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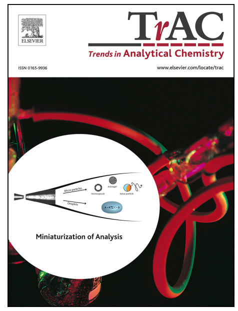

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PII: S0165-9936(17)30456-9

DOI: 10.1016/j.trac.2018.05.011

Reference: TRAC 15155

To appear in: *Trends in Analytical Chemistry*

Received Date: 12 November 2017

Accepted Date: 18 May 2018

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Abstract

An extensive *in situ* Raman spectroscopic campaign was performed on archaeological sites in three different provinces in Patagonia, Argentina (Neuquén, Río Negro and Chubut). 16 open air shelters located in different environments (forests, ecotones, steppes) were investigated and interpreted in terms of pigments used and the identification of substrata. Special attention was given to the alteration products and accretions that were found on the rock art paintings of the shelters and on the surface of the rock walls, as they can affect and damage this magnificent works of art. Haematite (α-Fe_2O_3) was the main chromophore that was found on the red paintings of the most of the shelters studied. The green earth glauconite, was identified only in one case, by using a red (785 nm) and a green laser (532 nm). Other minerals and silicates were found on the couloured areas but also on the rock support. Calcite ($CaCO_3$) and gypsum ($CaSO_4{\bullet}2H_2O$) crystallization was identified on the paintings, crusts and rock surfaces, in combination or alone, and are associated with weathering. In some cases the shelters were so severely degraded that no Raman signal of pigments and/or other components could be retrieved. Calcium oxalates were also detected in several figures and motifs in different shelters.

Keywords

In-situ Raman spectroscopy; rock art; pigment; degradation; Patagonia

1. Introduction

Physicochemical analysis of the composition of materials and pigments is currently becoming a standard analytical procedure in archaeology and particularly in rock art studies [1-3]. In this way, the analysis of pigments from both rocky supports and excavated samples allows us to answer key archaeological questions related to their technological, stylistic and/or temporal aspects [4-8]. As a consequence, the active and continuous communication between archaeologists, chemists and physicists has promoted interdisciplinary investigations, generating working protocols to reach methodological and even interpretive consensus [9].

Patagonia (Argentina) hosts a remarkable amount of painted rock art found quite commonly from the North to the South. The rock art paintings can be found ranging of single multi- and/or mono-coloured panels to more sophisticated multipanel ones. The examination of these prehistoric works of art, combined with archaeological studies in the Patagonian field from several archaeological sites, provides rich knowledge of the local hunter gatherers populations and a deeper understanding on their practice inside the environmental systems (forests, ecotones, steppes). Within these different, hostile and remote environments, hunter-gatherers groups demonstrated great mobility [10-11].

In general, micro-Raman spectroscopy is a powerful tool of the investigation of pigments, degradation products and substrata in rock art paintings [12-15]. Minimal samples can be brought in the laboratory and measured *in vitro* down to a micrometer-scale [16]. In cases that the invasive character of this approach cannot be justified, mobile Raman instrumentation can be employed. In fact, there are several studies in literature describing the use of portable Raman spectrometers [11, 17-18] in field studies with excellent results on the characterization of pigments, crusts and substrata. Moreover, by bringing such instrumentation to the site the preservation state of the work art can be monitored directly.

Studies in Argentina focused mainly on the characterization of pigments from different archaeological contexts by means of multiple, non-portable techniques [5, 9, 12, 19-27]. However, most of these studies did not specifically address the degradation processes that affect the rock art motifs and the preservation state of the archaeological sites in general. Moreover, severe degradation and/or thick encrustations encapsulate the actual painting in between layers to the point that it might be not visible anymore. Therefore, we consider it necessary, next to the pigments identification, to study also those factors in detail that cause the deterioration of the rock art paintings and have important implications when studying the main chromophores used by the hunters and gatherers societies. These factors are usually described macroscopically in the field and afterwards investigated microscopically in the laboratory. In fact, there are few studies dedicated to the *in situ* analysis of degradation and taphonomic processes of rock art pigments and rock supports [28-30].

The current research focusses on the *in situ* investigation of rock art paintings in 16 open air shelters found in the forests and ecotones of Neuquén and Río Negro and the steppe at Chubut. The study includes the identification of pigments and substrata. Great attention is given to the alteration products and accretions that were found on the paintings of the shelters and on the surface of the rock walls, as they affect and damage the rock art paintings. This work builds on a previous study on the evaluation of our portable Raman spectrometer to analyse rock art paintings under extreme conditions in Patagonia (Argentina) where a more detailed description of the literature and the possibilities of Raman spectroscopy on rock art paintings is given [11].

The information obtained by on field measurements is of great importance as an initial step prior to the physicochemical characterization of the rock art pigments, since by this way we can identify and differentiate on site between natural processes and the intentional (cultural) ones. In this sense, the use of portable instruments gives us critical information regarding the different sectors of the site that may be affected by different processes. At the same time, the information retrieved from this kind of analysis allows us to select in a more objective way those motifs that, due to their distinguishable characteristics and/or archaeological interest, should be further investigated, or eventually, conclude if extraction of samples is necessary for a more comprehensive analysis at the laboratory.

2. Experimental

In situ Raman spectroscopy was performed with a portable EZRaman-I dual Raman analyser from TSI Inc. [31]. The fibre-optics-based spectrometer is a double laser system coupled with a red diode laser (785 nm) and a green Nd:YAG laser (532 nm). The spectrometer is equipped with three interchangeable lenses for each wavelength: a standard lens (STD), a long working distance lens (LWD) and a high numerical aperture lens (HiNA). For measuring the Patagonian rock art paintings the standard objective lens was selected that has a focal length of ca. 7 mm and a circular spot size of 74 ± 2 µm and 88 ± 2 µm for the 785 nm and 532 nm laser, respectively. The laser power was kept low, to avoid alterations of the components measured: ca. <30 mW (785 nm) and <8mW (532 nm). The spectrometer is a two grating system, with a spectral resolution of 6-7 cm^{-1} and spectral ranges of 100 – 2350 cm^{-1} and 100 – 3200 cm^{-1}, for the red and green laser, respectively which includes a TEC-cooled (-50°C) charge-coupled-device (CCD) detector. The portable EZRaman-I dual Raman analyser is equipped with 5 m long fibre-optic cables for measuring remotely from the object and with an internal and an external Li-ion battery that secures the autonomy of the system. The laptop for recording the spectra and all components of the spectrometer are built-in in a suitcase (55 x 35.5 x 24 cm, ca. 17 kg). The suitcase can be carried on a metallic exoskeleton for easy transportation in the field. To avoid interference of ambient light a plastic tube with a protective foam layer was slid over the standard objective lens. The probehead was manually positioned, perpendicular and in complete contact with the selected area. For maintaining the focussing during the process, measurement time and number of accumulations were selected to obtain good spectra with acceptable signal-to-noise (S/N) ratios. Wavelength calibration was performed with sulphur, epsilon-caprolactone (Acros Organics), cyclohexane (Kaiser), polystyrene pellets (Aldrich) and acetonitrile (Panreac) toluene (UCB) (mixed in 50/50 volume%) [32]. Data post-processing performed by using Thermo Grams/AI 8.0® suite software (Thermo Fischer Scientific).

3. Results and discussion

3.1 Environments, Shelters and Rock Art Painting Studied

The portable Raman measurement campaign started in North Patagonia, investigating the Shelter Cueva Olate (Neuquén province) and ended in the steppe in Piedra Parada Valley

(Chubut province). Different environmental conditions affect the paintings, and also environmental pollution adds damage to the artefacts. In the wet forests, rock art paintings are found high in the mountains on remote places, away from busy road arteries. In the steppes, the shelters are much closer to the road and are accessible to possible visitors [11]. As a consequence, are more vulnerable to vandalism. Moreover, as all sites are in open air, they can also serve as shelters for animals. This can increase their decay and further damage the artefacts.

3.1.1 Traful Area, Neuquén Province

The archaeological sites of Traful are located in forest areas of the northern coast of Lake Traful, Nahuel Huapi National Park, and in the middle and upper valley of the homonymous river, in south of the Neuquén Province. Currently, in general terms the weather is cool, temperate and humid, with an average annual rainfall for the area estimated close to 1,400 mm [33]. The average temperature in the hottest month (January) is ranging from 14 to 16 °C and in the coldest month (July) from 2 to 4 °C with frequent snowfalls. The rainfall regime is determined by the humid winds of the Pacific anticyclone and the Andes mountain range, which acts as a natural barrier in its movement towards the east.

From the phytogeographic point of view, the area is located within the subhumid mixed forest of “coihue” (*Nothofagus dombeyi*), “cypress” (*Austrocedrus chilensis*), "ñire" (*Nothofagus antarctica*) and "lenga" (Nothofagus pumilio), corresponding to the eastern part of the Valdivian District, Subantarctic Province [34]. In general, in the northwest of Patagonia, the forest becomes denser towards the west in the subhumid forest of coihue

(*Nothofagus dombeyi*), cypress, and even more "closed" in the humid forests of coihue and cane “coligüe” (*Chusquea culeu*). According to V. Markgraf in 1989 [35], the cypress/coihue-steppe line is found in the 800 mm isohieta and from 2000 mm on, the first elements of the "Valdivian forest" appear.

Archaeological research in the area of the Nahuel Huapi Lake-Traful National Park, Neuquén province, Argentina-began in the 1980s, by M. Silveira, in order to discuss the human use of natural forest environment [36]. During this project, excavations and surveys were conducted at different archaeological sites situated 300 to 3500 meters away from the northern bank of the Traful Lake and in the middle- and upper-valley of the Traful River. The cultural remains correspond to hunter-gatherers occupations, dating since 4000 years BP. The landscape is characterized as an ecotonal environment between the rain forest and the steppe, showing a high diversity and availability of minerals, fauna and plant resources. At Los Cipreses (North of Traful Lake), which was sampled before, the rock art consists of red and yellow colours, with simple geometric shapes [37]. Currently, a high degree of degradation is observed on the aforementioned site. The paintings of the shelter Alero Las Mellizas are mostly geometric shapes, with some figurative motifs (animals and humans) (fig. 1 a) combining red, yellow, orange, white, black and green pigments [38]. On the south side of the lake, the shelter Cueva Olate is located. This particular shelter is well preserved and has a special interest as its rock art presents a different painting technique: all the motifs were outlined with a white line and filled in another colour, mostly red, green and black (fig. 1 b). Moreover, the lines are mostly staggered. Diamonds, circles and humanoids were designed from the union of two triangles.

On a white rock art painting of the shelter Cueva Olate, band attributed to (Fig. 2 a) whewellite ($CaC_2O_4 \cdot H_2O$) [17, 39-41], α-quartz [42-43] and anatase (TiO_2) [44] are identified, where on a red rock art painting (Fig. 2 b) the main chromophore corresponds to haematite (α-Fe_2O_3) [39, 45]. Moreover α-quartz [42-43] and anatase [44] are also present in the red mixture. The band at 512 cm^{-1} (Fig. 2 b) can also be attributed to the strongest Raman band, I_a, of potassium-rich alkali feldspar (K-feldspar) [46]. In addition to the Raman spectra, the general analysis of the site revealed the presence of gypsum ($CaSO_4 \cdot 2H_2O$) on the white rock art paintings but also on some of the red ones. For the green and black rock art paintings no information about the main chromophore is obtained via portable Raman spectroscopy except from mixtures of components that were already identified on other coloured areas. A weak signal of whewellite was, also, observed on the rock surface of the shelter.

Bands of gypsum [47-48] and haematite [39, 45] (Fig. 2 c) are identified on a red rock art painting from the shelter Alero Las Mellizas. It is worth mentioning that, some bands, with difference in intensities, of haematite and gypsum are overlapping the overall Raman signal for these wavenumbers is affected by both compounds in the mixture. The presence of a band at 657 cm^{-1} corresponds to distortion of the degree of crystallinity of the haematite matrix [45]. Gypsum [47-48] was identified on a green rock art painting (Fig. 2 d) but also on all the coloured (white, red, yellow, black) figures measured and on the rock surface. Probably, gypsum is the main chromophore of the white paintings although can also be related to a post-degradation process or accretion on top of the rock wall affecting figures and motifs. More studies should be carried in order to positively attributed its presence as a pigment. Special attention should be given to the vibrations arising at 1023 and 630 cm^{-1} (Fig. 2 d) as these can be attributed to more than one sulphate species. The band at ca. 1024 cm^{-1}, was observed, on spectra collected from red, green and white (in mixture with red) rock art paintings. Calcium oxalates in the form of whewellite and weddellite ($CaC_2O_4 \cdot 2H_2O$) and α-quartz are also present mostly on the coloured figurative motifs of the shelter.

3.1.2 Limay River, Nahuel Huapi Lake, Gutierrez Lake and Mascardi Lake Areas, Río Negro Province

In the area containing the upper basin of the Limay river and large lakes such as Nahuel Huapi, Gutiérrez, and Mascardi, a total of 8 sites with rupestrian paintings were analyzed. This area covers an extensive region in the Province of Rio Negro, with different environments ranging from the pasture steppe, passing through an intermediate or ecotone area, to an area full of native Andean Patagonian forest. In this area the forest environment has very similar characteristics with those from the Traful area described above. In contrast to this, the Limay River valley, located about 60 km east of the Andes mountain range, is already in a typical herbaceous steppe environment composed of "sweet coirón" (*Festuca pallecens*), various *Stipa* species and small isolated bushes. Towards the east the "neneo" (*Molinum spinosum*) becomes more frequent. The annual average precipitations are inferior to the forest and ecotone with an average of 600 to 800 mm per year [33].

Archaeological evidence from this area accounts for human occupations of hunter-gatherer groups from ca. 10600 years BP until post-conquest periods [49]. These groups would have had access to a wide variety of resources in a relatively short distance of about 30 km. In this sense, mobility and subsistence patterns have been proven by archaeological evidence, to be focused on the supply and use of these resources from different environments [50].

The archaeological site Alero Maqui (Fig. 1 c) is located ca. 55 km to the south from the source of the Limay Superior River. This small shelter is located at the base of a high wall formed by tuffs and is surrounded by vegetation, characteristic for the ecotone steppe forest. The site presents a total of 28 non-figurative motifs of geometric shapes, simple as well as compound. One of its most remarkable features is the presence of different colours that are combined a bichromatic and polychromatic paintings: red, yellow, white and green [51]. The physicochemical studies previously carried out on the different pigments of the motifs showed the presence of haematite, limonite, gypsum and muscovite [52]. Rocks near the site were analyzed and identified as possible sources of raw materials for the preparation of the paintings except for the green colour [52].

Another set of analyzed sites are very close to each other, located in the forest lake environment about 20 km west of the city of San Carlos de Bariloche, and near the El Trébol lagoon, Lake Nahuel Huapi and Lake Moreno. The site El Trébol is a wide shelter of Toba rock near the lagoon of the same name and records an extensive chronology of human occupations that began some ca. 10600 BP [49]. As for their rock paintings, a total of 28 motifs have been identified mainly in red and yellow, where simple and complex non-figurative designs predominate, and some anthropo-zoomorphic designs stand out [53-54]. Preliminary chemical analyses of rock pigments and pigments from the stratigraphy of the site confirmed the presence of akaganeite in both contexts for red and albite and gypsum for yellow motifs [55-56]. Finally, the analysis of the support rock tend to support that the pigments used for the paintings may have been obtained from the same shelter [55]. The sites Campanario I and II, are located about 1000 m from the previous site and in this case also their paintings are in red and present geometric designs similar to those observed in other sites of the area [57]. In the Lake Moreno, ca. 2.5 km from Nahuel Huapi Lake, the site that we have called Lago Moreno East is located on the east coast and also has rock paintings of similar characteristics, made in red and also with figurative designs similar to those of the site El Trébol [53].

The third set of sites are located further south in the middle of the Patagonian Andean forest and near the Gutiérrez, Mascardi and Guillelmo Lakes. The site Queutre Inalef (Fig. 1 d), located 1 km from Lake Gutierrez, is a large isolated rock block of granite origin, which registers a total of 60 motifs made in red and its shades with simple as well as complex geometric designs [58]. On the other hand, the site that we call Lake Guillelmo (by the near lake with the same name) also presents similar characteristics on the designs, all painted out with red color, although it presents other types of motifs, mainly quadruple zoomorph [58]. Finally, the site Los Rápidos, is very close to Lake Mascardi and to the springs of the Upper Manso River, in the middle of the forest. It is a small cave with paintings also red and with mainly geometric motifs.

In situ Raman analysis carried out on the shelter Alero Maqui revealed severe degradation in all the coloured features found on its rock wall. Gypsum [47-48] was identified on the crust found on top of the rock (Fig. 3 a) and on an macroscopically free crust area of the rock surface, as well as, on red (Fig. 3 b), yellow, green and white rock art paintings. Gypsum is the main component found on white motifs, although the spectra might contain also contributions from the degradation crust. Calcite ($CaCO_3$) signal [59-60] was more evident on red (Fig. 3 b), yellow, green and weaker in white areas. Weddellite was also observed in the case of a white painting. Fluorescence caused by the encrustrations in the shelter Alero Maqui completely blocked or overwhelmed the Raman signal in such a way that the identification of main chromophores was impossible. Only, calcite was identified on the red motifs of Guillelmo Lake while on the rock surface albite ($NaAlSi_3O_8$) [46, 61] (Fig. 3 c) is present. Haematite [39, 45] along with α-quartz [42-43] (Fig. 3 d) and calcite [59-60] (Fig. 3 e), were observed on a red rock painting from the shelter Los Rapidos and the white crust from the shelter Lago Moreno East, respectively. For the latter, haematite and carotenoids can be found on the red figures as well as weak signals of albite in the rock surface. Calcite and gypsum were commonly identified on different coloured areas of the shelter El Trébol with gypsum found and on a crust on the rock. The red pigment used is haematite [39, 45] (Fig. 3 f). Furthermore, anatase [44] and α-quartz [42-43] are present on both rock surface and pigmented areas (Fig. 3 g-h).

The main red chromophore found in the shelters Queutre Inalef, Cerro Campanario and Cerro Campanario 2 is haematite. Some other components that were identified are α-quartz and calcite for the first shelter and α-quartz only for the other two. α-quartz is the main phase found on the rock surface.

3.1.3 Lower Manso River Area, Río Negro Province

The lower Manso area is located in a glacially modified landscape ranging between 1700 and 550 meters above sea level (at the bottom of the Manso River valley). Climatic and phytogeographic characteristics are similar to Traful, Nahuel Huapi Lake, Gutierrez Lake and Mascardi Lake areas described above. On slopes and riverbanks, mixed forests of deciduous *Nothofagus* with grassland patches predominate. The climate is moderately continental cold with high annual temperature variance. Precipitation is scarce in summer (700 mm) but in fall-winter it can reach 2000 mm/m^2 at the western part of the valley, among the Andes range.

21 rock art sites are known at the lower Manso and Foyel river valleys. The oldest human occupation was dated at 8200 years BP in a site where scarce bone and stone tools were found. From that moment the forest inhabitants where hunter-gatherers and their main staple was an autochthonous deer ("huemul") and other smaller forest species. At ca. 1600 years BP the archaeological record increased and from 1200 years BP on, rock art sites are recorded.

Two archaeological sites are discussed in the current study, Campamento Argentino and Paredón Lanfré. The first one is a small rock shelter that is 6 meters high and 2.5 meters wide. Human occupation corresponds to hunter-gatherer groups, dated at 570 and 230 years BP. Rock art is very scarce: only two red semi-circles were identified [62]. Paredón Lanfré (Fig. 1 e-f) is a rocky wall and shelter where hunter-gatherer occupations are dated between 1500 to 500 BP. The numerous paintings are arranged along a 42 meters multipanel wall (Fig. 1 e). Most motifs are geometric: rectilinear, stepped, crenellated, curvilinear lines, zig zags etc. are combined in different ways, shaping crosses, suns, hourglasses, concentric circles, framed motifs, etc. Although there are some figurative zoomorphic motifs, representing two "guanacos" (*Lama guanicoe*) recycled as horses by adding tails and hooves (Fig. 1 f), along with anthropomorphic figures. Red colour predominates in all the tonalities. Yellow and green were also used to a lesser extent [63]. Paintings of both sites were made on granite rock, therefore, microexfoliation is facilitated. Also high humidity encourages the growth of lichens and fungi which are most likely responsible for the formation of calcium oxalate on paints [26].

In fig. 4 spectra collected from rock supports near paintings 58 and 51 (a-b) and 28a (red guanaco painting(c), from the shelter Paredón Lanfré, are presented. Albite [46, 61] and α-quartz [42-43] can be found on the rock surfaces but also inside coloured figures while haematite [39, 45] is the main chromophore of all the red paintings. In the case of the red guanaco painting the band at 658 cm^{-1} corresponds to iron oxide with low degree of crystallinity [45]. For the yellow and green paintings no coloured components were identified due to fluorescence and the strong Raman signal of the substrata.

The wall of the shelter Campamento Argentino is severely degraded. Even the main chromophore of the red paintings could not be identified, due to superimposed crusts of calcite [59-60] found on the natural white crust of the rock (fig. 4 e). In some other cases, only the dominant band of α-quartz [42-43] could be identified in red areas (fig. 4 d). In another area of the wall where a patina/crust was macroscopically observed the presence of anatase [44] was verified via its Raman spectrum (fig. 4 f). Moreover, a weak Raman signal of a feldspar was also observed on the rock surface.

3.1.4 Piedra Parada Area, Chubut Province

Piedra Parada area is located at the Chubut River Basin one of the five largest rivers in Patagonia, which springs at the Andes flanks and flows to the Atlantic Ocean. Piedra Parada area is located in its middle course, at 400-500 meters above sea level. The river modeled the landscape over volcanic ancient rocks dated between 57 - 45 million years ago [64]. The region is arid (138 mm/m^2 annual precipitation), with main precipitation in winter (as snow). The predominant vegetation is a shrub steppe. Temperature ranges between ca. 37º C in January to 3º C in July. In the last 100 years overgrazing has provoked desertification. An important climatic characteristic in Patagonia is the strong western winds (Westerlies) occurring specially in summer.

The area was populated by hunter-gatherers since 5000 years ago. There are evidences of this first occupation in only one rock shelter. From 3000 years BP to 450 BP, changes in settlement patterns and an increase in demography is detected. 36 Rock art sites were detected and analysed. A stylistic sequence was elaborated: a) an initial period (previous 2500 years BP) characterized by simple geometric motifs and stencil hand prints; b) a second moment, including geometrical engravings and paintings (around 1300 years BP); and c) a final period when the so called "Grecas" style appears (around 500 years BP) [65].

Piedra Parada 1, Angostura Blanca, Campo Cerda 1 and Campo Moncada 1 are archaeological sites situated in the Piedra Parada Valley. All of them are rock shelters located in volcanic formations along both margins of Chubut River. Piedra Parada 1 (Fig. 1 h) is the only one that shows stencil hand prints in yellow, white and green, and the use of black colour in other geometric motifs. Also, there are dotted lines and straight and curved lines in green, black, red and yellow. All these motifs are characteristics of an earlier period. The other three rock art sites show some of the most frequent motifs of the geometric "Grecas" style, as irregular lines, crosses, crenellated designs, guards, etc. (Fig g-i). In the latter period, motifs are less polychromatic than Piedra Parada 1 rock art;

because red colour predominates, in other colours as white, green and yellow are less frequent [66].

Glauconite [(K,Na)(Fe^{3+},Al,Mg)$_2$(Si,Al)$_4$$O_{10}$$(OH)_2$] (Fig. 5) is the only green pigment identified only in the case Nr. 10 green rock art painting from the shelter Angostura Blanca (Fig. 1 i). From the spectra, although they appear to be noisy, the presence of a green earth could be verified. Furthermore, taking into account the resonance behaviour and the position of the diagnostic bands of glauconite [67], rather than celadonite [K[(Al,Fe^{3+}),(Fe^{2+},Mg)](AlSi_3,Si_4)O_{10}(OH_2)$_2$], is more likely to be present. In general, green earths are not very good Raman scatterers and as a consequence, few *in situ* Raman spectra of this pigment were reported. Due to resonance Raman effect, band shifts are observed when comparing the spectra as recorded with a red (785 nm) and green (532 nm) laser. In previous studies, made in Chubut province and the shelter Campo Moncada 1, was suggested that also green earths was the main component of green samples [26].

Haematite [39, 45] is the iron oxide found on all the red rock art paintings of the 4 shelters measured in Piedra Parada Valley with representative spectra presented in fig. 6 (a) (i) (m). Microcline ($KAlSi_3O_8$) [46, 61] was identified on red rock art painting Nr. 11 (Fig. 6 a) and rock surface (Fig. 6 b) of the shelter Angostura Blanca but also in different panels of the shelter Piedra Parada Valley 1. Albite was also present in spectra collected from a red rock art painting from the shelter Angostura Blanca. Gypsum [47-48] is one of the major components found on the paintings and the rock surfaces and rock art paintings of the shelters Piedra Parada 1, Campo Cerda 1 and Campo Moncada 1 (Fig. 6 c-f, i-m). Its present in the shelter Angostura Blanca needs further investigation as weak signal found only in two points (in mixture with K-feldspars). On the PP1_10 black rock art painting of panel 6 (Piedra Parada 1) (fig. 6 d) anhydrite II/natural anhydrite was also identified [48]. Gypsum is the main white component that was detected in the white negatives of hands of panel 2 (Piedra Parada 1) (Fig. 6 h). A different composition was observed for the case of Nr. 15 white negative of a hand of panel 1 (Piedra Parada 1). The phyllosilicate, muscovite [$KAl_2(AlSi_3O1_0)(F,OH)_2$] [39, 42] was positively identified, together with α-quartz [42-43] and anatase [44] (although the presence of a feldspar cannot fully be excluded) (Fig. 6 g). On the yellow negative of hand found in panel 2 of the shelter Piedra Parada 1, microcline was identified (although gypsum might also be present). Calcium oxalates, in the form of whewhellite [17, 39-41] were also present on a red rock art painting PP1_6 of panel 5 of the shelter Piedra Parada 1 and a yellow flowers rock art painting Nr. 17 Campo Moncada 1 (Fig. 6 e and j, respectively). In general, weak Raman bands of calcium oxalates were, also, in some cases observed. The orthosilicate olivine [$(Fe,Mg)_2SiO_4$], [68] is one of the components measured on the rock surface of the shelter Campo Cerda 1 (Fig. 6 n). α-quartz was also identified in a white pigmented area of the shelter Campo Cerda 1. As in the case of the shelter Alero Las Mellizas, a band at ca. 1024 cm^{-1} is observed (Fig. 6 c-d, k, m) in combination with a band at 632 cm^{-1} (Fig. 6 m) on 3 different shelters, and different colouring hues of Piedra Parada Valley, namely: blue green, green, yellow, black of the shelter Piedra Parada Valley 1; green of the shelter Campo Moncada 1; red of the shelter Campo Cerda 1. On a white crust of panel 2 of the shelter Piedra Parada 1 thenardite (Na_2SO_4), also, detected.

3.2 Comparison Between the Different Archaeological Sites

An overview of the shelters that were analysed along with the major components that were positively identified, by *in situ* Raman spectroscopy in Table I. In the next paragraphs, we will focus on the analysis of chromophores, possible encrustations and the source of oxalates.

In general, the main chromophore of the red rock paintings is haematite. In some cases the shelters where so severely altered and degraded that no signal from haematite could be retrieved. Bands at 657 cm^{-1} (red rock art painting from the shelter Alero Las Mellizas), 658 cm^{-1} (Nr. 28a red guanaco from the shelter Paredón Lanfré) and 660 cm^{-1} (red rock art painting from the shelter Queutre Inalef) can be attributed to an IR active longitudinal (LO) mode which is symmetry forbidden in Raman spectra and is appearing due to a low degree of crystallinity associated with disordered structures [43, 45, 69-71]. However, in the literature it is also mentioned that this band can be assigned to traces of magnetite contributing to the haematite spectra, though this should be considered with caution [72-73]. Consequently, bands arising at these wavenumbers are often debated [74-75] especially when magnetite and haematite are present.

For the most of the yellow, green and black paintings no information from the main colourant could be obtained. Gypsum and calcite are commonly found and cause severe degradation on most of the shelters measured. Gypsum was more frequently identified at the provinces of Neuquén and Chubut, while on Río Negro and lower Rio Manso (Río Negro) calcite was present. Both degradation factors are found on pigmented and as well as nonpigmented areas (crusts). As gypsum was also identified on the white rock art paintings, results should be conceived with caution as it is also a major decaying compound of the rock surfaces. The gypsum accretion should have an impact on the actual Raman signal of the white chromophore, even if gypsum seems as a logical selection of white pigment. An archaeological question was if gypsum was introduced also in other coloured mixtures as an extender or to change the hue. This question cannot be answered with portable Raman instrumentation alone. The only observation was that in the cases that no gypsum was identified in the crusts, it was also not, present in the coloured mixtures. Another important information is that sometimes the populations used to paint on already degraded surfaces in order to achieve a homogeneous background.

The most important challenge related of the correct attribution of the Raman bands to the exact compound is coming from the vibrations arising at ca. 1022-1026 cm^{-1}, found on the shelters Alero Las Mellizas (along with a band at 630 cm^{-1}), Neuquén province and the shelters Piedra Parada 1, Campo Moncada 1, Campo Cerda 1 (along with a band at 632 cm^{-1}) located in Piedra Parada valley. By reviewing the literature on the analysis, the resulted outcome was interesting. Prinsloo et al. [69], studies in 2008 a red pigment on a shard from San rock art (South Africa), referring to a band at 1022 cm^{-1} as anhydrite. Tournié et al. [17], in 2011, measuring San rock art in site (South Africa), assigned also a band at 1025 cm^{-1}, from a yellow figure, as anhydrite ($CaSO_4$). Moreover, pointed out the literature for bassanite ($CaSO_4 \cdot 0.5(H_2O)$) and natural anhydrite and the transition between gypsum and the latter two compounds, concluding that more research should be conducted to verify this vibration.

Iriarte et al. [76], in 2013, when studying violet microparticles of a bluish black pigment from the shelter Abrigo Remacha (Spain), assigned the bands at 1170, 1027 (vvs), 676, 634 and 493 cm^{-1} to paracoquimbite [($Fe_2(SO4)_3 \cdot 9H_2O$)]. Calcite, α-quartz, carbon black and Ca-oxalates were also found in the mixture. Pitarch et al. [41], in 2014, when analysing blackish pictographs from the Los Chaparros shelter (Spain) attributed a band at 1027 cm^{-1} to gypsum (among other bands of calcium sulphate dehydrate). Hernanz et al. [61], in 2016, measuring hand stencils from the Yabrai Mountain (China) assigned a band at ca. 1028 cm^{-1}, found on rock surfaces and red paintings, as anhydrite III while also gypsum and anhydrite II were also present.

The band ca. 1022-1026 cm^{-1} along with the ones at 630 and 632 cm^{-1}, found on the Patagonian shelters, can be attributed to one of the five phases of $CaSO_4/H_2O$ system [48]. This is likely to be soluble anhydrite, γ-$CaSO_4$/anhydrite III, a compound with metastable thermodynamic stability. The Raman spectra of this compound consist of bands at 1167, 1025, 673, 630, 490 and 420 cm^{-1} [48]. Moreover, it is suggested that microconditions in the sample, under influence of the laser power, can promote the transformation of gypsum to anhydrite III [48]. When performing *in situ* Raman measurements in the Patagonian field the laser power density was kept low in order to avoid any transformation of the matrices.

From the other hand, a band at ca. 1025 cm^{-1} can also be attributed to the iron (III) sulfate nonahydrate (para)coquimbite. Maguregui et al. [77], in 2010, described a three step decaying pathway of the formation of the iron sulphate as a result of atmospheric SO_2 attack on the walls of a Pompeian house. For such a reaction, haematite and calcite should be involved, in the presence of sulphuric pollutants, resulting in the formation of (para)coquimbite and gypsum.

For what concerns the Patagonian shelters, the aforementioned Raman band was observed in spectra collected from red, green and white (in mixture with red) rock art paintings from the shelter Alero Las Mellizas, Neuquén province and it also appeared in Piedra Parada Valley on blue green, green, yellow and black rock art paintings of the shelter Piedra Parada 1, on a green rock art painting of the shelter Campo Moncada 1 and on a red rock art painting of the shelter Campo Cerda 1. In the red haematitic figures and motifs no calcite was detected due to a chemical reaction, hence the interpretation as (para)coquimbite cannot be prompted. In general, no calcite was detected in the shelters on which this band appear. However, while investigating the wall of the shelter Campo Cerda 1, we realised that calcite was present in a hidden way in a natural dual layered encrustation on top of the rock. Calcite and gypsum was measured in a layer composed on top of the rock surface while measuring on top of the latter layer only gypsum was found (Table I). If we assume that the band at 1025 cm^{-1} is assigned to (para)coquimbite then other hypotheses should be addressed. If it is a matter of origin and natural sources in Patagonia, Argentina, then it is necessary to examine possible sources of deposits, as related to the distance to the archaeological sites. In general, (para)coquimbite can also be formed by the flow of acid water on possible ferric sulphates [76] or by evaporation of acid, sulphate pools/brines as a consequence of a pyrite oxidation [78].

It is worth mentioning, that some spectra from the Patagonian rock art sites contained a band at ca. 1022-1026 cm^{-1}. This band position seems to correspond to that of anhydrite III as identified by Hernanz in the red paintings of Yabrai Mountain (China) [61]. In our observations, this band was always identified in zones where gypsum was observed.

Though not completely conclusive, Raman spectroscopy identified the vibrational mode of the sulphate anion (ca. 1022-1026 cm^{-1}) but the attribution to the correct compound needs further research. The identification, via Raman spectroscopy, is more difficult than initially thought, especially in mixtures of gypsum and iron oxides, and moreover some anhydrite III and (para)coquimbite bands are overlapping. The sulphate vibration band was found in various colours on the pigmented areas of shelters that are located on different provinces. More research should be conducted, including other analytical techniques that reveal the molecular/crystalline structures, in order to verify the presence of anhydrite III and further investigate possible formation pathways in the case of (para)coquimbite in the Patagonian environments.

Calcium oxalates, in the form of whewellite and weddellite, were identified by their strong Raman bands on the shelters of Neuquén province, on the shelter Alero Maqui, Río Negro province and the shelters Piedra Parada 1 and Campo Moncada 1, Chubut province. Oxalic acid production from the attack or metabolic acivity of fungi, lichens or bacteria on top of Ca-based substratum, is the biological explanation of the deposition of the hydrated calcium oxalates [8, 39, 70]. Furthermore, the chemical explanation for the formation of such compounds, is the decay of organic media and/or binders, containing oxalic acid of calcium oxalates [8, 70]. Lofrumento et al. [70], in 2012, when investigating Ethiopian prehistoric rock painting, suggested the use of a binder as the source of Ca-oxalate by comparing, via Raman mapping image, the concentration on a red fragment and on a hematite area. The Ca-oxalate appeared inhomogeneous and scattered. Another hypothesis for the presence of oxalates inside rock art mixtures [70, 79] was suggested as intentionally incorporation of Ca-oxalate for the composition of the pigment itself.

Although lichen activity was very obvious in some shelters, Ca-oxalates were found mainly on pigmented zones rather than on top of crusts and rock surfaces. When oxalates were found on the crusts, the Raman signal was very weak. Although, this tends to support the thesis of intentional admixture of oxalates and/or the decay of organic binders, this should not be considered as fully conclusive. In the sites measured, lichen activity could be macroscopically confirmed and due to limited measurement time, the number of measurements points was somehow restricted, compared to the extent of the sites of the rock art panels. A more elaborated study, completed with the analysis of cross sections, could further clarify the issue.

The presence of Ca-oxalates, on crust surfaces can be of importance for dating the pictorial layers. As described by Hernanz et al. [59], in 2014, if thick Ca-oxalate crusts are present on top of the motif/figure an "*ante quem*" date, by radiocarbon dating, can be established for the rock art paintings. Moreover, if the pictorial layer is encapsulated/sandwiched in between Ca-oxalate layers, an "*ante quem* and *post quem* radiocarbon dating" of the event can be determined [39-40, 59, 80]. For the case of the shelters of Patagonia, we propose perpendicular sampling of the pigmented and nonpigmented areas of the sites, where Ca-oxalates where found, to evaluate the homogeneity of the crusts, for further radiocarbon analysis.

4. Conclusions

In situ Raman spectroscopy was performed on 16 open air shelters, in Patagonia (Argentina), in the provinces of Neuquén and Río Negro and Chubut. The purpose of the current study is the identification of pigments and substrata. The main focus of the research was the positive identification of alteration products and encrustations, found on the rock art paintings of the shelters and on the surface of the rock walls. Apart, from the pigment identification, compounds attributed to decaying mechanisms and weathering of the shelters were discussed. Although in some cases, the results were not completely conclusive, portable Raman spectroscopy shed light on the main chromophores used and characterized substrata and alteration products in a non invasive way. The results demostrated in this article are not reflecting the complete variety of components that can be found on the walls of the shelters due to restrictions of the portable instrumentation and across restrictions due to limited measurement time.

The information obtained by on-site measurements is of great importance regarding the preservation state of this invaluable works of art. The results retrieved from this analysis allows the selection of rock art paintings that, due to their degradation state and/or archaeological interest, should be further investigated, by extraction of samples for laboratory analysis, possibly with multiple analytical techniques. The documentation and physicochemical characterization of the Patagonian rock art paintings is set as a priority, as these art works made by hunter-gatherer populations are doomed to be consumed by nature and/or human activity.

Acknowledgements

The authors would like to thank for their financial help: FWO (project K204416N-Travel Grant for a short stay abroad), Ghent University, through the concerted research actions programme (GOA), Consejo Nacional de Investigaciones Científicas y Técnicas

(CONICET) through PIP 365. For their valuable support, Emilio Eugenio (IMHICIHU, CONICET) and Lisandro Lopez (UBA) are greatly acknowledged.

References

[1] M. W. Rowe, Physical and chemical analysis, In: D. S. Whitley (Eds.), Handbook of Rock Art Research, AltaMira Press, Walnut Creek, California, 2001, pp. 190–220.

[2] G. D. Smith, R. J. H. Clark, Raman microscopy in archaeological science, J. Archaeol. Sci. 31 (2004) 1137–1160.

[3] R. C. Bednarik, D. Fiore, M. Basile, G. Kumar, T. Huisheng, Palaeoart and Materiality: The Scientific Study of Rock Art, Archaeopress Publishing Ltd, Oxford, 2016.

[4] E. Chalmin, M. Menu, C. Vigneaud, Analysis of rock art painting and technology of palaeolithic painters, Meas. Sci. Technol. 14 (2003) 1590- 1597.

[5] D. Fiore, M. Maier, S. D. Parera, L. Orquera, E. Piana, Chemical analyses of the earliest pigment residues from the uttermost part of the planet (Beagle Channel region, Tierra del Fuego, Southern South America), J. Archaeol. Sci. 35 (2008) 3047-3056.

[6] M. Tascon, N. Mastrangelo, L. Gheco, M. Gastaldi, M. Quesada, F. Marte, 2016 Micro-spectroscopic analysis of pigments and carbonization layers on prehispanic rock art at the Oyola's caves, Argentina, using a stratigraphic approach, Microchem. J. 129 (2016) 297–304.

[7] A. Bonneau, D. G. Pearce, A. M. Pollard A multi-technique characterization and provenance study of the pigments used in San rock art, South Africa, J. Archaeol. Sci. 39 (2012) 87-294

[8] M. Mas, A. García, G. Beatriz, S. Mónica, P. Enrique, P-P. Perez, Minateda rock shelters (Albacete) and post-palaeolithic art of the Mediterranean Basin in Spain: Pigments, surfaces and patinas, J. Archaeol. Sci. 40 (2013) 4635-4647.

[9] E. Tomasini, M. Basile, M. Maier, N. Ratto, Relevant issues for the design of a protocol for the interdisciplinary study of rock art, in: R. G. Bednarik, D. Fiore, M. Basile, G. Kumar and T. Huisheng (Eds.), Palaeoart and Materiality, The Scientific Study of Rock Art, Archaeopress Publishing Ltd, Oxford, 2016, pp. 1-13.

[10] C. Bellelli, F. X. Pereyra, M. Carballido, Obsidian localization and circulation innorthwestern Patagonia (Argentina): sources and archaeological record, in: M. Maggetti, B. Messiga (Eds), Geomaterials in Cultural Heritage, The Geological Society, London, 2006, pp. 241-255.

[11] A. Rousaki, C. Vázquez, V. Aldazábal , C. Bellelli, M. Carballido Calatayud, A. Hajduk, E. Vargas, O. Palacios, P. Vandenabeele, L. Moens, The first use of portable Raman instrumentation for the in situ study of prehistoric rock paintings in Patagonian sites, J. Raman Spectrosc. 48 (2017) 1459–1467.

[12] A. Rousaki, C. Bellelli, M. Carballido Calatayud, V. Aldazábal,G. Custo, L. Moens, P. Vandenabeele, C. Vázquez, Micro-Raman analysis of pigments fromhunter–gatherer archaeological sites of North Patagonia (Argentina), J. Raman Spectrosc. 46 (2015) 1016–1024.

[13] H. G. M. Edwards, E. M. Newton, J. Russ, Raman spectroscopic analysis of pigments and substrata in prehistoric rock art, J. Mol. Struct. 550–551 (2000) 245-256.

[14] H. Gomes, P. Rosina, H. Parviz, T. Solomon, C. Vaccaro, Identification of pigments used in rock art paintings in Gode Roriso-Ethiopia using Micro-Raman spectroscopy, J. Archaeol. Sci. 40 (2013) 4073-4082.

[15] F. Ospitali, D. C. Smith, M. Lorblanchet, Preliminary investigations by Raman microscopy of prehistoric pigments in the wall-painted cave at Roucadour, Quercy, France, J. Raman, Spectrosc. 37 (2006) 1063–1071.

[16] P. Vandenabeele, L Moens, Some ideas on the definition of Raman spectroscopic detection limits for the analysisof art and archaeological objects, J. Raman Spectrosc. 43 (2012) 1545–1550.

[17] A. Tournié, L. C. Prinsloo, C. Paris, P. Colomban, B. Smith, The first in situ Raman spectroscopic study of San rock art in South Africa: procedures and preliminary results, J. Raman Spectrosc. 42 (2011) 399–406.

[18] S. Lahlil, M. Lebon, L. Beck, H. Rousselière, C. Vignaud, I. Reiche, M. Menu, P. Paillet, F. Plassard, The first in situ micro-Raman spectroscopic analysis of prehistoric cave art of Rouffignac St-Cernin, France, J. Raman Spectrosc. 43 (2012) 1637–1643.

[19] M. T. Boschin, A. M. Seldes, M. Maier, R. M. Casamiquela, R. E. Ledesma, G. E. Abad, Análisis de las fracciones inorgánicas y orgánicas de pinturas rupestres y pastas de sitios arqueológicos de la Patagonia septentrional Argentina, Zephyrvs 55 (2002) 183-198.

[20] C. Vázquez, M. Maier, S. D. Parera, H. Yacobaccio, P. Solá, Combining TXRF, FT-IR and GC–MS information for identification of inorganic and organic

components in black pigments of rock art from Alero Hornillos 2 (Jujuy, Argentina), Anal. Bioanal. Chem. 391 (2008) 1381-1387.

[21] N. M. Carden, R. V. Blanco, D. G. Poiré, C. I. Genazzini, L. A. Magnin, P. J. García Análisis de pigmentos del macizo del deseado: el abastecimiento de materias primas y la producción de pinturas rupestres en Cueva Mmaripe (Santa Cruz, Argentina), Relac. Soc. Argent. Antropol. 39 (2014) 483-508.

[22] A. M. Iñiguez, C. J. Gradin, Análisis mineralógico por difracción de rayos X de muestras de pinturas de la Cueva de las Manos, Estancia Alto Río Pinturas. Relaciones 11 (1978) 121-128.

[23] C.E. Barbosa, G. E Rial, Análisis mineralógico por difracción de rayos X de muestras de pintura de Cerro Casa de Piedra, sitio CCP-5, Provincia de Santa Cruz, República Argentina, Museo Chileno de Arte Precolombino, Santiago de Chile, Primeras Jornadas de Arte y Arqueología, 1985, 21-24.

[24] C. E. Barbosa, C. J. Gradin, Estudio composicional por difracción de Rayos X de los pigmentos provenientes de la excavación del Alero Cárdenas (Provincia de Santa Cruz), Relaciones 17 (1988) 143-171.

[25] J. B. Belardi, A. Súnico, D.N. Puebla, Análisis de pigmentos minerales y sus fuentes potenciales de aprovisionamiento en el Área del Lago Roca (Sector Chorrillo Malo), Provincia de Santa Cruz (Argentina), An. Inst. Patagon. 28 (2000) 291-304.

[26] I. N. M. Wainwright, K. Helwig, M. M. Podestá, C. Bellelli, Analysis of pigments from rock painting sites in Rio Negro and Chubut Provinces, Argentina, in: M. M. Podestá, M. de Hoyos (Eds.), Arte en las Rocas, Sociedad Argentina de Antropología, AINA, Buenos Aires, 2000, p. 203-206.

[27] I. N. M. Wainwright, K. Helwig, D. S. Rolandi, C. A. Aschero, C. Gradin, M. M. Podestá, M. Onetto, C. Bellelli, Identification of pigments from rock painting sites in Argentina, 10° Journées d'etudes de la Section Francaise de l'Institut International de Conservation, Paris, 2002, pp. 15-24.

[28] J. Huntley, Taphonomy Or paint recipe: in situ portable x-ray fluorescence analysis of two anthropomorphic motifs from the Woronora Plateau, New South Wales, Aust. Archaeol. 75 (2012) 78-94.

[29] F. Gázquez, F. Rull, A. Sanz-Arranz, J. Medina, J. M. Calaforra, C. de las Heras, J. A. Lasheras, In situ Raman characterization of minerals and degradation processes in a variety of cultural and geological heritage sites, Spectrochim. Acta A 172 (2017) 48–57

[30] J. Huntley, C. F. Galamban, The Material scientific investigation of rock art: contributions from non-Invasive X-ray techniques, in: R. G. Bednarik, D. Fiore, M. Basile, G. Kumar and T. Huisheng (Eds.), Palaeoart and Materiality: The

Scientific Study of Rock Art, Archaeopress Publishing Ltd, Oxford, 2016, pp. 41-57.

[31] D. Lauwers, A. G. Hutado, V. Tanevska, L. Moens, D. Bersani, P. Vandenabeele, Characterisation of a portable Raman spectrometer for in situ analysis of art objects, Spectrochim. Acta A 118 (2014) 294-301.

[32] D. Hutsebaut, P. Vandenabeele, L. Moens, Evaluation of an accurate calibration and spectral standardization procedure for Raman spectroscopy, Analyst 130 (2005) 1204-1214.

[33] V. Barros, V.H. Cordón, C.L. Moyano, R.J. Mendez, J.C. Forquera, O. Pizzio, Cartas de precipitación de la zona oeste de las provincias de Río Negro y Neuquén. Primera Contribución, Centro Nacional Patagónico (CONICET)-Universidad Nacional del Comahue Dirección de Bosques y Praderas (Río Negro) - Secretaría de Estado del Copade (Neuquén) - Departamento Provincial de Aguas (Río Negro), 1983.

[34] A. L. Cabrera, Regiones fitogeográficas Argentinas, in: W. F. Kugler (Ed.), Enciclopedia Argentina de Agricultura y Jardinería, segunda ed., tomo II, fascículo 1, ACME S.A.C.I., Buenos Aires, 1976, pp. 1-85.

[35] V. Markgraf, Paleoclimates of central and south America since 18.000 years BP based on pollen and lake level records, Quat. Sci. Rev. 8 (1989) 1-24.

[36] M. J. Silveira, L. López, V. Aldazábal, El uso del espacio durante el Holoceno tardío - últimos 3500 años - en el bosque andino de Patagonia septentrional, lago Traful, sudoeste de la provincia de Neuquén, Anuario de Arqueología 5 (2013) 85-101.

[37] M. J. Silveira, Alero Los Cipreses, in: J. G. Otero (Ed.), Arqueología Solo Patagonia, Ponencias de las Segundas Jornadas de Arqueología de la Patagonia, CENPAT-CONICET, Puerto Madryn, Argentina, 1996, pp. 107–118.

[38] M. J. Silveira, L. G. López, V. Aldazabal, Investigaciones arqueológicas en el alero Las Mellizas, bosque andino de Patagonia Septentrional, sudoeste de la provincia de Neuquén, Comechingonia Virtual. 8 (2014) 157-190.

[39] A. Hernanz, J. M. Gavira-Vallejo, J. F. Ruiz-López, H. G. M. Edwards, A comprehensive micro-Raman spectroscopic study of prehistoric rock paintings from the Sierra de las Cuerdas, Cuenca, Spain, J. Raman Spectrosc. 39 (2008) 972–984.

[40] A. Hernanz, J. F. Ruiz-López, J. M. Gavira-Vallejo, S. Martin, E. Gavrilenko, Raman microscopy of prehistoric rock paintings from the Hoz de Vicente, Minglanilla, Cuenca, Spain, J. Raman Spectrosc. 41 (2010) 1394–1399.

[41] A. Pitarch, J. F. Ruiz, S. Fdez-Ortiz de Vallejuelo, A. Hernanz, M. Maguregui, J. M. Madariaga, In situ characterization by Raman and X-ray fluorescence spectroscopy of post-Paleolithic blackish pictographs exposed to the open air in

Los Chaparros shelter (Albalate del Arzobispo, Teruel, Spain), Anal. Methods 6 (2014) 6641-6650.

[42] M. L. Frezzotti, F. Tecce, A. Casagli, Raman spectroscopy for fluid inclusion analysis, J. Geochemical Explor. 112 (2012) 1-20.

[43] A. Hernanz, J. M. Gavira-Vallejo, J. F. Ruiz-López, S. Martin, A. Maroto-Valiente, R. de Balbín-Behrmann, M. Menéndez, J. J. Alcolea-González, Spectroscopy of Palaeolithic rock paintings from the Tito Bustillo and El Buxu Caves,Asturias, SpainJ. Raman Spectrosc. 43 (2012) 1644–1650.

[44] U. Balachandran, N.G.Eror, Raman spectra of titanium dioxide, J. Solid State Chem. 42 (1982) 276-282.

[45] D. L. A. de Faria, F. N. Lopes, Heated goethite and natural hematite: Can Raman spectroscopy be used to differentiate them?, Vib. Spectrosc. 45 (2007) 117-121.

[46] J. J. Freeman, A.Wang, K. E. Kuebler, B. L. Jolliff, L. A. Haskin, Characterization of natural feldspars by Raman spectroscopy for future planetary exploration, Can. Mineral. 46 (2008) 1477-1500

[47] J. Jehlička, P. Vítek, H. G. M. Edwards, M. D. Hargreaves, T. Čapoun, Fast detection of sulphate minerals (gypsum, anglesite, baryte) by a portable Raman spectrometer, J. Raman Spectrosc. 40 (2009) 1082–1086.

[48] N. Prieto-Taboada, O. Gomez-Laserna, I. Martizez-Arkarazo, M. Angeles Olazabal, J. M. Madariaga, Raman Spectra of the different phases in the $CaSO_4$–H_2O system, Anal. Chem 86 (2014) 10131–10137.

[49] A. Hajduk, A. M. Albornoz, M. Lezcano, P. Arias, The first occupations of the El Trebol site during the Pleistocene-Holcene Transition (Nahuel Huapi Lake, Patagonia Argentina), in: L. Miotti, M. Salemme, N. Flegenheimer, T. Goebel (Eds.), Southbound Late Pleistocene Peopling of Latin America, Special Edition of Current Research in the Pleistocene, Center for the Study of the First Americans, Department of Anthropology, Texas A&M University, 2012, 117-120.

[50] M. J. Lezcano, A. Hajduk, A. M. Albornoz, El menú a la carta en el bosque ¿entrada o plato principal?: una perspectiva comparada desde la Zooarqueología del sitio el Trébol (Parque Nacional Nahuel Huapi, Pcia. de Río Negro), in: M. De Nigris, P. M. Fernández, M. Giardina, A. F. Gil, M. A. Gutiérrez, A. Izeta, G. Neme, H. D. Yacobaccio (Eds.), Zooarqueología a Principios del Siglo XXI: Aportes Teóricos, Metodológicos y Casos de Estudio, Ediciones del Espinillo, Argentina, 2010, pp. 243-257.

[51] A. Hajduk, A. M. Albornoz, El sitio Valle Encantado I, su vinculación con otros sitios: un esbozo de la problemática local diversa del Nahuel Huapi, in: J. B. Belardi, P M. Fernández, R. A. Goñi, A. G. Guráieb & M. De Nigris (Eds.),

Soplando en el Viento, Neuquén-Buenos Aires: Universidad Nacional del Comahue-inapl, 1999, pp. 371-391.

[52] C. Vázquez, A. M Albornoz., A. Hajduk, S. A. Maury, S. Boeykens, Patrimonio rupestre en el Alero El Maqui, valle encantado, Patagonia: caracterización química inorgánica de pigmentos, in: O. Palacio, C. Vazquez (Eds), Patrimonio Cultural: la Gestión, el Arte, la Arqueología y las Ciencias exactas aplicadas. Editorial Talleres Gráficos Centro Atómico Constituyentes. CONEA, Argentina, 2010, pp. 225-232.

[53] A. M. Albornoz, A. Hajduk, "Ladran sancho' jinetes y caballos en el arte rupestre en la arqueología y la etnohistoria del área del Nahuel Huapi, XII Jornadas Interescuelas, Departamento de Historia, Eje Nº 12, Representaciones Intelectuales y Culturales, Mesa 12.5, Las Manifestaciones del Simbolismo Prehistórico: Arte Rupestre y Arte Mobiliar, Publicado en CD con referato, Puede Consultarse el Trabajo, http://es.scribd.com/doc/129690568/Albornoz-y-Hajduk-2009-Caballos-en-El-Arte-Rupestre, 2009 (accessed 1 November 1017).

[54] A. M. Albornoz, Sitios con Arte Rupestre en los alrededores del Lago Nahuel Huapi, Segundas Jornadas de Arqueología de la Patagonia; Madryn, in: J. G. Otero (Ed.), Arqueología Solo Patagonia: Ponencias de las Segundas Jornadas de Arqueología de la Patagonia, CENPAT Madryn., 1996, p.p 123-130.

[55] A. M. Albornoz, A. Hajduk, S. P. Fornels, A. Caneiro, C. Vázquez, Sitio El Trébol: identificación de pigmentos presentes en manifestaciones rupestres del ámbito boscoso lacustre del Nahuel Huapí, Río Negro, Argentina, in: C. Vázquez, O. Palacios (Eds.), Patrimonio Cultural: la Gestión, el Arte, la Arqueología y las Ciencias exactas aplicadas Editorial Talleres Gráficos Centro Atómico Constituyentes, CNEA, 2008, pp. 175-194.

[56] C. Vázquez, A. Caneiro, S. P. Fornells, A. M. Albornoz, A. Hajduk, Caracterización de pigmentos por técnicas de difracción de rayos x y microscopia electrónica: sitio arqueológico el Trébol: Nahuel Huapi, Argentina, En Avances en Técnicas de Rayos X, 14 (2008) 271- 276.

[57] A. M. Albornoz, E. Cúneo, Análisis comparativo de sitios con pictografías en ambientes lacustres boscosos de Patagonia septentrional, in: M. M. Podestá, M. de Hoyos (Eds.), En Arte en Las Rocas. Arte Rupestre, Menhires y Piedras de Colores en Argentina, Buenos Aires: Sociedad Argentina de Antropología y Asociación Amigos del Instituto Nacional de Antropología, 2000, pp. 163-174.

[58] A. M. Albornoz, L. C. Teira Mayolín, Documentación de yacimientos con arte rupestre del entorno del Parque Nacional Nahuel Huapi, III Jornadas de Historia de la Patagonia, Universidad Nacional del Comahue, CONICET, Agencia Nacional de Promoción Científica y Tecnológica, Editadas en CD con referato: Historia de la Patagonia: 3eras Jornadas; 1era Ed Neuquén, Universidad Nacional del Comahue, 2008.

[59] A. Hernanz, J. F. Ruiz-López, J. M. Madariaga, E. Gavrilenko, M. Maguregui, S. Fdez-Ortiz de Vallejuelo, Ir. Martínez-Arkarazo, R. Alloza-Izquierdo, V. Baldellou-Martínez, R. Viñas-Vallverdu, A. Rubio i Mora, A. Pitarch, A. Giakoumaki, Spectroscopic characterisation of crusts interstratified with prehistoric paintings preserved in open-air rock art shelters, J. Raman Spectrosc. 45 (2014) 1236–1243.

[60] H. G.M. Edwards, S. E. Jorge Villar, J. Jehlick, Tasnim Munshi, FT–Raman spectroscopic study of calcium-rich and magnesium-rich carbonate minerals, Spectrochim. Acta A, 61 (2005) 2273–2280

[61] A. Hernanz, J. Chang, M. Iriarte, J. M. Gavira-Vallejo, R. de Balbín-Behrmann, P. Bueno-Ramírez, A. Maroto-Valiente, Raman microscopy of hand stencils rock art from the Yabrai Mountain, Inner Mongolia Autonomous Region, China, Appl. Phys. A 122 (2016) 699.

[62] P.M. Fernández, M. Carballido Calatayud, C. Bellelli, M.G. Fernández,, Las ocupaciones del bosque durante los tiempos históricos, Libro de Resúmenes, X Jornadas de Arqueología de la Patagonia, IDEAUS-CONICET, Puerto Madryn, 2017, pp. 91.

[63] M. M. Podestá, A. M. Albornoz, El arte rupestre del sitio Paredón Lanfré dentro del contexto arqueológico del valle del río Manso inferior (Pcia. de Río Negro), Tras las huellas de la materialidad, XVI Congreso Nacional de Arqueología Argentina, Tomo III, Editorial Universidad Nacional de Jujuy, 2007, pp. 429-434.

[64] E. Aragón, M. Mazzoni Geología y estratigrafía del complejo volcánico piroclástico del río Chubut medio (Eoceno), Chubut, Argentina, Rev. Asoc. Geol. Argent. 52 (1997) 243-256.

[65] M. Onetto, Propuesta para la integración del arte rupestre dentro del sistema de comportamiento de los cazadores-recolectores del valle de Piedra Parada, Curso medio del río Chubut, in: M. M. Podestá, M. I. Hernández Llosas, S. F. Renard de Coquet (Eds.), El Arte Rupestre en la Arqueología Contemporánea, Buenos Aires, 1991, pp. 123-131.

[66] C. Aschero, C. Bellelli, A. Fisher, L. Nacuzzi, M. Onetto, C. Pérez de Micou Arqueología del Chubut. El Valle de Piedra Parada. Dirección Provincial de Cultura del Chubut, Rawson, 1983.

[67] F. Ospitali, D. Bersani, G. Di Lonardo, P. P. Lottici, ‘Green earths’: vibrational and elemental characterization of glauconites, celadonites and historical pigments, J. Raman Spectrosc. 39 (2008) 1066–1073.

[68] H. G. M Edwards, D. W. Farwell, M. MGrady, D. D Wynn-Williams, I. P. Wright, Comparative Raman microscopy of a Martian meteorite and Antarctic lithic analogues, Planet. Space Sci. 47 (1999) 353-362.

[69] L. Prinsloo, W. Barnard, I. Meiklejohn, K. Hall, The first Raman spectroscopic study of San rock art in the Ukhahlamba Drakensberg Park, South Africa, J. Raman Spectrosc. 39 (2008) 646–654.

[70] C. Lofrumento, M. Ricci, L. Bachechi, D. De Feo, E. M. Castellucci, The first spectroscopic analysis of Ethiopian prehistoric rock painting, J. Raman Spectrosc. 43 (2012) 809–816.

[71] D. Bersani, P. P. Lottici, A. Montenero, Micro-Raman investigation of iron oxide films and powders produced by sol–gel syntheses J. Raman Spectr. 30 (1999) 355–360.

[72] D. A. de Faria, S.V. Silva, M. T. de Oliveira, Raman microspectroscopy of some iron oxides and oxyhydroxides, J. Raman Spectr. 28 (1997) 873-878.

[73] F. Bordignon, P. Postorino, P. Dore, G. F. Guidi, G. Trojsi, V. Bellelli, In search of Etruscan colours: a spectroscopic study of a painted terracotta slab from Ceri, Archaeometry 49 (2007) 87-100.

[74] I. Aliatis, D. Bersani, E. Campani, A. Casoli, P. P. Lottici, S. Mantovan, I.-G. Marino, Pigments used in Roman wall paintings in the Vesuvian area, J. Raman Spectrosc. 41 (2010) 1537–1542.

[75] D. Bersani, P. P. Lottici, Raman spectroscopy of minerals and mineral pigments in archaeometry, J. Raman Spectr. 47 (2016) 499–530.

[76] M. Iriarte, A. Hernanz, J. F. Ruiz-López, Santiago Martín, μ-Raman spectroscopy of prehistoric paintings from the Abrigo Remacha rock shelter (Villaseca, Segovia, Spain), J. Raman Spectrosc. 44 (2013) 1557–1562.

[77] M. Maguregui, U. Knuutinen, K. Castro, J. M. Madariaga, Raman spectroscopy as a tool to diagnose the impact and conservation state of Pompeian second and fourth style wall paintings exposed to diverse environments (House of Marcus Lucretius), J. Raman Spectr. 41 (2010) 1400-1409.

[78] D. C. Fernández-Remolara, R. V. Morris, J. E. Gruener, R. Amilsa, A. H. Knoll, The Río Tinto Basin, Spain: mineralogy, sedimentary geobiology, and implications for interpretation of outcrop rocks at Meridiani Planum, Mars, Earth Planet. Sci. Lett. 240 (2005) 149 – 167.

[79] R. E. M. Hedges, C. B. Ramsey, G. J. Van Klinken, P. B. Pettitt, C.Nielsen-Marsh, A. Etchegoyen, J. O. Fernandez Niello, M. T. Boschin, A. M. Llamazares, Methodological issues in the 14C dating of rock paintings, Radiocarbon 40 (1998) 35-44.

[80] J. F. Ruiz, A. Hernanz, R-A. Armitage, M. W. Rowe, R. Viñas, J. M. Gavira-Vallejo, A. Rubio, Calcium oxalate AMS 14C dating and chronology of post-Palaeolithic rock paintings in the Iberian Peninsula. Two dates from Abrigo de los Oculados (Henarejos, Cuenca, Spain), J. Archaeol. Sci. 39 (2012) 2655-2667.

Figure Captions

Figure 1: Details from rock art paintings found at (a) the shelter Alero Las Mellizas (El Neuquén) and (b) the shelter Cueva Olate (Neuquén). (c) Overview of the rock art painting from the shelter Alero Maqui (Río Negro) and (d) red detail from the painting found at the shelter Queutre Inalef (Río Negro). (e) A complete view of the multipanel wall of the shelter Paredón Lanfré, (Río Negro) and (f) measurment of a horse (Motif 28) in one of its panels. Initially the figure was a guanaco but when the local population started riding horses, tail and hooves were added in order to resemble a horse. (g) Figure of yellow and red flowers from the shelter Campo Moncada 1 (Chubut), (h) Raman portable instrument set up placed in the shelter Piedra Parada 1 (Chubut) and (i) a red and green figure (Nr.10) from the shelter Angostura Blanca (Chubut).

Figure 2: Raman spectra of representative points of: (a) white rock art painting (b) red rock art painting from the shelter Cueva Olate, Neuquén province and (c) red rock art painting (d) green rock art painting from the shelter Alero Las Mellizas, Neuquén province. Labels: wh, whewellite; an, anatase; q, α-quartz; f, feldspar; h, haematite; g, gypsum.

Figure 3: Raman spectra of representative points of: (a) crust on top of the rock surface and (b) red rock art painting from the shelter Alero Maqui; (c) rock support from the shelter Guillelmo Lake; (d) red rock art painting from the shelter Los Rápidos; (e) white crust found on the rock surface from the shelter Lago Moreno East; (f-h) red rock art painting, rock support and yellow rock art painting, respectively, from the shelter El Trébol, all loacated in Río Negro province. Labels: g, gypsum; c-calcite; alb-albite; q, α-quartz; h, haematite; an, anatase.

Figure 4:. Raman spectra of representative points of: (a-b) rock support near paintings Nr. 58 and Nr. 51, respectively and (c) Nr. 28a, red guanaco painting from the shelter Paredón Lanfré; (d) Nr. 4, red rock art painting and (e-f) natural white crust and rock surface with a patina, respectively, near painting Nr.1 from the shelter Campamento Argentino, all located in lower Manso River area, Río Negro province. Labels: alb-albite; q, α-quartz; h, haematite; c-calcite; an, anatase.

Figure 5: Raman spectra of representative points of Nr. 10 green rock art painting from the shelter Angostura Blanca, Chubut province measured (a) with the 785 nm laser and (b) with the 532 nm laser, revealing the characteristic bands of glauconite (gl).

Figure 6: Raman spectra of representative points of: (a) Nr. 11 red rock art painting and (b) rock support, from the shelter Angostura Blanca; (c) PP1_9 yellow rock art painting of panel 5, (d) PP1_10 black rock art painting of panel 6, (e) PP1_6 red rock art painting of panel 5, (f) rock support of panel 2, (g) Nr. 15 white negative of a hand of panel 1, (h) PP1_2 white negative of a hand of panel 2, from the shelter Piedra Parada 1; (i) Nr. 20

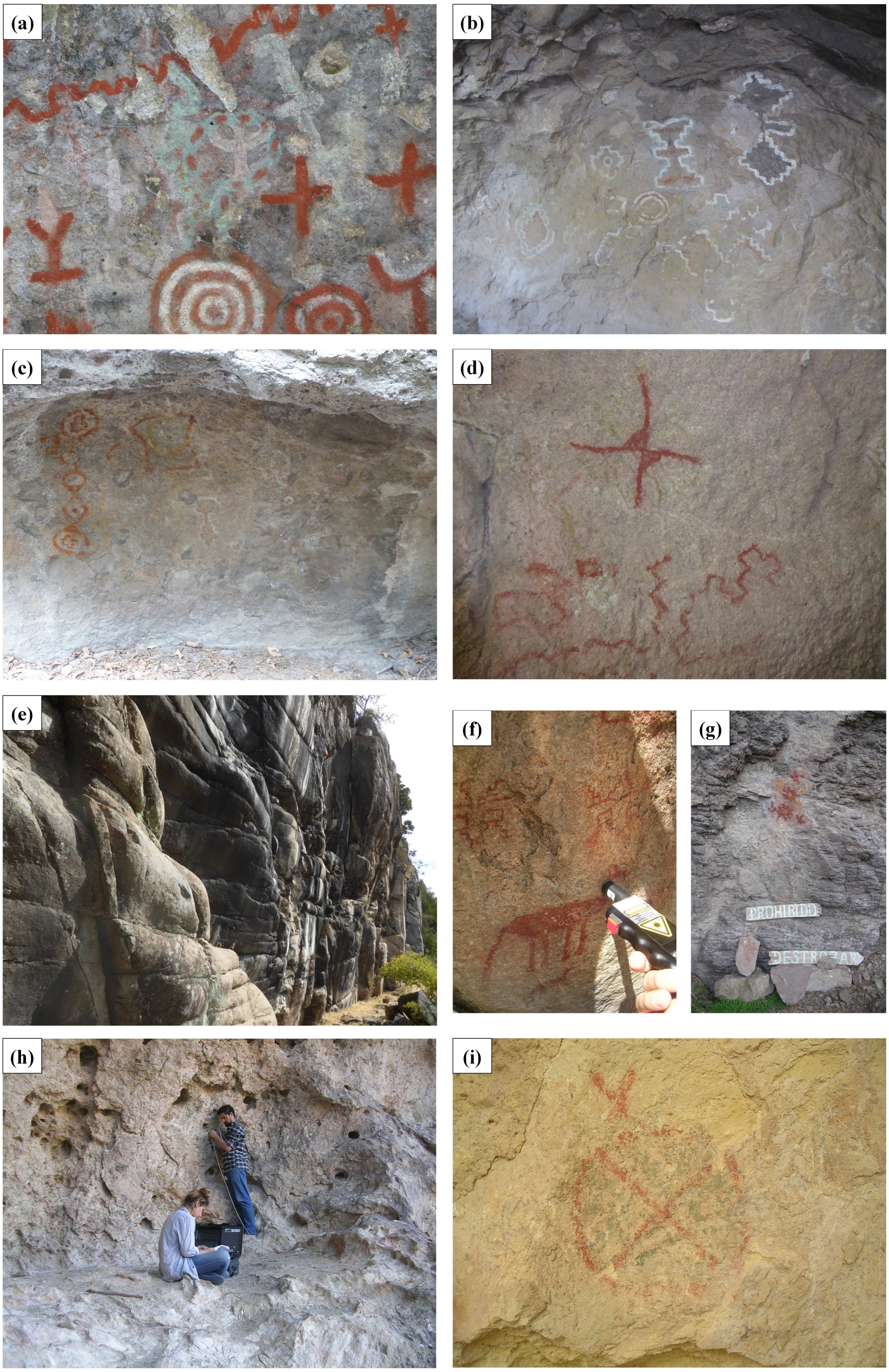
dark red rock art painting, (j) Nr. 17 yellow flowers rock art painting, (k) CM1_3 green rock art painting, (l) rock surface, from the shelter Campo Moncada 1; (m) M2 red rock art painting and (n) rock surface from the shelter Campo Cerda 1, all located in Chubut province. Labels: h, haematite; micro, microcline; g, gypsum; an II, anhydrite II, wh, whewellite; an, anatase; f, feldspar; q, α-quartz; mv, muscovite; ol, olivine.

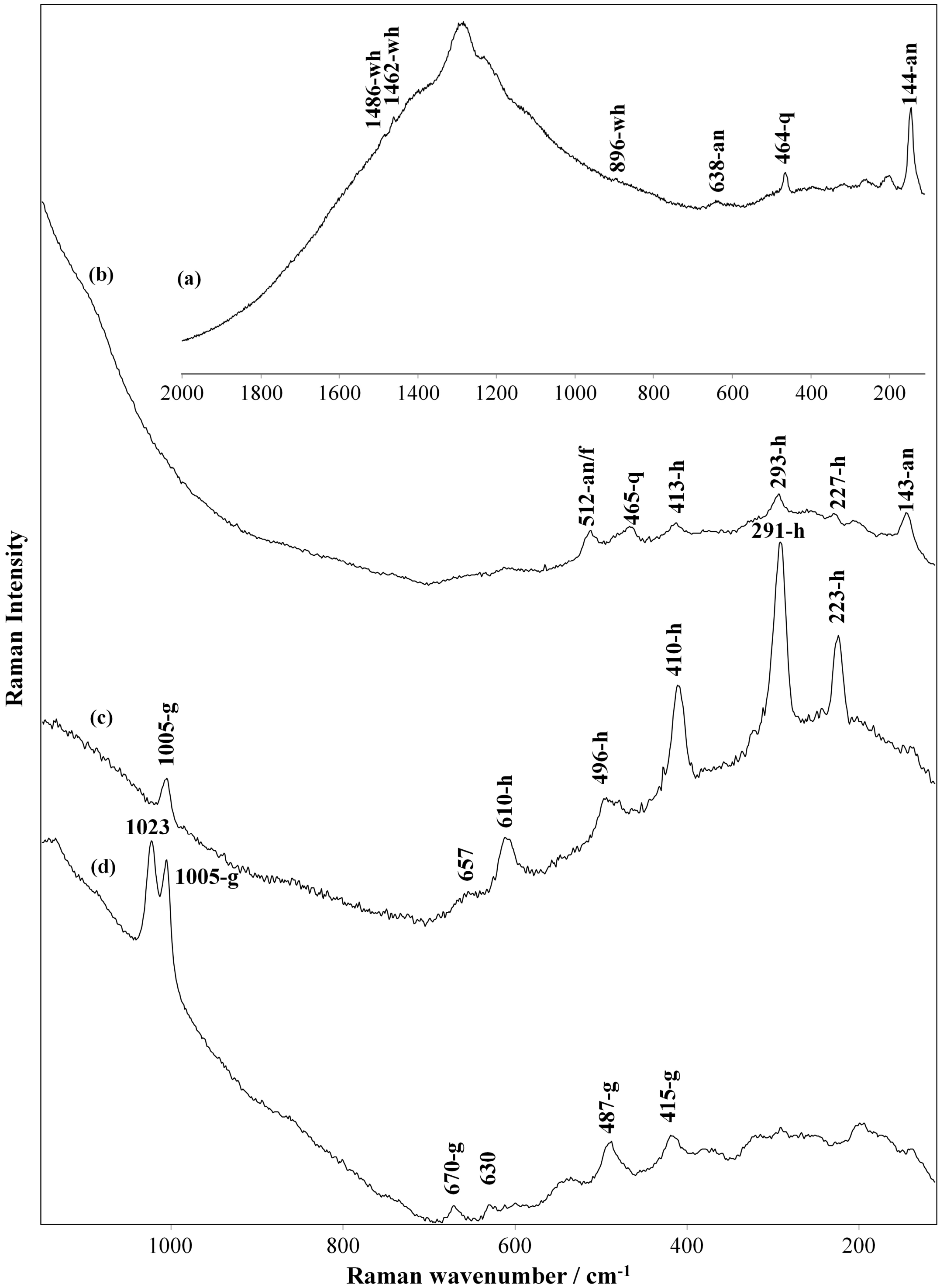
Table Captions

Table I: An overview of archaeological sites that were analysed along with the major components that were positively identified, by *in situ* Raman spectroscopy.

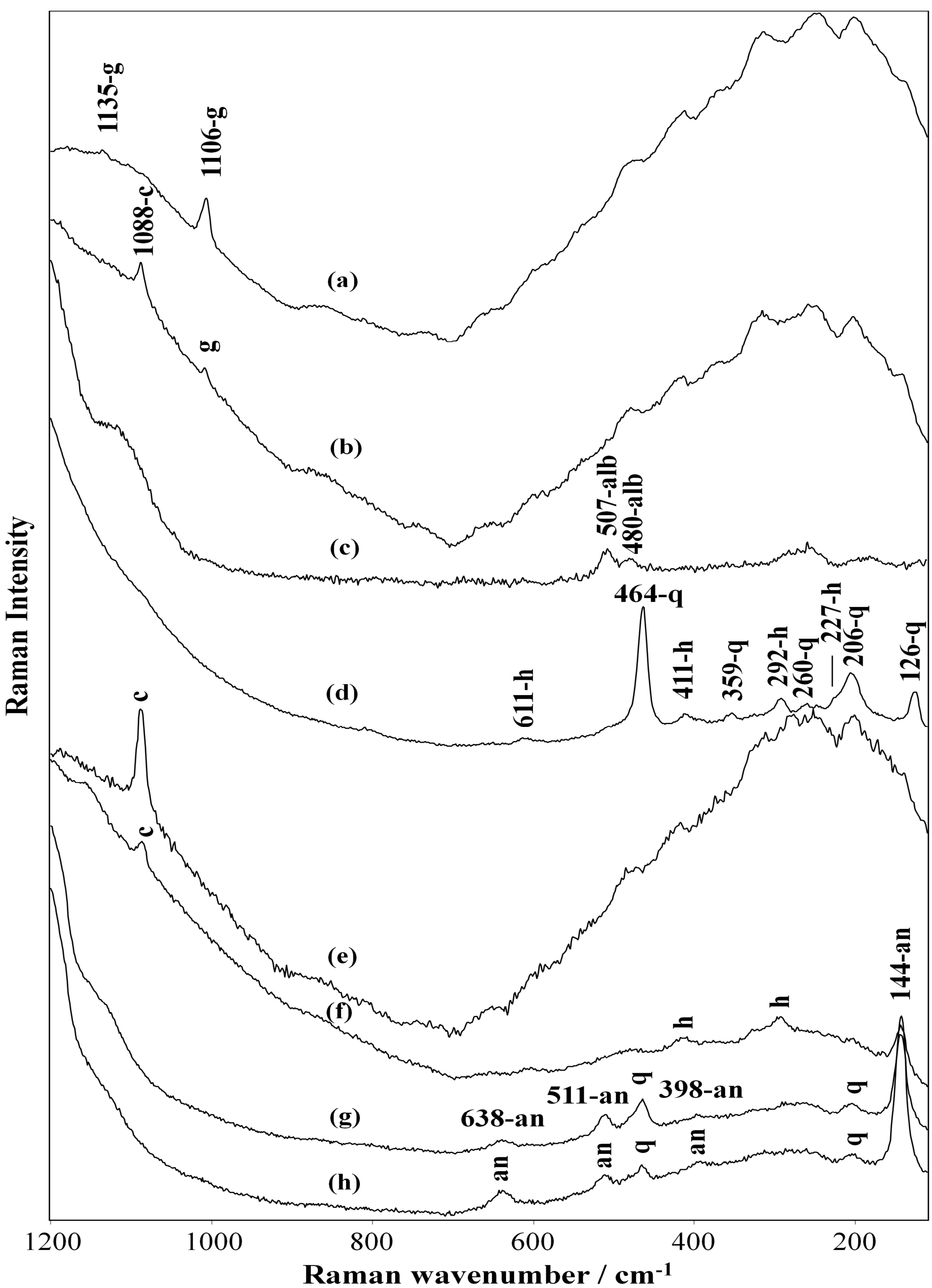
Province	**Shelter**	**Colours Measured**	**# motifs measured**	**Haematite** [39, 45]	**Gypsum** [47-458	**Calcite** [59-60]	**α-quartz** [42-43]	**Ca-oxalates** [17, 39-41]	**Titanium dioxide** [44]	**Anhydrite III** [48]	**Feldspars** [42, 46, 61]	**Other**
Neuquén	Cueva Olate	Red, white, green, black	3	x	x		x	x	x		x?	
	Alero Las Mellizas	Red, white, green, black, yellow	12	x	x		x	x		x		
Río Negro	Alero Maqui	Red, white, green, yellow	3		x	x		x				
	Queutre Inalef	Red	5	x		x	x					
	Guillelmo Lake	Red	1			x					X	
	Los Rápidos	Red	1	x			x					
	Cerro Campanario	Red	1	x			x					
	Cerro Campanario 2	Red	1	x			x					
	Lago Moreno East	Red	2	x		x					X	Carotenoids
	El Trébol	Red, yellow	5	x	x	x	x		x			
Río Negro (Rio Manso)	Paredón Lanfré	Red, yellow, green	10	x			x				X	
	Campamento Argentino	Red	3			x	x		x		x?	
Chubut	Angostura Blanca	Red, green	4	x	x?						X	Green earth
	Piedra Parada 1	Red, white, green, black	14	x	x		x	x	x	x	X	Anhydrite II, muscovite, thenardite
	Campo Moncada 1	Red, white, green, yellow	8	x	x			x		x		
	Campo Cerda 1	Red, white,	11	x	x	(x)*	x			x		Olivine

		orange, yellow										

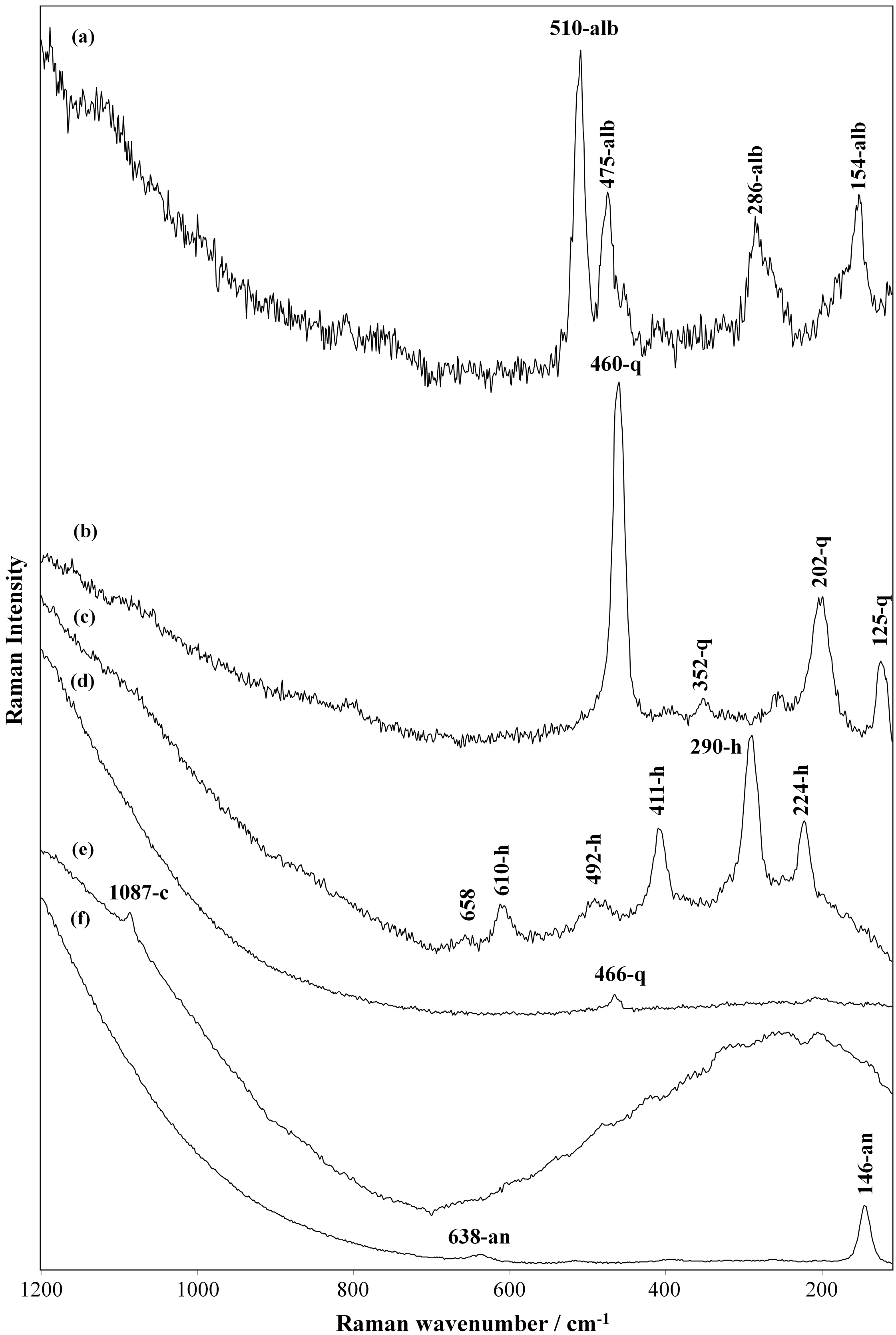

(a)
(b)
(c)
(d)
(e)
(f)
(g)
PROHIBIDO
(h)
(i)



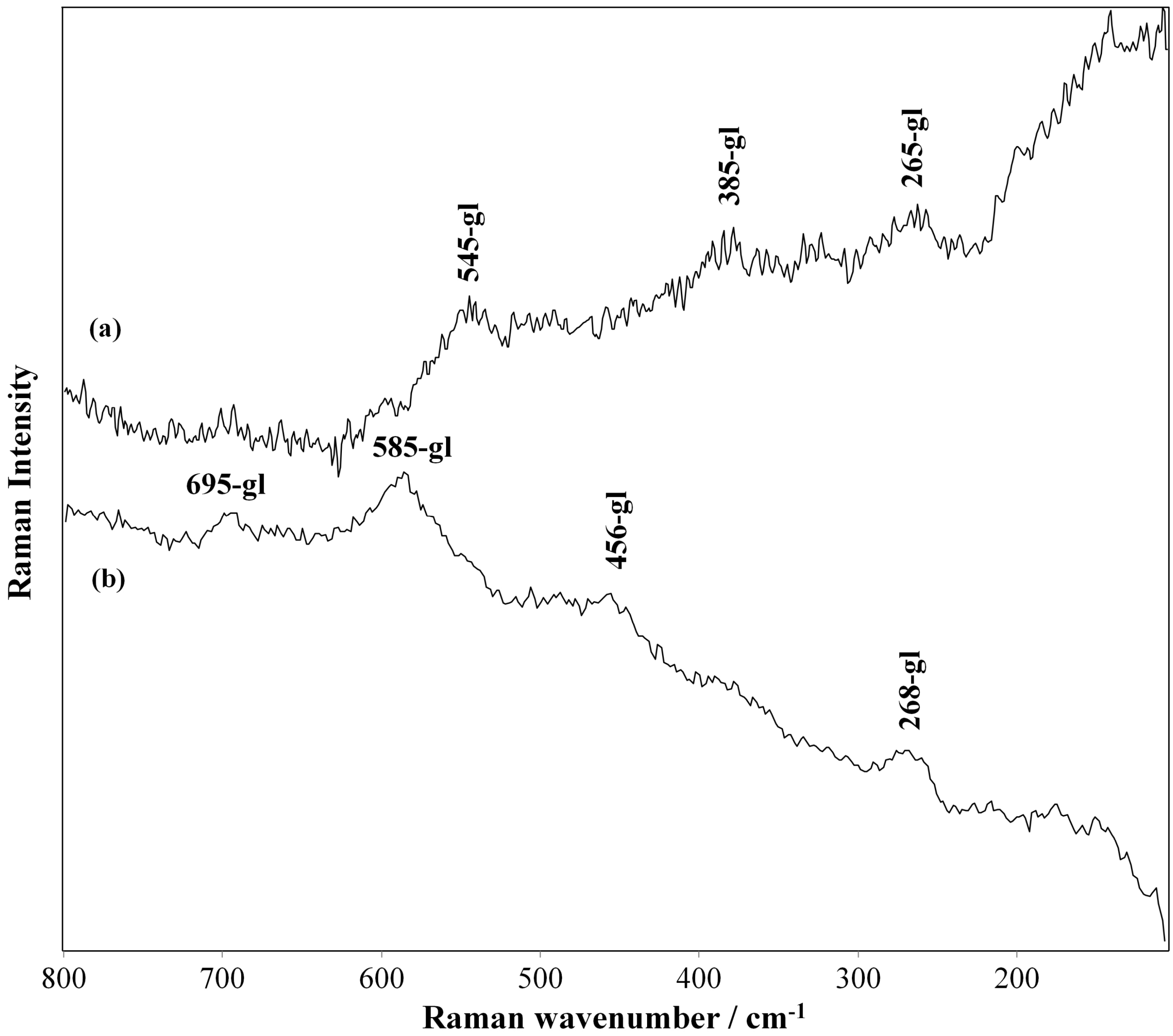
1486-wh
1462-wh
896-wh
638-an
464-q
144-an
(a)
(b)
2000
1800
1600
1400
1200
1000
800
600
400
200
512-an/f
465-q
413-h
293-h
227-h
143-an
291-h
223-h
410-h
Raman Intensity
(c)
1005-g
496-h
610-h
657
1023
(d)
1005-g
487-g
415-g
670-g
630
1000
800
600
400
200
Raman wavenumber / cm-1



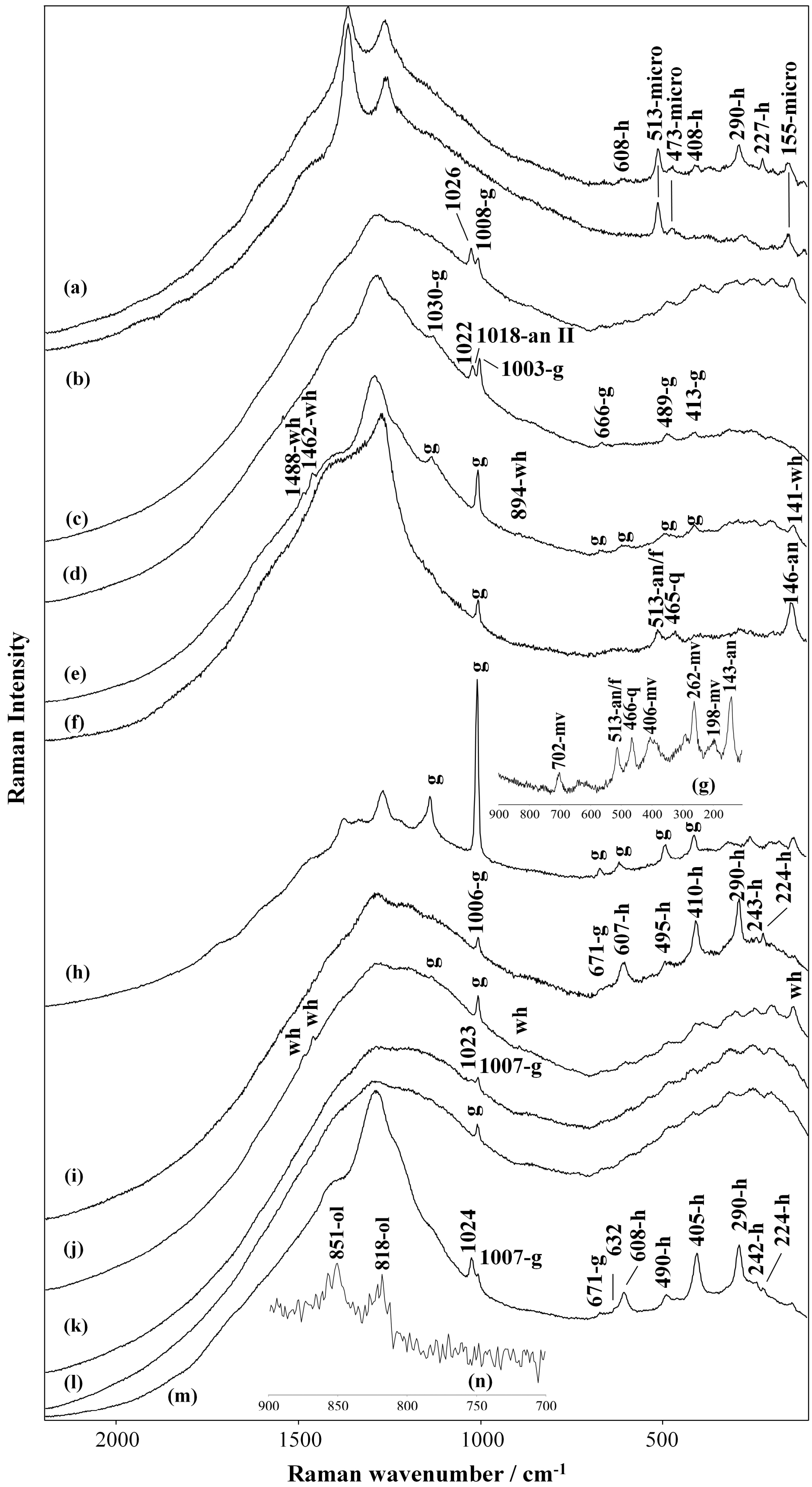
Raman Intensity
1135-g
1106-g
1088-c
(a)
g
(b)
507-alb
480-alb
(c)
464-q
611-h
411-h
359-q
292-h
260-q
227-h
206-q
126-q
(d)
c
c
(e)
(f)
h
h
144-an
638-an
511-an
q
398-an
q
(g)
an
an
q
an
q
(h)
1200
1000
800
600
400
200
Raman wavenumber / cm-1



(a)
510-alb
475-alb
286-alb
154-alb
460-q
(b)
(c)
(d)
202-q
125-q
352-q
290-h
411-h
224-h
492-h
610-h
658
(e)
1087-c
(f)
466-q
146-an
638-an
Raman Intensity
1200
1000
800
600
400
200
Raman wavenumber / cm-1



(a)
(b)
545-gl
385-gl
265-gl
695-gl
585-gl
456-gl
268-gl
Raman Intensity
800
700
600
500
400
300
200
Raman wavenumber / cm-1


Raman Intensity
Raman wavenumber / cm-1
2000
1500
1000
500
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)
(m)
(n)
608-h
513-micro
473-micro
408-h
290-h
227-h
155-micro
1026
1008-g
1030-g
1022
1018-an II
1003-g
666-g
489-g
413-g
1488-wh
1462-wh
894-wh
141-wh
513-an/f
465-q
146-an
702-mv
513-an/f
466-q
406-mv
262-mv
198-mv
143-an
1006-g
671-g
607-h
495-h
410-h
290-h
243-h
224-h
1023
1007-g
1024
1007-g
671-g
632
608-h
490-h
405-h
290-h
242-h
224-h
851-ol
818-ol
900
800
700
600
500
400
300
200
850
750

On-field Raman Spectroscopy of Patagonian Prehistoric Rock Art: Pigments, Alteration Products and Substrata

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Highlights:

- *In situ* Raman spectroscopy was performed on rock art from 16 open air shelters found in the provinces of Neuquén and Río Negro and Chubut, in Patagonia, Argentina.
- Pigments, alteration products and substrata was positively characterized by the technique.
- Special attention is given on the decaying products (biological and chemical attack, encrustations and accretions) found in the shelters and can affect their preservation state.