrate at ca. 5 mm below the surface of samples VQ1-1 and VQ2-2, show clear matches to sanidine [$K(AlSi_3O_8)$], calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), quartz (α-SiO_2), kaolinite [$Al_2Si_2O_5(OH)_4$], and phlogopite (an often-black Mg-mica). The XRD data indicate that the main crystalline component of the rock is sanidine, and the presence of such a potassium-rich feldspar is consistent with the geological history of the Deseado Massif (Páez et al., 2010). The concentrations of the secondary mineral components appear relatively constant across the samples, aside from some variations in gypsum/calcite content. A clear Raman signal for calcium oxalate monohydrate ($CaC_2O_4{\cdot}H_2O$), identified by its distinctive pair of peaks just below 1500 cm^{-1} (Frost and Weier, 2003), originated from white grains in the VQ1-1 substrate (Fig. 5f). These grains also exhibited Raman signals for gypsum, as well as ill-defined organics indicated by broad peaks in the range 1200–1500 cm^{-1}. Calcium oxalate monohydrate, also known as the mineral whewhellite, is a natural product of lichens and certain plants (Franceschi and Nakata, 2005; Gadd, 2006). The presence of both calcium oxalate monohydrate and organics within the substrate (ca. 5 mm from the surface) of VQ1-1 suggests that non-native substances have penetrated the porous rock. An alternate interpretation of the broad peaks between 1200 and 1500 cm^{-1} is that they originate from disordered aluminosilicates (Bonneau, Pearce, et al., 2017); however, their association with organics here is supported by AMS dating and further Raman results (vide infra).

Based on these initial findings that suggest the possibility of organics in the substrate, we set out to explore the extent to which the substrates of the VQ1-1 and VQ2-2 samples contain organic material and, if so, how this might vary with depth. To do this, we conducted Raman analysis of: 1) paint (p spectra); 2) painted surfaces, where most of the paint had been removed for dating (ps spectra); and 3) shallow substrate (ss spectra) ≤ 5 mm below the exposed surface. As a part of our effort to understand how organic matter in substrate can affect dating of rock paintings, we also attempted to date an unpainted rock surface near the VQ1-1 motifs.

To achieve these objectives, samples VQ1-1 and VQ2-2 were cut vertically (along the short axis) into fragments, and then some fragments were cut horizontally (along the long axis). This produced fragments A-D from VQ1-1 and fragments E-I from VQ2-2, and exposed a variety of substrate profiles for Raman analysis (Fig. 6a–d). We examined the "horizontal" cut surface of VQ1-1 fragment B, ca. 3 mm below the substrate surface (ss spectra), as well as its upper rough surface from which the paint of the left reddish dot in Fig. 3a was removed (ps spectra). Four VQ2-2 surfaces were studied: painted (p spectra) and scraped (ps spectra) areas on the upper surface of fragment F; the rough, upper surface of fragment G, from which paint was removed for dating, but still retaining vestiges of paint (ps spectra); and both smooth cut surfaces and rough areas of fragment I at ca. 3 mm depth (ss spectra). Both "rough" and "smooth" surfaces were examined; rough areas were produced when paint was scraped from the rock surfaces using a rotary tool (Dremel) with a diamond bit, and smooth surfaces are either the original painted or unpainted substrate surface or untouched saw-cut surfaces. Sometimes, as in the case of the cut surface in fragment B of VQ1-1 (Fig. 6 b), smooth surfaces had areas of roughness where large grains were present; these were sometimes also examined in more detail. In general, both types of surface produced similar Raman signals (e.g., including quartz, sanidine, calcite etc.). However, the signal/noise ratio for the spectra were sometimes better for rough areas because usually the scans of smooth surfaces covered a larger surface area, whereas scans of the rough surfaces focused on colored particles or colored areas (usually looking for paint) and so generally covered a much smaller area.

Several Raman scans of the VQ1-1ss surface showed peaks consistent with organics (e.g., spectra e-h in Fig. 6). Scans of black, light brown and grey-brown rough areas of the surface provided less evidence of organic material (e.g., spectra j–l in Fig. 6). Peaks matching hematite, quartz, gypsum, and sanidine were also observed as in our

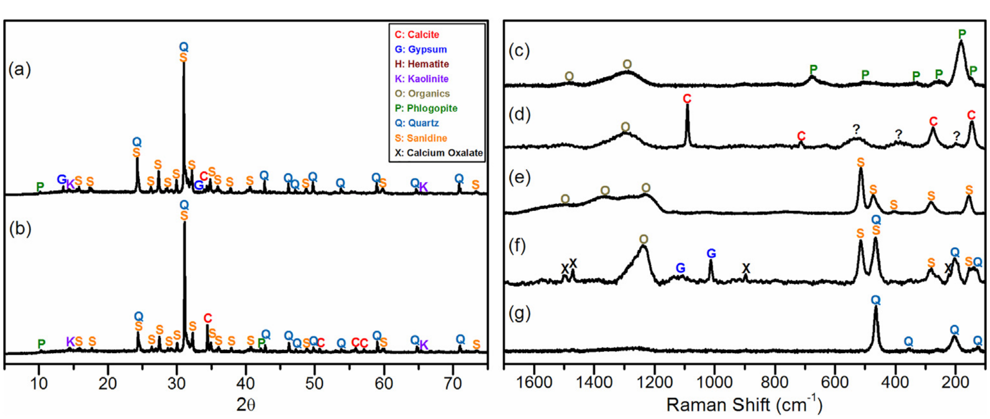


Fig. 5. Left panel: Powder XRD data from the rock substrate of samples VQ1-1 (a) and VQ2-2 (b) with phase identification (legend). **Right panel:** Micro-Raman spectroscopy (785 nm laser) of individual grains in the rock substrate from sample VQ1-1: black grain (c), black grain (d), light brown grain (e), white grain (f), and light grey grain (g). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

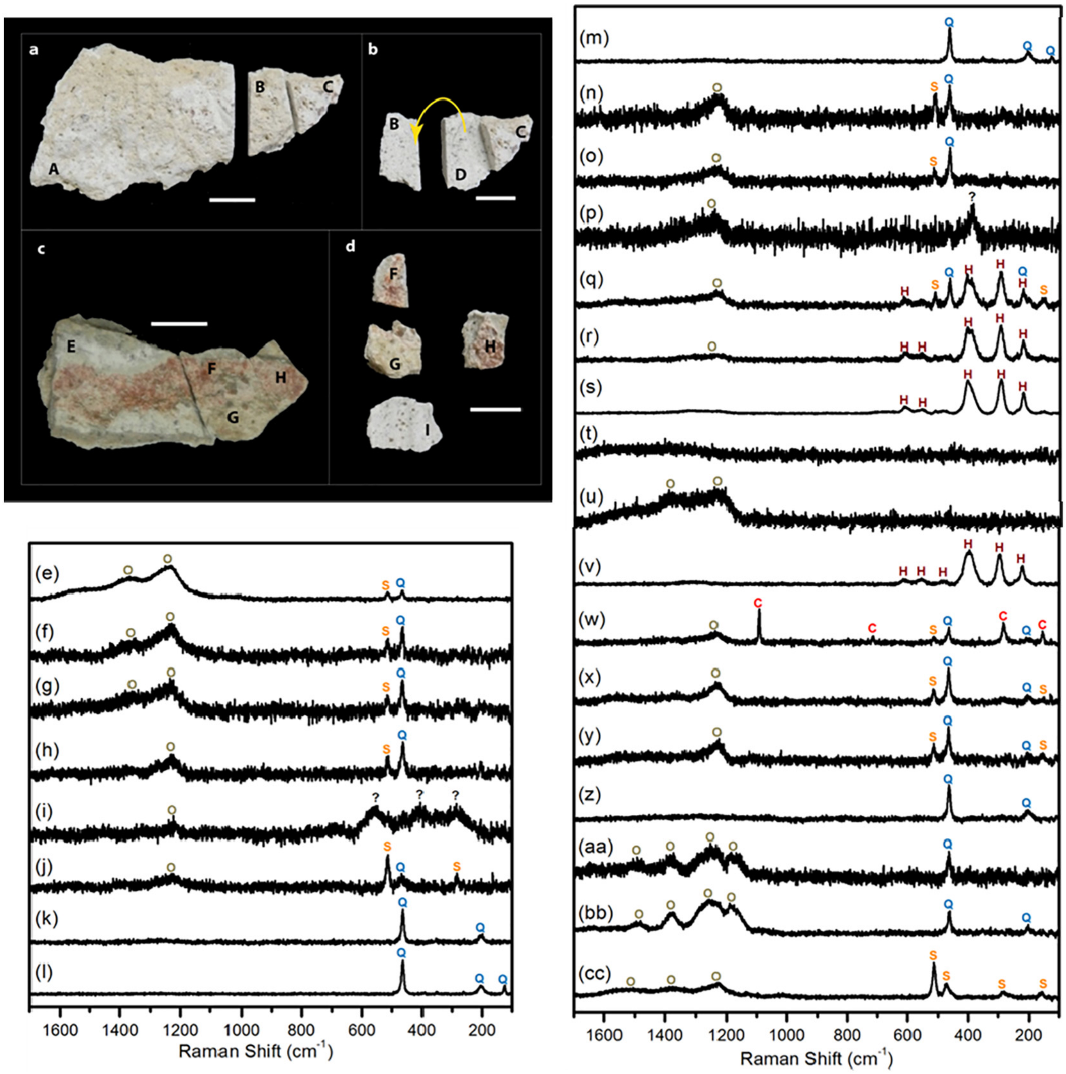


Fig. 6. Raman spectra of samples VQ1-1 (upper left panel a, b) and VQ2-2 (upper left panel c, d) used to determine substrate characteristics. **VQ1-1:** Image (a) shows the upper surface of VQ1-1 with paint removed and two vertical saw cuts. Image (b) shows fragments B-D disassembled revealing the horizontal saw cut. Fragment B in (a) is shown flipped over in (b), as indicated by the arrow, revealing a flat, cut surface that is ca. 3 mm below the outside surface of the sample after paint was removed for dating. Fragment B is 1.9 × 1.0 × 0.3 cm in size and weighs 0.8 g. **VQ2-2:** Image (c) shows the entire sample with vertical saw cuts. Image (d) shows fragments F—I disassembled, revealing the horizontal saw cut separating upper fragment G and underlying basal fragment I. Fragments F, G, and I are 1.2 × 0.9 × 0.15 cm (0.39 g), 1.3 × 1.25 × 0.4 cm (0.6 g), and 1.6 × 1.1 × 0.3 cm (0.9 g) in size, respectively. The upper surfaces of fragments F and G produced p and ps, and ps spectra, respectively. The cut surface of fragment I, shown clearly in Image (d), produced ss spectra. **Lower left panel:** Raman spectra (785 nm laser) of VQ1-1 fragment B; ss spectra (e) through (i) are from smooth areas of the cut surface whereas spectra (j) through (l) are from rough areas. **Right panel:** Raman spectra of VQ2-2. Spectra (m) through (p) are from the painted surface of fragment F, whereas spectra (q) through (s) are from rough areas on the surface where paint was removed. Spectra (t) and (u) are ps spectra from the roughened upper surface of fragment G. Spectra (v) through (z) are ss spectra from smooth cut surfaces of fragment I, whereas spectra (aa) through (cc) are from roughened areas. Labels are defined in the legend of Fig. 5.

characterization of the substrate in Fig. 5, and of the paint in Fig. 7.

In sample VQ2-2, peaks that might correspond to organics are apparent in Raman spectra for painted areas of fragment F (Fig. 6m–p) but are less apparent in areas where paint was removed. Instead, the ps spectra, which were obtained from small colored spots on the surface, show evidence of preserved paint indicated by numerous hematite peaks (Fig. 6q–s). The ps surface of fragment G also shows organic material in spectrum (u) of Fig. 6. Scans covering a larger area of the ss surface of fragment I show only minor evidence of organics (Fig. 6v–z). Spectrum (v) shows no evidence of organics but does record the presence of hematite in the fragment I ignimbrite, probably incorporated during the formation of the rock. Large orange and orange-brown particles in the rock do show Raman signals consistent with organics (Fig. 6aa–cc).

These data suggest that organic carbon is present at shallow depth within the ignimbrite substrate; this probably accumulated after a new surface was produced by mechanical weathering of the rock. It also suggests that it might be possible to estimate when a rock surface was first exposed by examining organic matter in the top few mm of the exposed surface. If true, the organic matter in substrate should provide a maximum age for any rock art that is present on the rock surface.

4.2. Paint characteristics

Optical microscopy images of fragments from the dot and negative hand motifs are shown in Fig. 7a–c. The paint layer of the dot art is clearly visible in the side view of the VQ1-1 fragment (Fig. 7a); it is relatively thick (20–40 μm) and continuous. In contrast, the paint on the negative hand motif is thinner (< 10 μm) and the coverage is irregular (Fig. 7b–c). This is consistent with the techniques used to apply

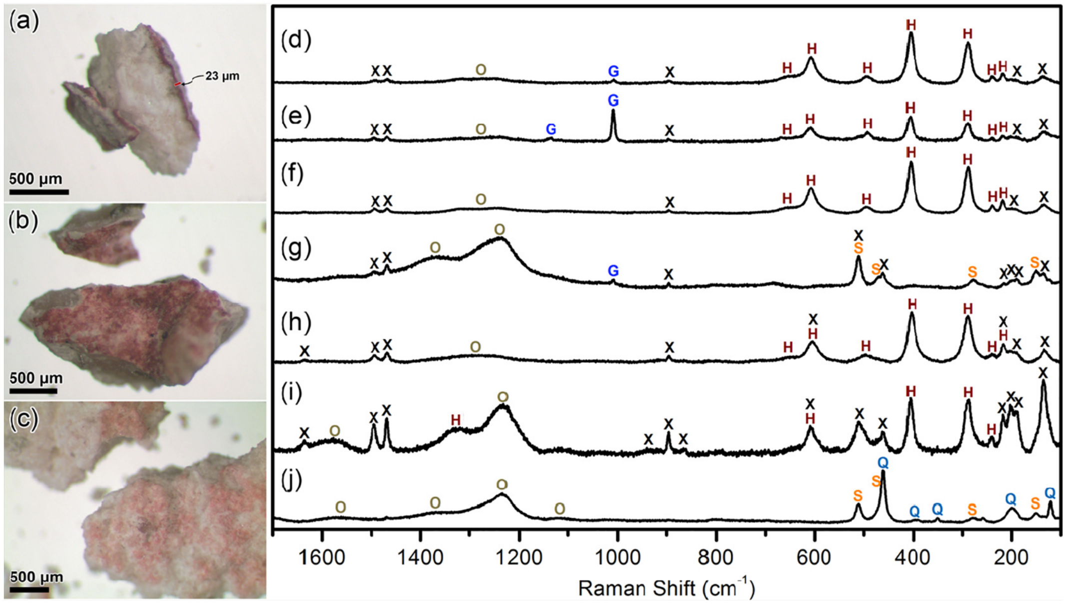


Fig. 7. Micro-Raman spectra (785 nm laser) of Viuda Quenzana rock art samples VQ1-1 (a) and VQ2-2 (b–c). Spectra (d–f) correspond to red and orange grains on the VQ1-1 paint; spectrum (g) corresponds to the freshly cleaved substrate beneath the paint. Spectra (h) and (i) correspond to red and orange grains on the VQ2-2 paint; spectrum (j) corresponds to the freshly cleaved substrate beneath the paint. Labels are defined in the legend of Fig. 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the paint in the creation of each motif: dots are generally produced by direct application of paint either by hand or using tools, which leave a continuous layer of paint. Negative hands are usually produced by spraying paint around a hand pressed onto the bedrock, thus leading to a discontinuous layer of paint (Fiore and Acevedo, 2016; Acevedo, 2017).

We next examined grains of pigment and the adjacent substrate with micro-Raman spectroscopy. Spectra from several red and orange grains of the dot motif VQ1-1 (Fig. 7d–f) indicate the presence of α–Fe_2O_3, along with gypsum ($CaSO_4{\cdot}2H_2O$), calcium oxalate monohydrate ($CaC_2O_4{\cdot}H_2O$), and traces of organics (very broad resonances at 1200–1400 cm^{-1}). In comparison, the freshly-cleaved substrate just below the paint layer (within 1 mm) (Fig. 7g) contains gypsum, calcium oxalate monohydrate, and sanidine, and a more pronounced organic component than in the paint layer.

Spectra from several red and orange grains of the hand motif VQ2-2 (Fig. 7h–i) show the presence of α–Fe_2O_3, substantial calcium oxalate monohydrate, and organics, whereas the substrate immediately below this paint layer (Fig. 7j) contains quartz, sanidine, and unknown organics. For both samples, we checked the Raman spectra of red and orange grains at a low laser power (0.1 W) to ensure that laser-induced heating was not causing the in situ conversion of iron oxides/hydroxides to α–Fe_2O_3 (de Faria and Lopes, 2007). We observed α–Fe_2O_3 consistently at all laser powers.

The presence of broad peaks in the two paints from 1200 to 1400 cm^{-1}, similar to some of the peaks in the substrate spectra (Figs. 5 and 7), was a curious feature in the micro-Raman data. Such peaks are consistent with undefined organics, i.e., complex mixtures or degradation products. By switching to another laser source (from 785 to 532 nm) we were able to identify this organic component in the VQ1-1 paint. The resolved spectra from the surface of the painted dot motif (Fig. 8a–b) are in excellent agreement with previously reported Raman data for animal fats (Boyacı et al., 2014; Prinsloo et al., 2008; Maier et al., 2005). The pattern of peaks at ca. 1600, 1400, 1350, 1300, and 1240 cm^{-1} is especially characteristic of C═O, C═C, and C–H vibrations of unsaturated triglyceride molecules (Prinsloo et al., 2008).

Scanning electron microscopy (SEM) provided more detailed views of the rock art, accompanied by elemental analysis through energy

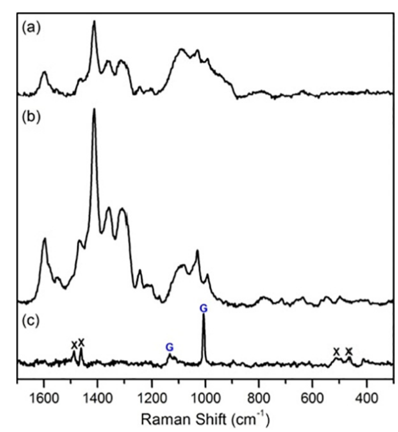
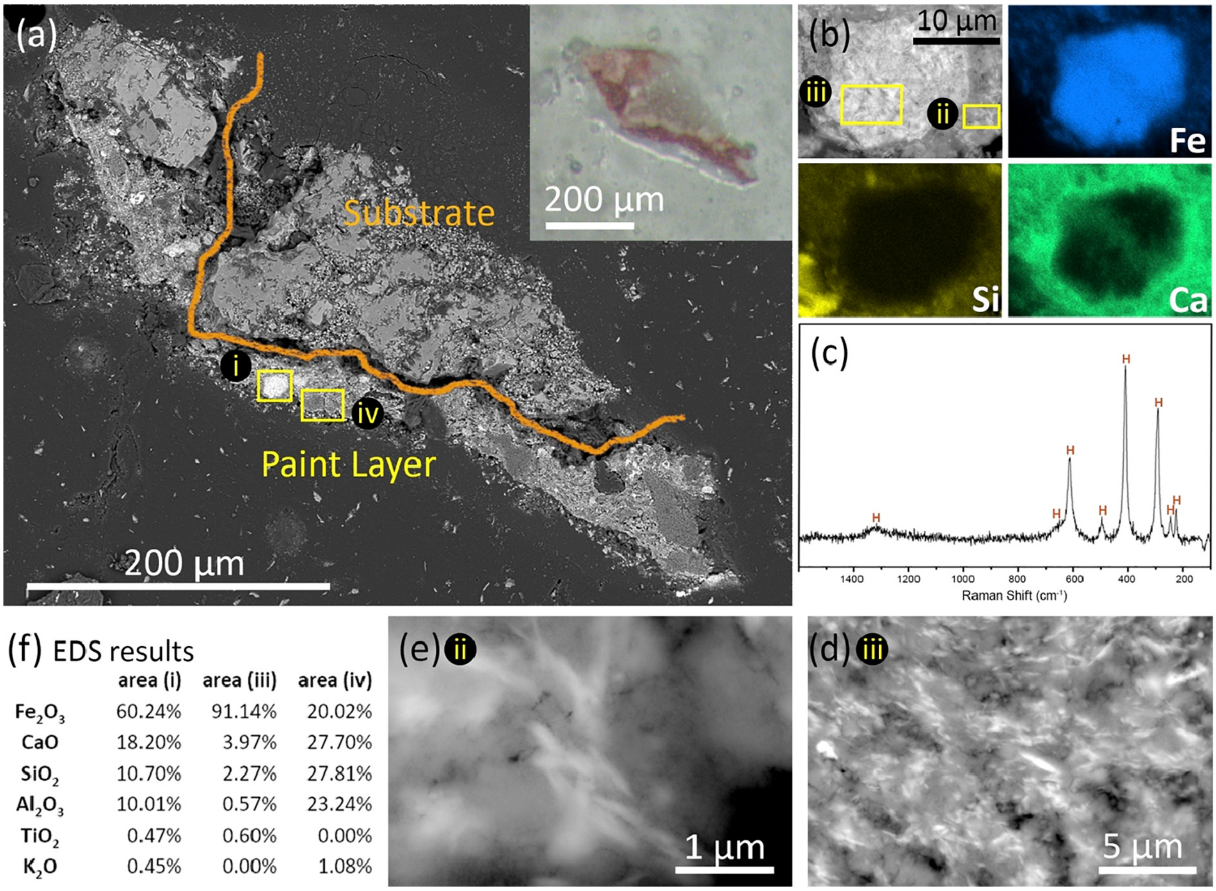


Fig. 8. Raman spectra from sample VQ1-1 (532 nm laser): two colored areas (a, b) and a substrate area (c). Labels are defined in the legend to Fig. 5.

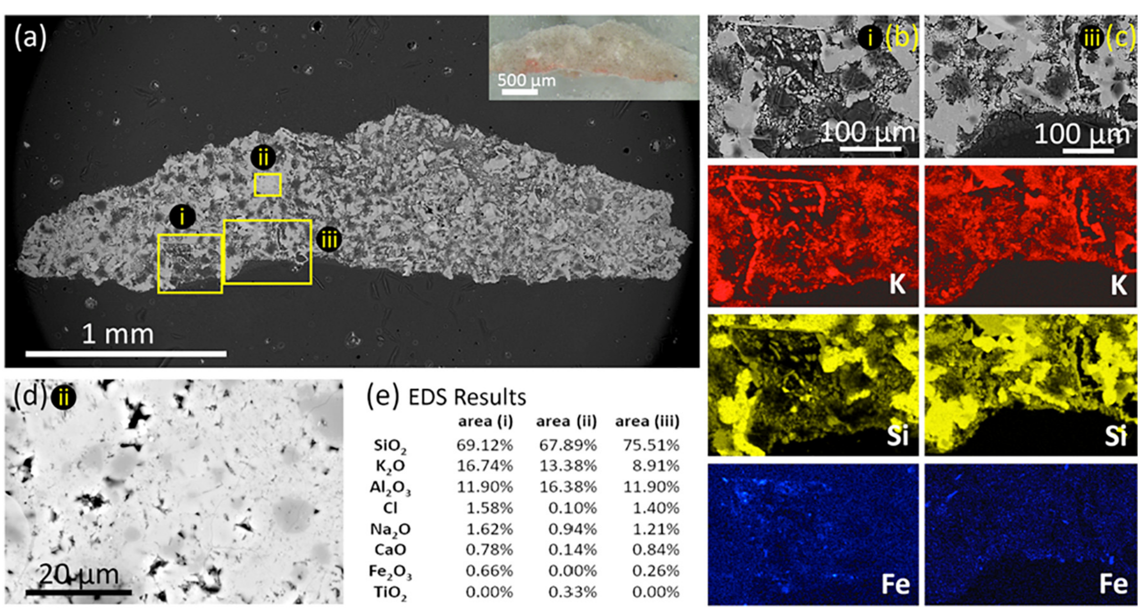
dispersive spectroscopy (EDS). Fig. 9a shows a polished cross-section from the dot art VQ1-1. Because this is a backscattered electron image, the bright areas correspond to concentrations of higher atomic number elements—in this case, iron—that are located within the paint layer, which delaminated from the substrate during polishing. EDS mapping of one particularly bright spot (Fig. 9b) shows a ca. 20 μm diameter patch of iron oxide surrounded by a Ca-, Si-, and Al-containing matrix. Raman spectroscopy at this spot (Fig. 9c) provided peaks for all eight vibrational modes for hematite (Jubb and Allen, 2010; Bonneau, Moyle et al., 2017), which confirmed that this iron oxide is specifically the α–Fe_2O_3 polymorph. Higher magnification inspection of this region revealed anisotropic structures (Fig. 9d–e) that are consistent with ca. 0.5–2 μm α–Fe_2O_3 platelets in cross-section. Thus the VQ1-1 paint is heterogeneous on the micron scale, containing areas with < 20% Fe_2O_3 adjacent to areas with > 91% Fe_2O_3; the balance of the material consists of Ca, Si, and Al (oxides or oxalates) with minor K and Ti content.

A detailed view of the negative hand print VQ2-2 is shown in Fig. 10. The thin, non-continuous paint of this motif means that very little of it is visible in cross section. Panels 10b and 10c show two areas with meager α-Fe_2O_3; these grains are most visible in the EDS maps of



	area (i)	area (iii)	area (iv)
Fe_2O_3	60.24%	91.14%	20.02%
CaO	18.20%	3.97%	27.70%
SiO_2	10.70%	2.27%	27.81%
Al_2O_3	10.01%	0.57%	23.24%
TiO_2	0.47%	0.60%	0.00%
K_2O	0.45%	0.00%	1.08%

Fig. 9. Characterization of sample VQ1-1 as a polished cross section. (a) Backscattered electron SEM image showing the paint layer on the substrate (optical microscopy inset). (b) Backscattered electron SEM image of area (i) along with EDS elemental maps. (c) Micro-Raman spectrum (785 nm laser) collected at area (i). (d, e) Higher magnification backscattered electron SEM images of areas (iii) and (ii), respectively, showing the microplaty hematite morphology. (f) Table summarizing metal oxide content for areas (i), (iii), and (iv) determined by EDS. In (c) H = hematite.



	area (i)	area (ii)	area (iii)
SiO_2	69.12%	67.89%	75.51%
K_2O	16.74%	13.38%	8.91%
Al_2O_3	11.90%	16.38%	11.90%
Cl	1.58%	0.10%	1.40%
Na_2O	1.62%	0.94%	1.21%
CaO	0.78%	0.14%	0.84%
Fe_2O_3	0.66%	0.00%	0.26%
TiO_2	0.00%	0.33%	0.00%

Fig. 10. Characterization of sample VQ2-2 as a polished cross section. (a) Backscattered electron SEM image showing fragmentary paint on the substrate (optical microscopy inset). (b, c) Higher magnification backscatter SEM images of areas (i) and (iii), respectively, along with EDS maps of potassium, silicon, and iron for the same areas. (d) Higher magnification backscatter SEM image of area (ii). (e) Table summarizing metal oxide content for areas (i), (ii), and (iii) determined by EDS.

Table 1
Radiocarbon ages for organic material from paint and substrate at Viuda Quenzana.

UGAMS ID	Sample ID	Material	δ^{13}C‰	Age (^{14}C BP)	Calibrated age (cal BP or cal CE)		
					1σ probability	2σ probability	Median probability
13612	VQ1–1a	Paint (dots)	−24.8	3050 ± 50	3079–3325 BP	3007–3357 BP	3194 BP
13612b	VQ1–1b	Substrate	−23.3	3440 ± 60	3564–3810 BP	3481–3829 BP	3648 BP
13613	VQ2–2a	Paint (hand)	−22.6	520 ± 50	498–540 BP 1410–1452 CE	341–624 BP 1326–1609 CE	518 BP 1432 CE

Table 2
Comparison of δ^{13}C values for dated VQ carbon with common natural materials in Patagonia, Argentina. Modern values have been corrected for the Suess effect by adding 1.5‰ so that they can be compared with archaeological samples. [1]Barberena et al. (2009) with information from Tessone et al. (2005), Carballo Marina et al. (1999), Borrero et al. (1998–1999, 2006, 2009), Campan et al. (2007), Barberena (2002), Franco and Borrero (2003), Franco et al. (1999), and Aschero et al. (2007); [2]Tessone et al. (2013) modern guanaco assemblages central west Santa Cruz province including Lago Cardiel area; [3]Tessone et al. (2009), Salitroso Lake; [4]Zangrando et al. (2004), Tierra del Fuego island (coast); [5]Politis et al. (2009), Pampa on Atlantic coast ca. 400 km south of Rio de la Plata; [6]Trees: Nothofagus spp. Bushes: caulk (Berberis spp.), neneo (*Mulinum spinosum*), primrose (*Colliguaja integerrima*), molle (*Schinus polygamus*) and tail piche (Nassauvia spp.). Grasses: coirones (Stipa spp., and Festuca spp.).

Material and location	δ^{13}C (‰)
Rock art paint pigment	
VQ1-1a carbon in paint sample from VQ1	−24.8
VQ2-2 carbon in paint sample from VQ2	−22.6
VQ1-1b carbon in substrate from VQ1	−23.3
Animals-herbivores	
Lama guanicoe collagen	
Southern Patagonia steppe[1]	−18.6 to −22.3
Southern Patagonia forest[1]	−19.0 to −24.9
Central-west Santa Cruz Province[2]	−16.7 to −21.2
Subcutaneous fat *L. guanicoe*[3]	−30.8
Medullary fat *L. guanicoe*[3]	−28.6
Muscle *L. guanicoe*[3]	−21.5 to −25.5
Choique (*Peterocnemia pennata*) collagen[3]	−19.7 to −22.6
Animals-carnivores	
Canine red fox (*Pseudalopex culpaeus*)[4]	−17.3
Canido[4]	−19.2
Canidae[5]	−13.5
Pseudalopex culpaeus and puma (*Felis concolor*) collagen[3]	−17.0 to −19.8
Bird eggs	
Choique-Pterocnemia Pennata & common cauquén-*Chloephaga picta*	
Egg white[3]	−24.2 to −24.9
Egg yolk[3]	−28.3 to −31.6
C_3 plants	
C_3 plants [3, 6]	−24.3 to −28.3
Calafate *(Berberis buxifolia)*[4]	−25.0
Mata verde *(Lepidophyllum cupressiforme)*[4]	−24.9
Coirón (*Festuca sp.*)[4]	−24.9
Nothofagus sp.[4]	−24.0
Archaeological charcoal Chico River basin (interior)	−22.0 to −23.7
Archaeological charcoal Santa Cruz River basin (interior)	−21.3 to −22.9
Archaeological charcoal Santa Cruz River basin (coast)	−22.5
C_4 and CAM plants	
C_4 plants [3, 6]	−13.0
Archaeological charcoal Santa Cruz River basin (coast)	−16.4

iron. A large sanidine grain in the substrate of VQ2-2 (Fig. 10d) allowed us to determine the chemical composition of this rock as $K_{0.9}Na_{0.1}(Al_{0.9}Si_{3.1}O_8)$, which is consistent with potassium-rich feldspar containing a minor contribution from the other end member of the series, albite [$Na(AlSi_3O_8)$]. In addition, the surface is covered with 0.5–10 µm grains of a silicon- and potassium-containing material comprising a 50–200 µm thick layer, which likely is wind-borne sanidine dust accumulation. Although the appearance of this layer is more obvious in sample VQ2-2, a similar thin layer of dust covers the paint of sample VQ1-1. No other accretion materials are visible on either sample, which is perhaps surprising in light of prior observations of distinct calcium oxalate or gypsum encrustations covering rock art (Hernanz et al., 2007, Wainwright, Helwig, Rolandi, Aschero al., 2002, Wainwright et al., 2004). To summarize, the microstratigraphy of VQ1-1 consists of a 20–40 µm thick α-Fe_2O_3-rich paint layer directly on the rock substrate surface, and this paint is covered with a thin layer of rock dust. The microstratigraphy of VQ2-2 consists of spotty α-Fe_2O_3-containing paint found directly on the rock substrate surface, and this paint also is covered with rock dust.

4.3. Radiocarbon dating

Organic material in the reddish dot paint of VQ1–1 dated to 3050 ± 50 ^{14}C BP (Table 1) or 3007–3357 cal BP (2σ probability; median probability age (MPA) = 3194 cal BP). Organic material in the pink negative hand paint dated to 520 ± 50 ^{14}C BP or 341–624 cal BP/ 1326–1609 CE (2σ, MPA = 518 cal BP or 1492 CE, Table 1) (Stuiver and Reimer, 1993; Reimer et al., 2013; Hogg et al., 2013). The sample from the weathered unpainted rock surface laterally adjacent to the reddish dots produced an age of 3440 ± 60 ^{14}C BP or 3481–3829 cal BP (2σ; MPA = 3648 cal BP) (Table 1). This last result complicates the interpretation of the age obtained for the reddish dot paint, because when paint was collected it was impossible not to include a small amount of substrate. The fact that the paint sample and its small amount of substrate (3007–3357 cal BP) is younger than the sample composed entirely of substrate with no paint present (3481–3829 cal BP) is to be expected because the paint must be younger than the substrate upon which it was applied.

A further point of importance is that the negative hand of VQ2-2 provided a much younger age than the VQ1-1 paint or the VQ1-1 unpainted substrate. In the rock shelters at VQ, the walls are fragile and so periodically thin rock slabs break away, being replaced by younger surfaces. The organic material that accumulates on these surfaces is a measure of when they were exposed and how long they have lasted. For this reason, we believe that the ages of substrates beneath rock art in this area do provide information on the ages of paints applied to them. At the very least, we believe that the dots of VQ1-1 are younger than 3007–3357 cal BP (MPA = 3194 cal BP) and the negative hand of VQ2-2 is of comparable age or younger than 341–624 cal BP or 1326–1609 CE (MPAs = 518 cal BP and 1432 CE). The two rock art ages are consistent with evidence of human occupation at La Gruta 1 and 3, about 25 km south of VQ, at 3707 cal BP and 521–305 cal BP (MPAs) (Brook et al., 2015), which is discussed more fully below. The pink, stenciled hand is relatively recent, which supports the notion that such artwork continued through the Late Holocene (defined as 4200 cal BP to present by Walker et al., 2012), despite changes in other artistic motifs.

4.4. Isotopic characteristics of dated organic material

As mentioned previously, the samples we used to date the VQ1-1 and VQ2-2 paints included some of the underlying rock substrate. We could not avoid this because there was a limited amount of paint on an irregular surface, thus some substrate was removed to recover all of the paint. Thus the question is, what was the organic material that we dated—animal fat or something else? The $\delta^{13}C$ values for the organic carbon we extracted from the two paint samples and from the unpainted substrate sample were −24.8‰, −22.6‰ and −23.3‰ and provide some information on what was dated.

Archaeological and modern isotope data for natural substances in Patagonia that might have been added to paint are shown in Table 2. From ca. 1750 CE, and particularly from the beginning of the Industrial Revolution in Europe around 1850, fossil fuel combustion has increased atmospheric CO_2 and decreased its $\delta^{13}C$ composition by 1.7–2‰, from ca. −6.4‰ in 1750 to −8.4‰ in 2012 (Bowling et al., 2014). This is known as the "Suess effect" (Suess, 1955; Revelle and Suess, 1957). Modern data listed in Table 2 have been corrected to account for the Suess effect by adding 1.5‰ to measured values (e.g., see Tessone and Panarello, 2009; Tessone et al., 2013; Marino and McElroy, 1991).

Fat and tissue of predator animals and C_4 and CAM organic material have $\delta^{13}C$ values that are much higher than the carbon we dated. However, fat and tissue of herbivores, C_3 plant organic material, and choique-*Pterocnemia pennata* and common cauquén-*Chloephaga picta* egg albumen do have $\delta^{13}C$ values that overlap those of the material dated. In the case of guanaco collagen, Barberena et al. (2009) report slightly higher $\delta^{13}C$ values for animals living in steppe environments (mean = −20.2 ± 0.8‰) compared to those living in or near forest (mean = −22.1 ± 1.8‰) although the mean values are statistically the same. Collagen $\delta^{13}C$ values for guanaco living in areas of steppe, which is the vegetation at VQ, are slightly higher than the values we obtained from the rock art paint (Table 2). However, guanaco muscle tissue and choique collagen both have $\delta^{13}C$ values similar to those of the carbon in the paint. We have not been able to find published values for lichens and mosses in continental Patagonia but $\delta^{13}C$ of terrestrial lichens and mosses in northern Iceland ranged from −22.9‰ and −25.2‰ (lichen) and −24.6‰ to −24.9‰ (moss) (Wang and Wooller, 2006), while lichens and mosses on xeric sites in northern Michigan, USA had $\delta^{13}C$ values ranging from −20.3‰ to −25.6‰ (Teeri, 1981). In both cases 1.5‰ was added to the measured modern values to account for the Suess effect so that they can be compared with archaeological carbon isotope data.

The data in Table 2 suggest that the carbon we extracted from the VQ paints and from the unpainted substrate of VQ1-1 is consistent with it being C_3 plant material, animal fat, tissue, or choique egg albumen, or a mixture of these substances. The isotopic characteristics of animal fat are absolutely consistent with our Raman evidence suggesting that animal fat was added as a binder to the VQ1-1 dot motif paint. The lack of evidence for animal fat in VQ2-2 and in the sample of unpainted substrate from VQ1-1 does not rule out its presence in these samples in small amounts. However, it means that we cannot rule out that the carbon we dated in these samples (and indeed some of the carbon in the reddish dot paint) came from choique egg albumen or C_3 plant material, or possibly even from fungal hyphae and cyanobacteria, which could have colonized the VQ rock shelter walls and ceilings in the past, and can be present in solid rock at depths of more than 10 mm below the surface (Edwards et al., 2000).

5. Discussion

5.1. Paint analysis

Iron oxide is the most widely used red pigment in prehistoric rock art worldwide (e.g., Cornell and Schwertmann, 2003). Furthermore, iron oxide-based pigments were used for body painting (Onelli, 1904; Fiore, 2002), burial and mummification practices (Franco et al., 2012, Sepúlveda et al., 2014), and decorating pottery and textiles (Bellelli, 1980; Goodall et al., 2009; Backes et al., 2012). Thus, it is not surprising that we find iron oxide-based paints used in the rock art at VQ. This observation is similar to findings at other rock art sites in Patagonia, including those in the Río Pinturas area (Iñíguez and Gradín, 1977; Barbosa and Gradin, 1986/87; Wainwright, Helwig, Rolandi, Gradin et al., 2002) and Río Negro province (Darchuk et al., 2010; Boschín et al., 2002; Maier et al., 2007; Vázquez et al., 2008; Wainwright et al., 2000). In these studies, various orange-red-brown pigments were identified as iron oxides using X-ray diffraction and Raman spectroscopy. Here we aim to make much more specific conclusions about the paint used at VQ (Table 3): in particular, both the reddish dot and pink negative hand motif studied were made using mineral hematite-based paints, and the reddish dot art was made specifically with a paint composed of microplaty hematite pigment and an animal fat binder.

Table 3
Summary of components identified in Viuda Quenzana rock art and substrates.

	Reddish dot motif (VQ1-1)	Pink negative hand motif (VQ2-2)
Substrate	Sanidine [$K(AlSi_3O_8)$] Phlogopite [$KMg_3(AlSi_3O_{10})(F,OH)_2$] Kaolinite [$Al_2Si_2O_5(OH)_4$] Calcite ($CaCO_3$) Gypsum ($CaSO_4{\cdot}2H_2O$) Quartz ($\alpha$-$SiO_2$) Whewhellite ($CaC_2O_4{\cdot}H_2O$) Unidentified organics	Sanidine [$K(AlSi_3O_8)$], including [$K_{0.9}Na_{0.1}(Al_{0.9}Si_{3.1}O_8)$] Phlogopite [$KMg_3(AlSi_3O_{10})(F,OH)_2$] Kaolinite [$Al_2Si_2O_5(OH)_4$] Calcite ($CaCO_3$) Quartz ($\alpha$-$SiO_2$) Unidentified organics
Paint	Hematite (α-Fe_2O_3) Gypsum ($CaSO_4{\cdot}2H_2O$) Whewhellite ($CaC_2O_4{\cdot}H_2O$) Animal fat Unidentified organics	Hematite (α-Fe_2O_3) Whewhellite ($CaC_2O_4{\cdot}H_2O$) Unidentified organics

Several lines of evidence lead to these conclusions. The first point is that hematite (the mineral form of α–Fe_2O_3) is the only pigment present in the VQ1-1 and VQ2-2 paint samples. The absence of a clay mineral (e.g., kaolinite) and quartz, typical components of ochre mixtures (Bikiaris et al., 1999), is consistent with a mineral hematite source. The absence of other iron oxide/hydroxide species, such as goethite (α-FeOOH), is also consistent with hematite rather than ochre. In addition, the α–Fe_2O_3 in the VQ1-1 and VQ2-2 paints is well-ordered (crystalline) according to Raman spectroscopy, in contrast to the disordered iron oxides that often characterize ochres (Cornell and Schwertmann, 2003; de Faria and Lopes, 2007). The observation of solely mineral hematite at VQ differs from the reports of multiple iron oxides (hematite, maghemite, goethite, ochres) in pink-red-brown pigment samples from other rock art sites in Patagonia, including La Cueva de las Manos, Cerro de los Indios, El Alero Cárdenas, Cueva Leleque I, Cueva Alonso I, Cueva Comallo I, Cueva Loncomán, and Carriqueo rock shelters (Iñíguez and Gradín, 1977; Barbosa and Gradin, 1986/87; Boschín et al., 2002; Maier et al., 2007; Darchuk et al., 2010).

Furthermore, maghemite (γ-Fe_2O_3) and carbon particles are not present in the VQ1-1 or VQ2-2 paints: such absence is not due to limitations of the methods carried out here, since they would be apparent in the Raman spectra. The absence of these components makes the possibility of α–Fe_2O_3 derived from a "roasted goethite" source unlikely (Mastrotheodoros et al., 2010; Cornell and Schwertmann, 2003). Although there is strong evidence for the intentional heat treatment of goethite to hematite by prehistoric people at locations in France, Italy, and Ethiopia (Gomes et al., 2013; Salomon et al., 2015; Gialanella et al., 2011)—for the purpose of producing the more desirable red α–Fe_2O_3 pigment—such pigment processing does not appear at VQ.

An additional point is the high α–Fe_2O_3 content of the reddish dot paint, which is consistent with a mineral hematite-based pigment. Although this paint is heterogeneous at the micron length scale, the overall α–Fe_2O_3 concentration is ca. 20% and reaches > 90% in certain spots. These values are high compared to the iron oxide content of other red rock art paints; quantitative studies are scarce, but examples include San rock art in South Africa (red paint containing ca. 3–15% Fe_2O_3) (Bonneau et al., 2012) and rock paintings in the Lower Pecos archaeological region, southwestern United States (red paint containing ca. 2–17% Fe_2O_3, red "crayons" containing ca. 13–62% Fe_2O_3) (Bu et al., 2013). Our examination of the reddish dot paint at > 15,000 × magnification revealed that the morphology of the α–Fe_2O_3 is 0.5–2 μm platelets (Fig. 9b, d, e); in the geological literature, this morphology is the so-called "microplaty hematite" (Morris, 2012). Such hematite is a typical component of banded iron formations (Sun and Li, 2017; Hagemann et al., 2016; Morris, 2012) and has been found at diverse iron ore sites, such as the Quadrilátero Ferrífero and Carajás Mineral Province, Brazil (Hensler et al., 2015; Figueiredo e Silva et al., 2013) and the Arabian shield in western Sinai, Egypt (Salem et al., 1998). Notably, microplaty hematite also has been identified in red iron oxide-based paints from two rock art sites in northern Chile (Sepúlveda et al., 2012), a rock art site in France (Salomon et al., 2015), and rock art in Canada (Bonneau, Moyle et al., 2017) by scanning electron microscope imaging. This distinctive morphology suggests the possibility of tracing the hematite source used to prepare the VQ1-1 paint to a specific geological location or locations. Efforts to establish the provenance of iron oxides used in prehistoric rock art paints have been successful in several studies so far (Eiselt et al., 2011; Bonneau et al., 2012; Bu et al., 2013; Prieto et al., 2016).

In comparing the colors of the reddish dot motif versus the pink negative hand print, we conclude that the color difference originates from the thickness of the remaining paint and the concentration of α–Fe_2O_3, with the dot motif containing substantially more pigment in its 20–40 μm thick continuous paint layer. It also is well known that the color of α–Fe_2O_3 particles varies with primary grain size and clustering, with micron-sized α–Fe_2O_3 particles typically appearing deep red-brown (Cornell and Schwertmann, 2003), as seen in VQ1-1. Also, as noted above, the different amount of paint found in each motif at the μm scale (thicker in the dot and thinner in the hand) is also consistent with the different paint application techniques identified during fieldwork for each motif type (Fiore and Acevedo, 2016; Acevedo, 2017).

The association of calcium oxalate monohydrate with both the paint and substrate of VQ1-1 and the paint of VQ2-2 points to two possibilities: either this material was present as an original constituent of the paint, or it has microbiological origins. In support of the first possibility, prior observations of calcium oxalate monohydrate in pigment samples from Catamarca Cave in northwestern Argentina (Edwards et al., 2000) were accompanied by the interesting proposal that it might originate from extracts of Cactaceae species that produce calcium oxalate biominerals (Franceschi and Loewus, 1995), which were intentionally added as a binder or diluent during paint preparation. A similar hypothesis has been explored in the context of Ethiopian and South African prehistoric rock paintings (Arocena et al., 2008; Lofrumento et al., 2012). Although no Cactaceae species are present currently in the VQ area, in fact the accumulation of calcium oxalates has been reported in over a thousand different genera of plants, where it is linked to the detoxification of calcium ions (Franceschi and Nakata, 2005).

Supporting the second possibility, it is well known that metal oxalates are generated from atmospheric CO_2 by the bioactivity of microorganisms (Martin et al., 2012; Gadd, 2006). For example, many saxicolous lichens excrete oxalic acid as a secondary metabolite, which then readily reacts with metal cations in the substrate (Jorge Villar, Edwards, Cockell et al., 2005; Jorge Villar, Edwards, Seaward, 2005; Ibarrondo et al., 2017). In the presence of calcium minerals, such as the calcite and gypsum present in the substrates of samples VQ1-1 and VQ2-2, this chemistry produces calcium oxalate monohydrate (whewellite) or dihydrate (weddellite); because these oxalates are only sparingly water-soluble, they can accumulate in significant quantities, even forming macroscopic surface encrustations (Russ et al., 1996; Girbal et al., 2001; Steelman et al., 2002; Edwards et al., 2003; Edwards, 2007). This biochemical restructuring, together with the growth of lichen hyphae up to 10 mm beneath the surface of colonized rocks, can contribute significantly to the biodeterioration of rocks (Gomez-Alarcon and de la Torre, 1994; Edwards et al., 2000; Edwards, 2007). Calcium oxalates, especially the monohydrate, frequently have been observed on rock art in widely varying environments. Examples occur at other sites within Patagonia (e.g., rock shelters in the Rio Pinturas Valley) (Wainwright, Helwig, Rolandi, Gradin et al. et al., 2002; Barbosa and Gradin, 1986/87), greater South America (e.g., rock art in Minas Gerais, Brazil) (de Faria et al., 2011), North America (Scott and Hyder, 1993; Bu et al., 2013), Europe (Hernanz et al., 2007; Mas et al., 2013), Africa (Prinsloo et al., 2008; Lofrumento et al., 2012), and Australia (Ford et al., 1994). The presence of calcium oxalates in these samples can be characterized by the unique Raman spectra of calcium oxalate mono- and dihydrates, which provide unambiguous identification, as well as the location of calcium content by EDS, which indicates the distribution of calcium-containing components.

In the present work, Raman spectroscopy of samples VQ1-1 and VQ2-2 indicates that calcium oxalate monohydrate is present in both paints as well as the VQ1-1 substrate ~0.5 cm below the surface (Fig. 5). In addition, EDS mapping shows that the calcium content in the VQ1-1 paint surrounds the Fe_2O_3-rich particles, with the concentration reaching ca. 27% CaO in these areas (Fig. 9b). Such an association could reflect the preferential colonization of the painted areas by lichens due to the nutrients provided by the iron oxide and organic binder (*vida infra*). Although presently there are no lichens, algae, or mosses visible on the painted walls of the VQ1 and VQ2 rock shelters (e.g., Figs. 3 and 4), it is possible that such species thrived during earlier, more humid environmental conditions (Brook et al., 2015). Based on the data at hand, however, it is not possible to make a final conclusion about the origin of the calcium oxalate monohydrate in VQ1-1 and VQ2-2.

A final point related to paint analysis concerns the binder material used at VQ. Raman spectra from the surface of the reddish dot motif VQ1-1 (Fig. 8a–b) match published Raman data for animal fats in a South African rock art context (Prinsloo et al., 2008), a simulated rock art study (Maier et al., 2005), as well as pure isolated animal fats (Boyacı et al., 2014). Although VQ2-2 paint was examined using the same methodology, neither animal fat nor another binder could be resolved. Animal fat is a well-known binder for rock art paints, and there are a significant number of instances where such organic material has been remarkably preserved. Notable examples from prehistoric sites in South America include proteinaceous material detected by Raman spectroscopy (similar to animal fats but not identical) in red rock art at a lowland site in the Limarí River Basin, Chile (Moya et al., 2016), fatty acids consistent with animal fats detected in yellow paint from the Leleque I site in northern Patagonia (Boschín et al., 2002), the detection of a proteinaceous component in paint on a rock fragment from Cerro de los Indios near Viuda Quenzana (Fig. 1) (Wainwright, Helwig, Rolandi, Gradin et al. et al., 2002), an oily material mixed with ground hematite-cinnabar mixtures (possibly shark or sea lion fat, or achiote seed oil) at Gramalote, Peru (Prieto et al., 2016), fatty acids found on lithic tools from the Argentinian Pampas region (Mazzia and Flegenheimer, 2015), and lipids detected on pigment samples from sites in the Beagle Channel region, the southernmost tip of South America (Fiore et al., 2008). According to Mazzia and Flegenheimer (2015), the preservation of animal fats in these samples is due to the environmental protection from the effects of temperature, water, light, oxygen, and microorganisms provided within porous rock substrates. Although porosity may play some role in the preservation of animal fat in sample VQ1-1, the 20–40 μm thickness of the reddish dot paint probably also contributes to the preservation of organics. We cannot be certain about the exact source of the animal fat used to prepare the VQ1-1 paint, but guanaco is a likely candidate. We note that guanaco bones were found during excavations at VQ7 and 8 (Franco et al., 2013 and pers. observ.) and at La Gruta 1, 2 and 3 rock shelters, 25 km from the Viuda Quenzana area (Brook et al., 2015), and accounts from 18th–19th century visitors to Patagonia describe a practice of mixing red clays with rhea or guanaco fat to produce paint (Onelli, 1904; Maier et al., 2007). On the basis of the combined analytical results, we conclude that the reddish dot motif of sample VQ1-1 was made by finely grinding a hematite-rich source, mixing this pigment powder with an animal fat, and then applying the resulting thick paint to the rock shelter wall using fingers or painting implements. Regarding the production of the negative hand, results suggest that fine grained hematite powder was probably mixed with a diluent substance which left no traces of organic remains; such dilution is a prerequisite for the spraying technique typically used in the production of this motif.

5.2. Dating analysis

Gradin et al. (1979) and Gradin (1988, 2001) note that hand negatives are present at different times across the full south-central Patagonian stylistic sequence (*Stylistic Groups A–E*), while dots have been associated with *Stylistic Groups A–C*, and are characteristic of *Stylistic Group B1* (Gradin et al., 1979; Gradin, 1988). As mentioned previously, Gradin and Aguerre (1983) attribute the art at VQ to *Stylistic Group B1* and estimate an age of around 4500 ^{14}C BP (ca. 5130 cal BP), which is not inconsistent with our radiocarbon MPA of 3194 cal BP for the dots of VQ1-1. Also, it is consistent with dates obtained for human occupation of the nearby La Martita Cueva 4 archaeological site (Rubinos Pérez, 2003). Gradin (1968) suggests that hand negatives were painted until at least ca. 3580 cal BP and possibly in more recent times (Gradin, 2001). Hand negatives are thought to have been produced in Patagonia over a considerable time period, and the MPA age we obtained for the VQ2-2 pink hand of 518 cal BP (1432 CE) is consistent with the youngest dates for human occupation of the Southern Deseado Massif (Brook et al., 2013; Franco et al., 2013) and for Cueva de las Manos (450 cal BP; cal 1500 CE; Gradin et al., 1976).

Our studies of the two painted motifs, and the substrates on which they are found, revealed organics in both the paints and in the shallow and deeper substrate materials. Importantly, Raman spectroscopy revealed the presence of animal fat in the paint used to create the reddish dot motif. In fact, in Patagonia during historical times, *Pterocnemia* fat was used as a binding agent in paints applied to animal hides (Onelli, 1904), and so it is possible that in the past it was used as a binder in paints applied to rock surfaces.

The age for the reddish dot motif is consistent with previous estimates of the age of the VQ rock art by Gradin and Aguerre (1983). Furthermore, we would expect the evidence for occupation of the VQ rock shelters, and other sites close enough to be within the home ranges of hunter-gatherers at these latitudes (e.g. Kelly, 1995), to include the period covered by the rock art, which is the Late Holocene. In fact, guanaco bones from the VQ8 rockshelter, with evidence of human action, have provided collagen ages of 4770 ± 25 ^{14}C BP (5470 cal BP) and 4740 ± 25 ^{14}C BP (5400 cal BP) (Franco et al., 2013), indicating human occupation in the period ca. 5500–5400 cal BP. A charcoal age of 1220 ± 20 ^{14}C BP (1080 cal BP or 865 CE) has been obtained from an excavation in the VQ7 rock shelter. In addition, Aguerre (2003) has obtained ages of ca. 4500, 2200 and 1600 ^{14}C BP (ca. 5100, 2160, and 1450 cal BP) for human occupation at La Martita Cueva 4, about 25 km north of VQ (Rubinos Pérez, 2003), and charcoal ages of 3500, 1890, 1830, and 1450 ^{14}C BP (MPAs of 3710, 1780, 1710, and 1315 cal BP) have been obtained for deposits at La Gruta 1, about 25 km to the south (see Table 1 in Brook et al., 2015). Finally, five ages have been obtained from bone and charcoal at La Gruta 1 and 3 (290–530 ^{14}C BP) indicating human occupation at 305–521 cal BP (MPAs).

Therefore, the available evidence shows that the broader VQ region, including VQ, La Martita, La Gruta and El Verano, was inhabited by hunter-gatherers during the later part of the Middle Holocene (Middle Holocene extends from 8200 to 4200 cal BP following Walker et al., 2012) and the Late Holocene (Aguerre, 2003; Brook et al., 2015; Durán et al., 2003; Franco et al., 2013), and stylistic similarities suggest that some paintings in these areas were produced at about the same time (Gradin, 2003; Durán et al., 2003; Fiore and Acevedo, 2016; Acevedo, 2017). Significantly, our age for the reddish dot motif of 3007–3357 cal BP (MPA = 3194 cal BP) correlates very closely with evidence of occupation at La Gruta 1 at 3594–3832 cal BP (MPA = 3707 cal BP), and our age for the pink negative hand of 341–624 cal BP or 1326–1609 CE (MPAs = 518 cal BP and 1432 CE) correlates closely with five charcoal ages indicating occupation of La Gruta 1 and 3 from 305 to 521 cal BP (MPAs). Thus, there is firm evidence of people being in the broader VQ area at the times our research shows that the reddish dots and pink negative hand were created.

Our ages for the two samples of paint, both of which included a small component of the underlying substrate, differ by about 2700 cal years. This could be because the two substrate surfaces beneath the paint were exposed at different times, or because the younger surface has a higher percentage of younger carbon than older carbon despite long exposure. The age difference could also be due to the carbon content of the organic binder used in the production of the paint mixture at VQ1-1 being older than that in the paint of VQ2-2. The first of these options seems the most likely. This means that in areas where the substrate is massive and resistant to breakdown, both due to granular disintegration and flaking, organic materials of considerable age can accumulate on the surface. However, in areas where the rock is highly susceptible to rapid breakdown, the organic material will differ in age depending on how recently the substrate surface was exposed. This is certainly the case at VQ, where the ignimbrite bedrock splits easily and granular disintegration appears rapid. For this reason, we believe that the ages we obtained define the maximum possible ages of the painted motifs and may even provide reasonable estimates of the actual ages of the motifs.

It is important that the ages we obtained for organic carbon in the reddish dot paint, and in the adjacent unpainted substrate of sample VQ1-1, were similar and much older than the age we obtained for the pink hand paint. Although we did not date unpainted substrate adjacent to the VQ2-2 paint, the very young age of this paint sample, which because of our sampling method must have included a small amount of the underlying substrate, suggests that the organics in the VQ2-2 substrate are either very close in age to the paint or not sufficiently older to significantly increase the very young age of the paint. This important observation suggests that organic material at or just below exposed rock surfaces in the VQ rockshelters, is not everywhere of the same age. In fact, we believe that organic carbon is added only when a new rock surface is exposed by disintegration of the rock shelter walls and ceiling, and that the age of this carbon provides a maximum age for any rock art associated with that surface. Thus, even if the paint used to create the rock art cannot be definitively dated, it is possible that the substrate can, and this can provide at least some information about the ages of different rock art motifs and possibly different stylistic groups.

6. Conclusions

This study of the rock art in the Viuda Quenzana archaeological locality has yielded new technological and chronological information about the production of rock art in central-southern Patagonia. In particular, it sheds new light on the materials and technical procedures used by hunter-gatherer populations in the creation of painted images applied to rock surfaces during different periods of human occupation of the area. Our research results suggest the following main conclusions:

i) α–Fe_2O_3 derived from the mineral hematite was used as a pigment in both samples of paint from VQ. Furthermore, the morphology of the α–Fe_2O_3 in the paint from VQ1–1 is a distinctive microplaty type, and so provides a significant marker that might allow a local source of the raw material for the pigment used by the hunter-gatherer populations that produced it to be identified.

ii) Calcium oxalate hydrate (whewhellite) is present in the paint of both samples but the analytical results do not allow us to distinguish the source (intentionally added plant source as part of a binder vs. microbiological degradation product). Raman analysis shows that whewhellite is also present in both substrates, suggesting that it is more likely to have been a microbiological degradation product accumulated before and/or after paint application.
iii) Raman analysis indicates that animal fat was added as a binding agent to the paint used to create the reddish dots of VQ1-1, yet it did not produce evidence of animal fat in the paint used to create the pink hand motif (sample VQ2-2). This result is consistent with the technique potentially used to produce hand motifs: spraying diluted paint, probably blowing it by mouth. We would not expect a binder to have been added because this paint would need to be liquid-like, rather than pasty, for effective application; however, saliva could have played a binding role, helping the pigment to adhere to the rocky surface.
iv) The $\delta^{13}C$ value of the carbon in the paint used to create the reddish dots is consistent with the Raman finding of animal fat in the paint and also with historical observations of hunter-gatherers using animal fat in paint at the time of European contact.
v) AMS radiocarbon ages suggest that the VQ reddish dot and negative hand motifs are younger than about 3200 cal BP and 500 cal BP, respectively. They provide the first absolute temporal references for artistic elements that previously have been related to numerous Stylistic Groups covering a broad temporal range, in the case of the pink hand, even until very recently, near the very end of the archaeological sequence of Patagonia.

Thus, rock art paint production at VQ involved two different processes. One entailed mixing a mineral coloring substance (microplaty hematite) with an organic binder (animal fat), which was then applied to the rock substrate with a painting tool and/or with the fingers (sample VQ1-1). The second entailed using a mineral coloring substance (hematite) with little to no binder (or with a binder that left no chemical trace), which was then applied to the rock substrate by spraying (sample VQ2-2). These results demonstrate an interesting technical variability in the preparation and application of paint during rock art production at VQ. Continuing detailed work on VQ rock art will reveal whether these production processes also are characteristic of particular periods of human occupation.

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