



# The first use of portable Raman instrumentation for the *in situ* study of prehistoric rock paintings in Patagonian sites

Anastasia Rousaki,<sup>a\*</sup>  Cristina Vázquez,<sup>b,c</sup> Verónica Aldazábal,<sup>d</sup> Cristina Bellelli,<sup>e</sup> Mariana Carballido Calatayud,<sup>e</sup> Adam Hajduk,<sup>f</sup> Emmanuel Vargas,<sup>g</sup> Oscar Palacios,<sup>h</sup> Peter Vandenabeele<sup>i</sup>  and Luc Moens<sup>a</sup>

Portable Raman spectroscopy is applied for the first time on rock art paintings from hunter-gatherers in three different provinces in Patagonia, Argentina (Neuquén, Río Negro and Chubut). Selected archaeological sites were examined, revealing the local 'palette' of the native population and, if possible, the technology used. Moreover, alteration products were investigated to obtain valuable information for a better conservation and preservation of these magnificent rock art paintings. During a single research campaign, 16 shelters and one cave were investigated, which makes this study as one of the most condensed expeditions on measuring rock art paintings. Here, we evaluate the use of our portable Raman instrument to analyse rock art paintings under extreme conditions in Patagonia, Argentina. Several improvements are proposed to maximize the quality of the research output in such condensed expeditions. Copyright © 2017 John Wiley & Sons, Ltd.

**Keywords:** portable Raman spectroscopy; *in situ* analysis; hunter-gatherers; Patagonia; rock art

## Introduction

Archaeometrical studies in Patagonia (Argentina) reveal useful information about the materials used by the population that inhabited the area. The North Patagonian region was occupied by hunter-gatherer populations since the transition between late Pleistocene-early Holocene (at least 10 000 years BP) to the last century. When crossing the landscape from west to east, relatively low temperatures (in the Andes region) are found, followed by the wet forest of the mountain, dry steppes and, finally, moderate temperatures and humidity of the Atlantic coast. Through the study of different archaeological contexts and materials (i.e. geochemical analysis of obsidian tools and sources), it has been established that these groups of hunter-gatherers had broad mobility or exchange systems that could include these environments, which are hundreds of kilometres distant.<sup>[1]</sup> In Patagonian archaeological sites, lithic materials, pottery and faunal remains are commonly found, as well as paintings or engravings on rocks, leather or textiles. The current work focuses on the direct investigation of prehistoric rock art paintings on 17 sites, in two different environmental regions of Patagonia, the forest at Neuquén and Río Negro and the steppe at Chubut. More specifically, we study their pigments, the alteration products and the substrata.

Rock art paintings are relatively common in the Patagonian scenery, and thus, they play an important role in understanding the population dynamics of local hunter-gatherers groups. However, little information is available based on physicochemical investigation, to better understand their manufacturing techniques and to identify the painting materials.

The pioneer work on using X-ray methods, for the investigation of south Patagonian rock art was performed, among others, by

Gradin *et al.*,<sup>[2]</sup> Aschero,<sup>[3]</sup> and Barbosa *et al.*<sup>[4,5]</sup>; all using X-ray diffraction (XRD) (details on these studies in Patagonia can be found at Boschini *et al.* (2011)<sup>[6]</sup>). In 2002, Wainwright *et al.*<sup>[7]</sup> combining XRD, Fourier transform infrared spectroscopy and/or polarizing microscopy determined the composition of pigments from two south and six north rock art sites. From Tierra del Fuego island (Southern South America), Fiore *et al.*<sup>[8]</sup> analysed the organic and

\* Correspondence to: Anastasia Rousaki, Department of Analytical Chemistry, Ghent University, Krijgslaan 281(S-12), B-9000 Ghent, Belgium.  
E-mail: raman@ugent.be

a Department of Analytical Chemistry, Ghent University, Krijgslaan 281(S-12), B-9000, Ghent, Belgium

b Gerencia Química, Comisión Nacional de Energía Atómica, Av. Gral Paz 1499. (1650), San Martín, Argentina

c Facultad de Ingeniería, Universidad de Buenos Aires, Av. P. Colón 850 (1063), Buenos Aires, Argentina

d IMHICIHU, CONICET, Saavedra 15, 5°, (1083), Buenos Aires, Argentina

e CONICET-INAPL-UBA, 3 de Febrero 1370. (1426), Buenos Aires, Argentina

f Museo de la Patagonia, Francisco P. Moreno, Centro Cívico s/n, Bariloche, Argentina

g CONICET-IIDyPCA-UNRN, Mitre 630, San Carlos de Bariloche, Argentina

h CONICET, Godoy Cruz 2290, 9no, Piso, Buenos Aires, Argentina

i Department of Archaeology, Ghent University, Sint-Pietersnieuwstraat 35, B-9000, Ghent, Belgium

inorganic fractions of pigments and coloured sediments recovered in excavations with a multidisciplinary analytical protocol.

In 2000, Wainwright *et al.*<sup>[9]</sup> analysed seven samples from forest sites in North Patagonia and one sample from Campo Moncada 1, a site located in the same steppe (Chubut province) as we are discussing in this paper. Samples of rock art from El Trébol site, close to Bariloche (Río Negro province), were studied with XRD and energy-dispersive X-ray spectroscopy (SEM EDX) by Vázquez *et al.*<sup>[10]</sup> The span of human occupation in El Trébol site<sup>[11]</sup> is dated around 10600 ± 130 BP to 5731 ± 70 BP. In 2009, Darchuk *et al.*<sup>[12]</sup> investigated pigment samples from Carriqueo rock shelter (Neuquén province), and in 2010, Vázquez *et al.*<sup>[13]</sup> reported the analysis of pigments found in different levels of the same archaeological site (Carriqueo). For the later study, the pigment samples of orange, red and brown hues were investigated by synchrotron radiation XRD. In 2012, Massaferro *et al.*<sup>[14]</sup> applied XRD to determine the composition of rock art samples and whether if nearby outcrops were used for the pigments at Comallo I cave (Río Negro province). In 2014, Aldazabal *et al.*<sup>[15]</sup> analysed pottery, pigmented raw materials and some rock art fragments recovered during the excavations of four archaeological sites from Traful lake (Neuquén province). One of them (Las Mellizas shelter) was sampled during this archaeological campaign.

The first record of the use of Raman spectroscopy in North Patagonia is published by Maier *et al.*<sup>[16,17]</sup> combining spectroscopic and chromatographic methods to determine the composition of two archaeological pastes recovered at a stratigraphic layer of Loncoman cave (Río Negro province). An extensive analysis from 13 sites of Río Negro province and one sample from a leather blanket preserved in the Bariloche city museum was published by Boschin *et al.*<sup>[6]</sup> They analysed 107 samples of rock art, pastes, rocks, artefacts, leather fragments and control samples with XRD, energy-dispersive X-ray spectroscopy (SEM EDX), Fourier transform infrared spectroscopy and Raman spectroscopy. Furthermore, pigments found on leather artefacts from the archaeological site Campo Moncada 2 (Piedra Parada, Chubut province) were analysed with Raman spectroscopy by Bellelli *et al.*<sup>[18]</sup> Finally, in 2015, Rousaki *et al.*<sup>[19]</sup> reported the analysis of pigments, beads, grinding tools and pottery from archaeological excavation of hunter-gatherer archaeological sites from Traful Lake (Neuquén province) and Manso River areas (Río Negro province) using the combination of micro-Raman spectroscopy and X-ray fluorescence.

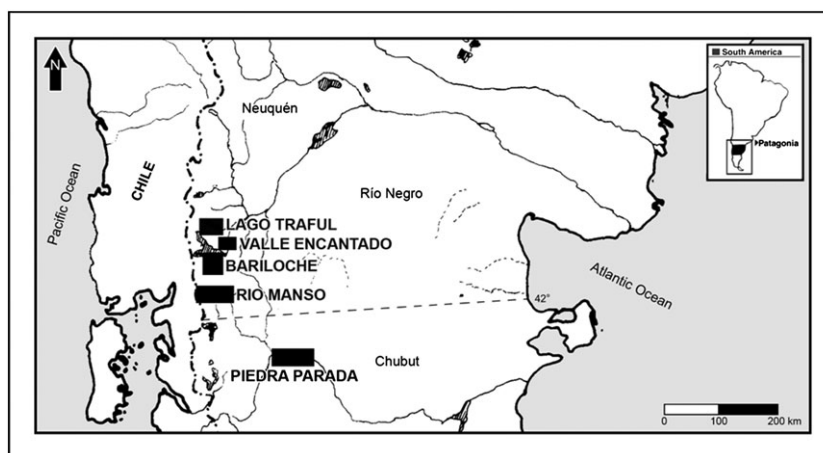
Raman spectroscopy has proven to be a powerful approach to study rock art paintings, substrata and alteration products on the rock surface. The technique was either used as a single approach<sup>[20–24]</sup> or in combination with complementary techniques.<sup>[25–36]</sup>

The use of portable instrumentation in rock art painting research has expanded the field of non-destructive and non-invasive investigation. Also, portable Raman instruments can be carried on site, to perform analysis of the artefacts without disturbing the work of art. In 2011, Tournié *et al.*<sup>[37]</sup> managed to study *in situ* San rock art in South Africa with an HE532 micro-Raman spectrometer (Jobin-Yvon-Horiba, Villeneuve d'Ascq, France). They positively identified red and white pigments, accretions and alteration products while testing their portable Raman instrument in extreme conditions. Although the analysis of the San rock art was successful, the portability of the instrument can be argued as its total weight including the supporting tripod was approximately 60 kg, and therefore, we would rather classify the instrument as transportable.<sup>[38]</sup> In 2012, Lahlii *et al.*<sup>[39]</sup> used the same instrument, for the analysis of prehistoric cave art in Rouffignac St-Cernin,

France, characterising the mineralogical nature of manganese pigments and underlining the presence of organic materials. In 2012, Ravidran *et al.*<sup>[40]</sup> reported the on-site analysis of rock-shelter paintings of the Bhimbetka site (India) using a B&W Tek portable Raman spectrometer. The spectra collected from the portable instrument were compared with the ones obtained from *in vitro* Raman equipments. It is worth mentioning that on-site analysis revealed mainly the inorganic components of the rock art paintings, and a possible organic binder was found from an extracted pigment sample. Olivares *et al.*<sup>[41]</sup> discussed the analysis of La Peña Cave in San Roman de Candamo, Spain, with a similar portable spectrometer, identifying red earths, amorphous carbon and manganese (handheld EDXRF) as main pigments along with products that indicate cyanobacterial growth (parietin, beta-carotene and lycopene), while a recent study<sup>[42]</sup> reported the use of a BWTEK innoRam 785H portable Raman microscope in selected open-air rock shelters in Iberian Peninsula, discussing the difficulties of measuring in open-air environments and presenting the analysis of pigments and crusts from the rock art paintings. In 2014, Pitarch *et al.*<sup>[43]</sup> analysed *in situ* the rock substrate and paintings of Los Chaparros shelter (Albalade del Arzobispo, Teruel, Spain), again with the use of a B&W Tek portable Raman spectrometer, obtaining information from the rock substrate, identifying alteration and accretion products and investigating the Mn-bearing minerals of the pigments used. The last five studies used also other auxiliary portable or laboratory instruments for combining the data. It is worth mentioning that the B&W Tek portable Raman spectrometers were significantly lower in weight (ca. 10 kg) opposite to the one Tournié *et al.*<sup>[37]</sup> used. The total weight of the instrument and the packaging could play a very important role in site-to-site transportation, especially when the rock shelters are difficult to reach or when the measuring comprise a large number of sites that needs to be studied in a short time. This is also an issue that is encountered in the current study.

The problem of weight can be solved by the use of ultramobile or handheld battery-operated instruments (<2 kg). These Raman spectrometers can perform analysis while held by one person.<sup>[44]</sup> Although these ultra light Raman spectrometers are not discussed in the literature of the analysis of rock art paintings, there are many studies that highlight their use outdoors, on-site and in extreme conditions. Moreover, handheld and palm-sized instruments have typically a single, fixed grating, in comparison with portable Raman instruments.<sup>[44]</sup> In some of the studies, handheld Raman instruments were used for detecting biomarkers in complex samples in a host geological matrix under Alpine conditions,<sup>[45]</sup> for the *in situ* identification of arsenate minerals at outcrops,<sup>[46]</sup> for field identification of several minerals,<sup>[47]</sup> for the analysis of stones and gemstones mounted in the sceptre of the Faculty of Science of Charles University in Prague,<sup>[48]</sup> and for detection of common gemstones in several complex religious artefacts and the Ring Monstrance from the Loreto treasury.<sup>[49]</sup> At the latter study also, a 0.8-kg palm-sized device was used.

The total weight, along with other drawbacks that might be faced when analysing rock art with portable instrumentation, will be extensively discussed in this work. Possible solutions are suggested. In this work, we also report for the first time the use of *in situ* Raman spectroscopy in rock art painting of 16 shelters and one cave in archaeological regions in three different Patagonian provinces (Neuquén, Río Negro and Chubut) (Fig. 1). The focus of this study is on the use of portable Raman spectroscopy on the analysis of the rock art materials, accretions and alterations products and substrata.

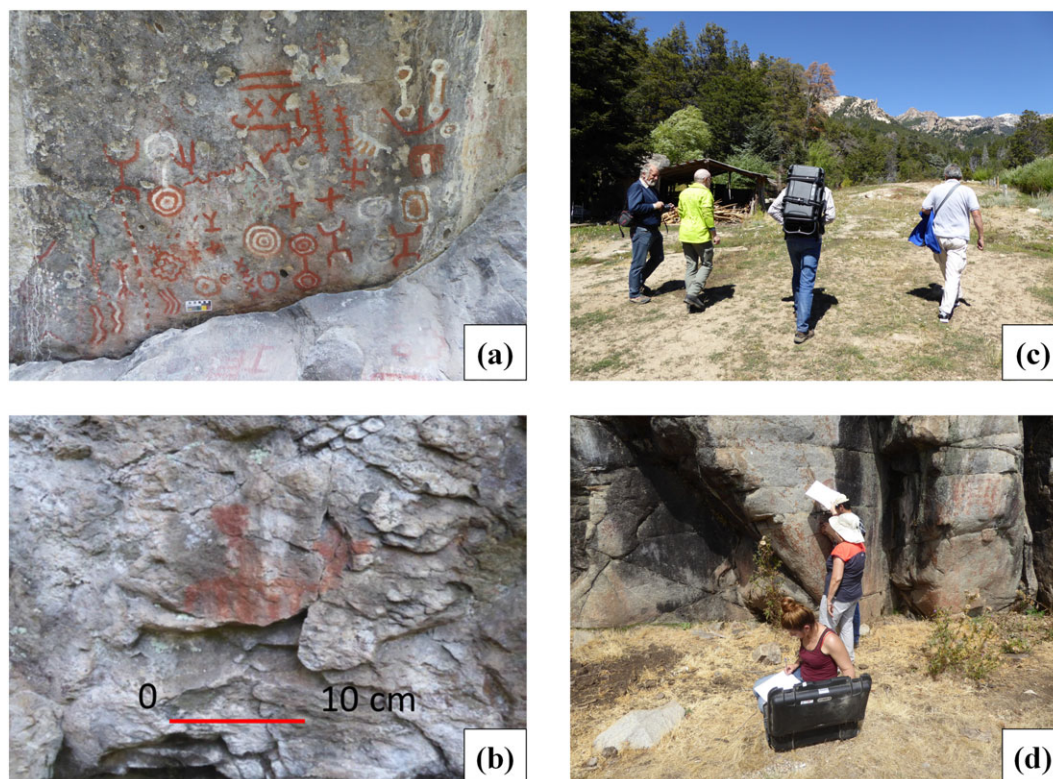


**Figure 1.** Map indicating the location of the different archaeological sites in three different Patagonian provinces (Neuquén, Río Negro and Chubut).

## Experimental

Sixteen shelters and one cave in Patagonia, Argentina, were investigated with portable Raman spectroscopy during a 9-day measuring campaign (Fig. 2(a)–(d)). An overview of these sites is given in Table 1. The instrument was carried into the field and used on painted rock surfaces, alteration and substrata. During this campaign, ca. 500 km was driven by car, often on non-asphalted roads. Although reaching the sites was not straightforward, as usually, the sites were not accessible by car.

All spectra were recorded using a portable EZRaman-I dual Raman analyser from TSI Inc.<sup>[38]</sup> The fibre optics-based spectrometer is coupled with two lasers, a red diode laser (785 nm) and a green Nd:YAG laser (532 nm). For each wavelength, three interchangeable lenses could be used, but most measurements were performed using the standard objective lens, with a typical experimental working distance of 7 or 8 mm and a spot size of  $74 \pm 2 \mu\text{m}$ . A plastic tube with a foam layer was slid over the objective lens tube to avoid interference of the ambient sunlight. The spectrometer is equipped with adjustable power controllers for



**Figure 2.** (a) Rock art painting from the shelter Las Mellizas (Neuquén). (b) Figure representing a man horse riding from the shelter Lago Moreno East (Río Negro). (c) Colleague carrying the portable Raman instrument up the mountain trail towards the shelter Cueva Olate (Neuquén). (d) Raman portable instrument setup in the shelter Paredón Lanfré (Río Negro).



**Table 1.** An overview of the archaeological sites that were investigated with portable Raman EZRAMAN-I dual analyser. 14C chronology indicates the span of human occupation in each site and not the rock art painting age

Area	Province	Number	Site	Sites chronology
Trafal	Neuquén	1	Shelter Cueva Olate	Late Holocene <sup>a</sup>
Trafal	Neuquén	2	Shelter Alero Las Mellizas	590 ± 90 BP
Valle Encantado	Río Negro	3	Cave Mirador de Castillo	Not dated
Valle Encantado	Río Negro	4	Shelter Alero Maqui	Not dated
San Carlos de Bariloche (Gutiérrez Lake)	Río Negro	5	Shelter Queutre Inalef	Not dated
San Carlos de Bariloche (Guillermo Lake)	Río Negro	6	Shelter Guillermo Lake	Not dated
San Carlos de Bariloche (Mascardi Lake)	Río Negro	7	Shelter Los Rápidos	Not dated
San Carlos de Bariloche	Río Negro	8	Shelter Cerro Campanario	Not dated
San Carlos de Bariloche	Río Negro	9	Shelter Cerro Campanario 2	Not dated
San Carlos de Bariloche	Río Negro	10	Shelter Lago Moreno East	Not dated
San Carlos de Bariloche	Río Negro	11	Shelter El Trébol	10600 ± 130 BP–5731 ± 70 BP
Río Manso	Río Negro	12	Shelter Paredón Lanfré	1570 ± 60 BP–330 ± 50 BP
Río Manso	Río Negro	13	Shelter Campamento Argentino	560 ± 60 BP–230 ± 70 BP
Piedra Parada Valley	Chubut	14	Shelter Angostura Blanca	2960 ± 60 BP–450 ± 110 BP
Piedra Parada Valley	Chubut	15	Shelter Piedra Parada 1	1330 ± 50 BP
Piedra Parada Valley	Chubut	16	Shelter Campo Moncada 1	Late Holocene <sup>a</sup>
Piedra Parada Valley	Chubut	17	Shelter Campo Cerda 1	2850 ± 50 BP–580 ± 60 BP

<sup>a</sup>Denotes Relative chronology.

each laser, with a maximum output power of 300 and 50 mW for the 785 and 532 nm lasers, respectively. However, typically, laser power was kept low, to avoid possible laser damage: ca. <30 mW (785 nm) and <8 mW (532 nm). The spectrometer is equipped with two gratings, allowing to record spectra with a spectral resolution of 6–7 cm<sup>-1</sup> (bandwidth as reported by the manufacturer) and projecting the spectra on a TEC-cooled (–50°C) charge-coupled device detector, allowing for spectral ranges of 100–2350 cm<sup>-1</sup> and 100–3200 cm<sup>-1</sup>, for the red and green laser, respectively. 5-m long fibre optic cables allow to record spectra remote from the instrument. A trigger is foreseen on the probe head, for starting the measurements easily. The instrument is controlled by a built-in laptop, allowing to visualise the spectra while performing the measurements. An internal and an external Li-ion battery allow for a total autonomy of ca. 12 h measuring. The instrument was modified with a built-in GPS tracking device that reports the coordinates of the system. Measurement times and number of accumulations were determined to obtain spectra with acceptable signal-to-noise (S/N) ratios, bearing in mind that focusing was performed manually, without rigid positioning equipment and knowing that the available time on site was limited. The entire system is built in a suitcase (55 × 35.5 × 24 cm, ca. 17 kg), which was carried on a metallic exoskeleton, to allow for transportation by a single person (Fig. 3).

Before starting to operate, the portable Raman spectrometer, and after each displacement of the instrument, wavenumber calibration was performed for both lasers. Five products were used for wavelength calibration: sulfur, epsilon-caprolactone (Acros Organics), cyclohexane (Kaiser), polystyrene pellets (Aldrich) and acetonitrile (Panreac)/ toluene (UCB) (mixed in 50/50 volume%).<sup>[50]</sup> The instrument was positioned on an even ground or a gentle slope. The probehead with the light blocker covered with foam was placed perpendicular and in complete contact with the selected spot. The foam layer protected the rock art from further damage. Positioning of the probehead was achieved by hand or on a stick to reach the highest rock art paintings. Thus, for every

**Figure 3.** Colleague carrying the portable Raman spectrometer on a metallic exoskeleton along a gentle slope in Piedra Parada Valley (Chubut) towards the shelter Piedra Parada 1.

single shelter or cave, spectra from the rock surface, the pictograms, the encrustations or alterations and the environment were collected.

Post-measurement data treatment was performed by using Thermo Grams/AI 8.0 suite software (Thermo Fisher Scientific).

## Results and discussion

### Practical considerations for the *in situ* Raman analysis of Patagonian rock art

The purpose of this work is to describe possible difficulties that are encountered during *in situ* Raman measurement of Patagonian pre-historic rock art, and some possible improvements are suggested. The portable Raman spectrometer used in this project was also applied in previous studies, covering a broad range of artefacts, such as the analysis of a mediaeval wall painting,<sup>[38]</sup> glass glyptics,<sup>[51]</sup> illuminated mediaeval manuscripts,<sup>[52]</sup> 16th century majolica tiles,<sup>[53]</sup> the 'Mad Meg' oil painting by Pieter Bruegel the Elder<sup>[54]</sup> and identification of different minerals.<sup>[55,56]</sup> Its application for the direct analysis of rock art paintings from Patagonia, Argentina, is described and discussed for the first time in this paper. Special for the current research project is that 17 sites were investigated in a single expedition, which makes this study as one of the most condensed on measuring rock art paintings that was published before. As a consequence, some challenges are related to bringing the equipment on site and reaching the areas of interest.

During this campaign, the first site was the Cueva Olate shelter in Neuquén province, Patagonia. The shelter was situated high in the mountains, and it was not easy accessible: 4 h (mostly uphill) walking or climbing. This site was the only one that surveyed in the area. The materials recovered from the archaeological site in combination with the actual rock art motives suggest a later chronology. The shelter Las Mellizas (Neuquén) is situated at the north bank of Lago Traful (Traful lake) and is reachable by boat and then on foot. This shelter was previously excavated, and the results pointed out an occupation dating around  $590 \pm 90$  BP. Dating of the archaeological site was based on  $^{14}\text{C}$  analysis on charcoal. As we measured on a windy day, the boat trip to the north bank was a challenge taking into account that the instrument could not suffer severe vibrations or water penetration. Also, a calm boat trip was necessary to reach the cave Mirador de Castillo and the shelter Alero Maqui in Valle Encantado in Río Negro province. The rest of the shelters in Río Negro province were more accessible as they could be reached on foot in a relatively moderate distance from the main driving arteries.

Another obstacle that was faced while reaching the shelters was the thick vegetation sometimes covering the path. This problem was more evident in a number of archaeological sites in the province of Neuquén and Río Negro as they are located inside forests. Opposite to this, the shelters in Chubut province located in Piedra Parada were more easy to reach because they are near the roads and in an opened steppe environment. Moreover, at the time of the campaign that was conducted during summer, the study needed to take place under extreme heat, which hampered transport to the site, but sunlight also interfered with the measurements.

When arriving on site, the rock art paintings were first evaluated and discussed with the archaeologists, to understand the state of the art on how the hunter-gatherers population created the rock art paintings. In some cases, the hunter-gatherers used to paint on top of already degraded rock surfaces to achieve a better contrast. This information was very helpful in understanding the paintings and their stratigraphy, which is obviously also of interest when interpreting the results. Pictograms that needed to be investigated were selected, and measurement points were determined with the

help of a small microscope. Preferentially, thick-paint layers were selected for Raman spectroscopic analysis, if possible without degradation crusts on top of them. In some cases, finding an appropriate spot was difficult, as some paintings and particularly yellow and green areas were severely damaged or degraded. Some shelters, such as Campanario 2, Río Negro, were completely covered with a white weathered crust.

The possibilities of the portable EZRaman-I dual Raman laser spectrometer were tested on rock art paintings in three different provinces in Patagonia. The main problem was not only the challenging conditions under which the spectra were recorded but also the transportation of the instrument from site to site, or from panel to panel within the same site, as this could interfere with wavenumber stability. The problem of transportation was partially due to the weight of the instrument (ca. 17 kg) and additional parts (e.g. external battery, calibration products, sample holder to record calibration products, lenses and light blockers). The instrument is constructed in a suitcase that we mounted on a metallic exoskeleton for backpack carrying. Moreover, in some cases, when steep slopes and climbing are involved, vibrations can affect the geometry of internal components and thus contribute to wavenumber instability, underlining the need of spectral calibration. Transport involved not only rough and steep paths but also travelling by boat to reach shelters at the north bank of the Traful Lake.

Most of the shelters and the cave in the provinces Neuquén and Río Negro were in the forests, on a long walking or climbing distance from roads or main cities. In the Río Manso area, in shelters like Paredón Lanfré and Piedra Parada sites (Chubut province), the environmental conditions changed dramatically. The environment was dry and warm, and most of the shelters were facing the sun. The spectra were recorded in direct sunlight, and metallic components and the laptop of the instrument were exposed.

On all the examined archaeological sites, before starting measurements, the instrument was calibrated for both lasers. It is known that changing the lasers (hence changing the grating position) could possibly affect the observed wavenumber stability.<sup>[38]</sup> In the case of the Patagonian sites, we were measuring three to four archaeological sites per day, and we were using both lasers on each site.

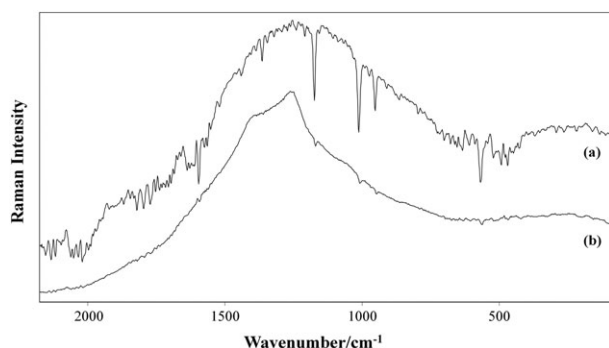
Concluding different sources can be distinguished that contributed to slight shifts in the observed Raman band positions, during measurements of Patagonian rock art paintings. These include (1) vibrations generated by the moving of the instrument as a backpack from site to site or caused by its transportation on rough roads, boat and so on and (2) temperature fluctuations coming from different environmental conditions when measuring in the forests of Neuquén and Río Negro to the dry steppes of the Chubut province. These variations should be tackled by the calibration procedure. However, small shifts can occur if changes in the instrument occur between the calibration and the recording of the spectrum of the unknown.

Another important aspect of measuring in the Patagonian field is the electrical power supply. The portable EZRaman-I dual Raman analyser has an internal battery and an external lithium-ion one. The latter has a live time of ca. 6 h and 30 min. However, frequently changing between the different lasers decreases this time. As it is reported by Lauwers *et al.*,<sup>[38]</sup> the laser output power decreases slightly in time, and this can influence the Raman signal intensity. After 2 h, a constant power output of 230 mW is reached until the battery is empty. The time needed for the batteries to be fully charged is 8.30 h. Working remotely with batteries in Patagonian rock art painting is a challenge. Furthermore, it is not possible to

fully recharge the batteries with no access to electrical power, while being far away from major cities. When visiting the shelters at the Chubut province, this problem was more evident as we stayed in an organized camping in the Piedra Parada Valley. The only source of electricity was a generator that was shut down at midnight and repowered at 7:00 h. Except from the first measuring day in the Chubut province, the spectra were collected with only half-charged batteries, which might have influenced the overall Raman signal intensity.

The spectrometer is equipped with two 5-m long fibre optic cables. This was in particular of use for the analysis of rock art paintings located at a higher level in shelters such as Alero Las Mellizas (Neuquén province). To collect spectra from higher located figures, the probehead was attached to a stick. Moreover, the positioning of the probehead in all the archaeological sites was made by hand. Although, the probehead should be sufficiently stable in order to allow focusing the laser beam on the rock art painting, we could not ensure that focusing was feasible in every case. In spectra that were recorded from the same spot in different measuring conditions, broader bands and low intensity spectra were observed when measuring longer. Focusing by hand is unavoidable while working in the Patagonian field. Using positioning equipment, like tripods, could slow down the set up and would introduce extra problems in mobility. Moreover, some shelters, like Cueva Olate (Neuquén province), are located on slopes in the mountains, and it is difficult to find flat areas for positioning the tripod.

An important aspect when measuring rock painting is the interference of ambient light. When measuring in the field with portable Raman spectrometers, it is advisable to work at night or in darkness. In the case of the Patagonian rock art paintings, all the shelters, except the Mirador de Castillo cave (Río Negro) were exposed directly to light. In the Chubut province, most of the shelters were facing the sun. For these reasons and in order to perform most of the measurements during daytime, a plastic tube with a foam layer (to prevent damage of the painting) was slid over the objective lens tube to avoid sunlight interference. These light blockers performed excellent on field. The only problem occurred the last measuring day in the Piedra Parada 1 shelter (Chubut province) while measuring black pigments. In Fig. 4, the spectrum of an environmental measurement is overlaid with the spectrum recorded from a black rock art painting, highlighting the interference of sunlight to the spectral acquisition. The protective foam was partially destroyed from the rough surfaces of the rocks and light reached the objective.



**Figure 4.** Raman spectra demonstrating the problem of light penetration during measurements. The spectra (a) represent an environmental measurement while the spectrum (b) was recorded the last measuring day at a black rock art painting from the shelter Piedra Parada 1, Chubut province.

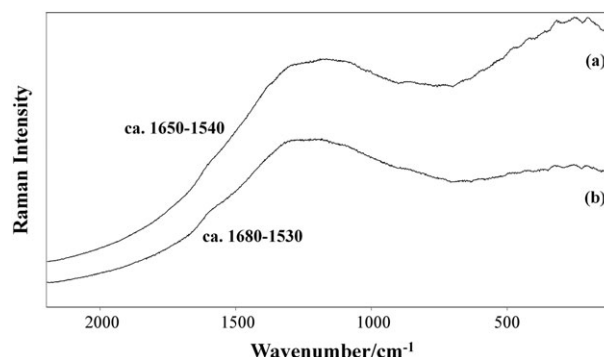
Although, in general the portable EZRaman-I dual Raman analyser performed well in rock art paintings analysis, there were some cases when the characterization of the components was difficult. For yellow pigmented rock art paintings, only the alteration products on top of the rock could be identified. For the green paintings, measured with both lasers, only in one case (painting Nr. 10, Angostura Blanca, Chubut province), we were able to attribute bands to celadonite  $[(\text{Al}, \text{Fe}^{3+}, \text{Fe}^{2+}, \text{Mg})](\text{AlSi}_3\text{Si}_4\text{O}_{10}(\text{OH})_2)]$  or glauconite  $[(\text{K}, \text{Na})(\text{Fe}^{3+}, \text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2]$ , but the strong interference of the substrata was obvious. High fluorescence was observed when measuring with both lasers, sometimes overwhelming the signal. In the case of the black pigments, as shown in Fig. 5, the attribution of bands in certain vibrations was impossible. Because of high fluorescence, probably from the substrata, a relative weak broad band assigned as  $\text{E}_{2g2}, \text{E}_{2g}$  vibrational modes is observed, in the absence of the  $\text{A}_{1g}$  vibrational mode<sup>[57]</sup> from 1301 to 1390  $\text{cm}^{-1}$ . Characterizing the black pigment as carbon base is rather impossible. No other bands, which in combination may be assigned to a different black material, were found. The manganese oxides, with Raman frequencies roughly from 300 to 700  $\text{cm}^{-1}$ , have a weak Raman activity<sup>[58]</sup> and would have been difficult to be investigated via our portable Raman instrument.

The problem of the fluorescence is coming partially from the substrata. In all the spectra we collected from the rock surfaces without degradation, broad features have been found between 1100 and 1600  $\text{cm}^{-1}$ . These features tend to shift from spectra to spectra and cause problems in the identification of components that give rise to Raman bands in that spectral region. A more elaborate study should be made before making final conclusions on the nature of these bands. Perhaps, these are attributed to the fluorescence effects related with the presence of some luminophores.

### Raman spectroscopic identification of pigments and minerals

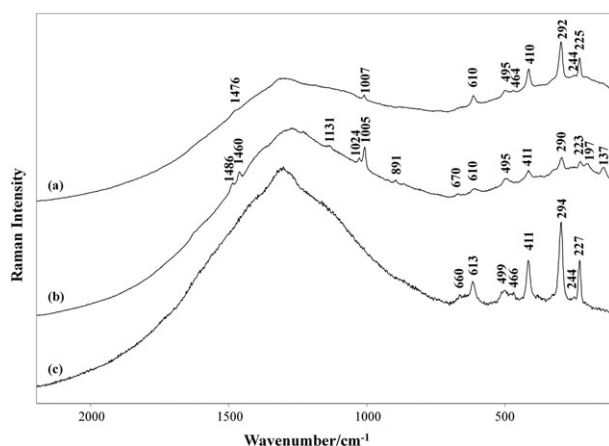
The portable EZRaman-I dual Raman analyser performed excellent in the identification of pigments of the red and the white features of rock art paintings, characterization of encrustations and weathering products on the top of the rock surface as well as investigation of the actual rock. In some cases, the spectra were noisy with high background, which was expected from a portable Raman instrument. Baseline correcting such spectra could possibly create problems by generating artificial features.

In Fig. 6, spectra collected from red rock art paintings from (a) the shelter Alero Las Mellizas, Neuquén province, and (c) the shelter



**Figure 5.** Raman spectra demonstrating the problem of the black pigments identification. The spectra are collected (a) from a black rock art painting from the shelter Alero Las Mellizas, Neuquén province, and (b) from a black rock art painting from the cave Mirador de Castillo, Río Negro province.





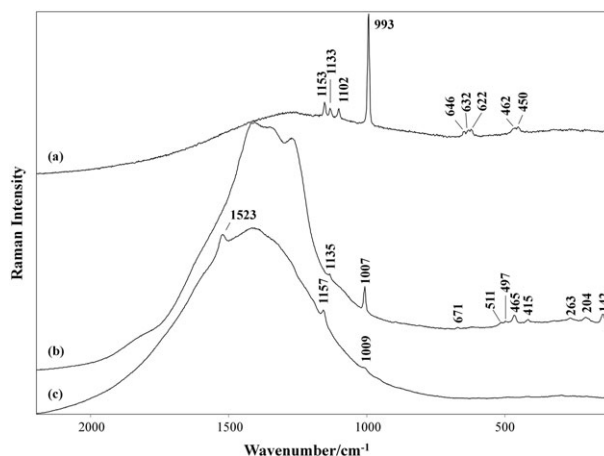
**Figure 6.** Raman spectra of representative points of (a) red rock art painting, (b) white-dot rock art painting from the shelter Alero Las Mellizas, Neuquén province, and (c) red rock painting from the shelter Queutre Inalef, Río Negro province.

Queutre Inalef, Río Negro province, are presented. The red chromophore of these two rock art paintings is haematite ( $\text{Fe}_2\text{O}_3$ ), which could be identified by the bands<sup>[27,59,60]</sup> at 610, 495, 410, 292, 244 and 225  $\text{cm}^{-1}$  for the shelter Alero Las Mellizas and bands<sup>[27,59,60]</sup> at 613, 499, 411, 294, 224 and 227  $\text{cm}^{-1}$  for shelter Queutre Inalef. Moreover, in the shelter Alero Las Mellizas, a band at 1476  $\text{cm}^{-1}$  can be attributed to weddellite ( $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ )<sup>[61]</sup> and bands at 1007 and 464  $\text{cm}^{-1}$  assigned to gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )<sup>[62]</sup> and  $\alpha$ -quartz,<sup>[63]</sup> respectively. The presence of a band at 660  $\text{cm}^{-1}$  at the spectrum of the shelter Queutre Inalef might be due to magnetite ( $\text{Fe}_3\text{O}_4$ ).<sup>[59,60,64]</sup> Magnetite is often associated with thermal treatment but also can be formed from microbiological attack on haematite and its oxy-hydroxides and serve as a decaying product.<sup>[19,21]</sup> Moreover, it is present in the nature. It is worth mentioning that the band at around 660  $\text{cm}^{-1}$  is under debate, especially when both haematite and magnetite are present.<sup>[65]</sup> In 1999, Bersani *et al.*<sup>[66]</sup> showed that in the absence of magnetite, haematite appears a band at 660  $\text{cm}^{-1}$  related to disorder effects and/or the presence of nanocrystals. In the presence of magnetite, the debated peak is enhanced. Among other spectra that were collected from the multicoloured paintings of the shelter Alero Las Mellizas, also, a white-dot rock art painting was measured (Fig. 6(b)). The white pigment of the painting is identified as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) by the bands<sup>[62]</sup> at 1131, 1005, 670 and 137  $\text{cm}^{-1}$ . Haematite ( $\text{Fe}_2\text{O}_3$ ) is also present in the white mixture (610, 495, 411, 290 and 223  $\text{cm}^{-1}$ ).<sup>[27,59,60]</sup> Bands of whewellite ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ )<sup>[27]</sup> were observed at 1486, 1460, 891 and 197  $\text{cm}^{-1}$ . The presence of hydrated Ca-oxalates, on the red and white dot rock art paintings of the shelter Alero Las Mellizas, can be explained biologically and chemically. Ca-oxalate layers are the result of metabolic activity of lichens, fungi or bacteria that colonize on top of Ca-rich substrates. Moreover, oxalates can be formed from the degradation of organic media and the alteration of some binders found in the paintings.<sup>[20,30,31]</sup> Special attention should be given to a band at 1024  $\text{cm}^{-1}$ . This band is attributed in the thermal studies as metastable soluble anhydrite (AIII). This compound is unstable and rehydrates very quickly.<sup>[67]</sup> In 2011, Tournié *et al.*<sup>[37]</sup> measuring *in situ* San rock art in South Africa attributed a band at 1025  $\text{cm}^{-1}$  as anhydrite discussing the instability of the compound. In the absence of other bands, the band at 1024  $\text{cm}^{-1}$  can also be attributed to the iron (III) sulfate nonahydrate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ). This chemical formula is shared by two polymorphs with almost identical Raman

spectra: coquimbite and paracoquimbite.<sup>[68]</sup> In environments rich in sulfuric aerosols, the formation of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  is the result of the reaction between iron oxides, in particular haematite, and the soluble sulfate from the formation of gypsum. It is worth mentioning although that the formation of coquimbite and paracoquimbite as a decaying product is well described in the case on wall paintings and modern mortars.<sup>[68,69]</sup>

The Raman spectra from the shelter Piedra Parada 1, Chubut province and shelter Lago Moreno East, Río Negro province, Fig. 7(a) and (c) represent degradation products and biological activity compounds, respectively. The thenardite ( $\text{Na}_2\text{SO}_4$ ) encrustation (bands at 1153, 1133, 1102, 993, 646, 632, 622, 462 and 450  $\text{cm}^{-1}$ )<sup>[70,71]</sup> was found near the rock art paintings of Panel 2 of the shelter Piedra Parada 1. The dry environment of the steppe can explain partially the formation of the anhydrous sodium sulfate and is a result of the atmospheric gases attack. At the spectrum of red man horseriding painting, from shelter Lago Moreno East, the bands at 1523, 1157 and 1009  $\text{cm}^{-1}$  are attributed to carotenoids.<sup>[27,61]</sup> Carotenoids are the result of photosynthetic bacteria or lichens containing these compounds. The precise species of carotenoid is difficult to be identified by the three bands alone.<sup>[27]</sup> At the white rock art painting from the shelter Cueva Olate, Neuquén province (Fig. 7(b)), the white pigment identified as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) by the bands<sup>[62]</sup> at 1135, 1007, 671, 497 and 415  $\text{cm}^{-1}$ . The bands at 511 and 142  $\text{cm}^{-1}$  correspond to titanium oxide (anatase)<sup>[29]</sup> while the bands at 467, 263 and 204  $\text{cm}^{-1}$  attributed to  $\alpha$ -quartz.<sup>[63]</sup>

Working with portable Raman instruments on rock art paintings allows measuring all the possible layers that may contribute to the Raman signal of the actual painting and thus attribute the bands to the proper compounds. Spectra collected from the rock surfaces, with and without alteration products, revealed the compounds of the substrata and the encrustations and contribute to the precise identification of the materials of the paintings. For the Patagonian sites, being able to create instant libraries of materials found on rocks improved our ability to intergrade bands and assigned them to the correct compound, especially in the cases of mixtures of iron oxides, different groups of silicates, anatase and degradation products like gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).



**Figure 7.** Raman spectra of representative points of: (a) white encrustation near the paintings of Panel 2 at the shelter Piedra Parada 1, Chubut province, (b) white rock art painting from the shelter Cueva Olate, Neuquén province and (c) red man horseriding from the shelter Lago Moreno East, Río Negro province.

## Suggestions for improvement of the portable EZRaman-I dual laser Raman spectrometer

The use of portable Raman spectroscopy on the analysis of the rock art materials, accretions and alterations products and substrata on rock art paintings from Patagonia was proven successful. In order to overcome difficulties presented during the *in situ* Raman measurement of Patagonian prehistoric rock art, possible improvements are suggested.

A very important aspect that needs special attention is the weight of the system. Although, our entire system is built-in in a suitcase of ca. 17 kg, its transportation was difficult especially when the sites were remote or situated high in the mountains. In order to reduce the total weight of the basic instrument, it is suggested that the battery and the computer, which are now fixed inside the suitcase, can be removed and carried separately. Moreover, a lighter suitcase material would be welcomed, for example, carbon fibres, titanium or aluminium, to further reduce the total weight of the basic instrument. Simultaneously, the new suitcase should protect the internal part of the instrument, from fine dust penetration and be waterproof. Instead of carrying the instrument on an exoskeleton, stripes are proposed to be incorporated at the back of the suitcase, in order to be used as a backpack.

Another aspect that needs to be considered is the life time of the batteries. Most of the sites in Patagonia are far from cities. The shelters in the Chubut province are situated near or in Piedra Parada Valley, where electrical power is unavailable. As a consequence, the batteries need to have a life time of more than 8 h, which is an average working day.

Another problem occurred while measuring in the steppes was the high temperature. When the suitcase is opened, all the metallic parts of the instrument are exposed to heat. Temperature fluctuations may disturb wavenumber stability, and thus, it is suggested either the metallic components to have a thermostable cover or insulator materials to be used.

Calibration is very important in order to ensure partially the wavenumber stability. Other parameters that can disturb wavenumber stability are temperature fluctuations, vibrations coming from moving the instrument and changing the grating while measuring with different lasers. As some of them are unavoidable when measuring in Patagonia, calibration cannot be entirely ensured. Although our instrument was tested for wavenumber stability,<sup>[38]</sup> this study was performed in laboratory environment. For the Patagonian sites, it is suggested to perform the calibration just before measuring the rock art painting for every single site, even when the sites are close by located. Also, every laser should be calibrated just before use in order to avoid wavenumber shift during changing the grating. Also, automatic calibration of the spectra can reduce the time of post-processing of the data.

Another suggestion is the use of a 1064-nm laser in order to decrease the fluorescence background and have better results as the noise and background is limited. Also the solid state detectors of near IR lasers are more sensitive at the C–H stretching region than charge-coupled device detectors. The main problem of coupling a 1064-nm laser on an instrument that works already with a 785-nm and 532-nm laser is that a different geometry, grating and detector should be applied. This might also change the dimension and the total weight of the instrument.

Measuring in Patagonia with tripods in order to focus the problem is not possible. Most of the sites are located on slopes, or the rough rocky ground is uneven. Moreover, if three or four sites need to be measured in the same day, carrying extra positioning

equipment is impossible. Positioning of the probehead by hand although is considered difficult is proven successful in measuring rock art paintings. It is suggested not to perform very long measurements when focusing by hand, as the focus fluctuates because of the instability of the hand. Moreover, in order to reach and focus paintings that are situated higher at the sites, an adjustable stick of 2 m in total with a rotary head of 180° is essential.

The plastic tubes with foam that were slid on the objective lens proved excellent on blocking the ambient light. The only problem occurred at the last measuring day was because the protective foam was damaged. Additional light blockers should be carried when measuring rock art paintings or change the soft foam on the edge of the plastic tube with a more hard material.

The portable EZRaman-I dual Raman analyser is not coupled with a microscope and that created problems as the focusing on the region of interest could not be inspected. The use of a microscope or camera with high magnification is highly recommended.

## Conclusions

The current research focuses on the direct investigation of prehistoric rock art paintings on 17 archaeological sites, in two broader Patagonia regions, El Neuquén, Rio Negro and Chubut. The purpose of this work is twofold: to describe possible difficulties occurring during *in situ* Raman measurements of Patagonian prehistoric rock art and to suggest some possible improvements. The portable Raman spectrometer used in the current study was also applied in previous projects, covering a broad range of artefacts, but was never used in the investigation of rock art paintings before. The portable EZRaman-Dual Raman spectrometer successfully characterized substrata, encrustations, degradation products and biological activity related compounds and most of the pigments used for rock art painting.

An extra challenge for the current research campaign is that a significant amount of rock art paintings from different archaeological sites were investigated in a single and short-time expedition, resulting in one of the most condensed studies on measuring rock art paintings that was published before.

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