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RESEARCH ARTICLE

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Colors and dyes of archaeological textiles from Tarapacá in the Atacama Desert (South Central Andes)

Marcela Sepúlveda^{1*} , Cecilia Lemp Urzúa², José Cárcamo-Vega³, Edgar Casanova-González⁴, Sebastián Gutiérrez⁵, Miguel Ángel Maynez-Rojas⁶, Benjamín Ballester³ and José Luis Ruvalcaba-Sil⁶

Abstract

This work concerns the study of colors and dyes identified on archaeological textiles from the Atacama Desert. The different garments and ornaments come from the excavation of two important pre-Columbian cemeteries of the Tarapacá region: Tarapacá-40 attributed to the Formative period (1100 BC–660 AD) and Pica-8 to the Late Intermediate period (900–1450 AD). For the first time, a multi-analytical approach with non-invasive techniques using FORS and SERS was applied on samples of less than 2 cm of length for physicochemical characterization of the raw materials and the dyes employed in the textile production of northern Chile. The fibers are from animal origin. Blue, green, and yellow are identified as indigo, but we cannot discard a mixture with other dyes to vary hue and shade; while carminic acid and alizarin—to a lesser extent—are found on red, orange, and brown samples. This research provides new elements for the discussion about the textile technology developed in this desertic region, its changes, and continuities along the history. Our results are compared to recent findings on neighboring regions from South-Central Andes, to improve the current knowledge and discuss the existence of dyeing textile cultural traditions.

Keywords: Dyes, Textiles, FORS, SERS, South america, Indigo, Alizarin, Carminic acid

Introduction

In South America, Andean textiles are recognized as a major art of the pre-Columbian societies that inhabited these territories. This tradition is still preserved and stands out for the variety of techniques and materials employed, their rich iconography and their wide chromatic palette visible from the first archaeological textiles testimonies. In the words of John Murra, an important Andean scholar: “No political, military, social, or religious event was complete without textiles being volunteered or bestowed, burned, exchanged, or sacrificed” [1]. And even if Murra is referring in this case to the Inca State, from the 14th to sixteenth centuries, we can easily

imagine a similar situation in previous periods. Textile testimonies are exhibited in famous museums around the world, acting as evidence of the great achievement of textile artisans. For their production, they used different types of fibers (animal, vegetal and human hair) spun, and weave with a variety of structural techniques, using naturally colored threads or others painted and dyed, with eventual decorations made of beads, colored minerals, metals, and feathers. The textile craft in the Andes involved the gradual development of a technological system, which began in the Late Pleistocene [2]. The use of dyes also evidences a long historic tradition, as recently proven by the identification of indigo on 5000-year-old textiles, the oldest record of the use of this type of dye in the world so far [3].

Today, the techniques, materials and polychromy recognized on certain objects raise textile production to a prominent position among the handcrafts of

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pre-Columbian Andean communities [1, 4–10]. The knowledge related to the acquisition of the diverse raw materials, the weaving and structure of textiles, as well as the mathematical logic applied to the elaboration of the textile is widely recognized [11, 12]. The chromatic attributes have also attracted great interest since it has been demonstrated that numerous plants and insects were used and prepared to achieve the wide color palette observed in textile dyeing [1, 13–22].

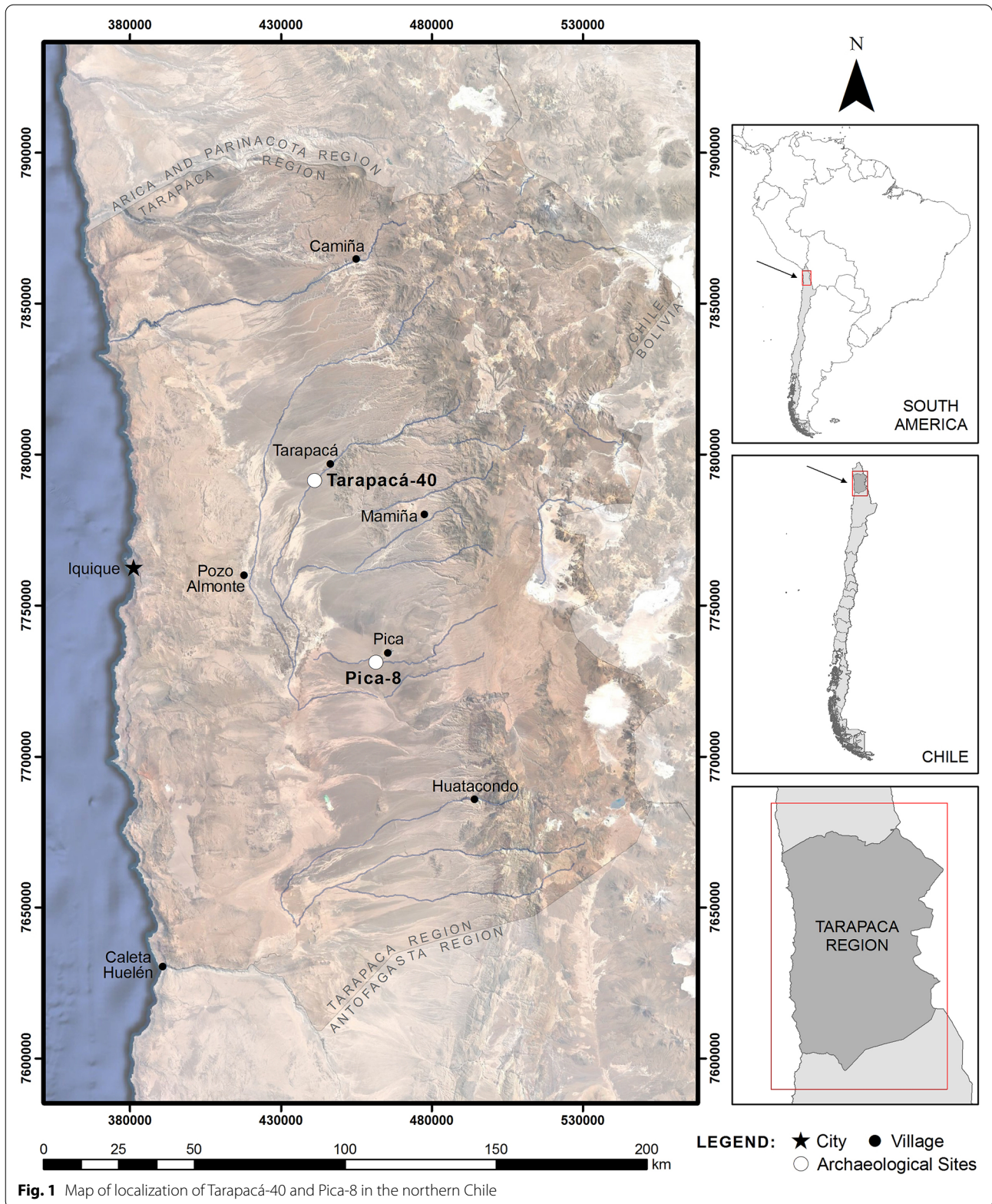
Textile manufacture involves several technological procedures related, on one side, with the procurement of the fibers and the preparation of the yarns, made from animal (mainly camelids and other mammals in a minor proportion), plants (cotton, *titora* and *junquillo*, among others) or human hair, which will become part of the textile structure (warp and weft). Such procedures are also related to the incorporation or application of color on yarns, to accomplish the design of the textiles. Color was incorporated through dyeing or painting, using organic dyestuffs or mineral pigments, collected, and prepared using other compounds that served as mordants or post-mordants, for ensuring a better adherence of the color on the fibers [9, 10, 19, 20]. A third element are the skills associated with the weaving or the construction of the textile [5, 23–25]. Moreover, the incorporation of symbols or figures through color constitute a true semiotic device. The final form of the textiles, as well as the choice of colors, the logics that shape the design, figures and elements elaborated on each textile, contribute to defining diverse styles and manufacturing traditions, often related to socio-cultural distinctions of status, gender or role, as well as ethnic or cultural identities, among others [26–35].

In the Andes, the color in archaeological textiles have been interpreted in terms of the prestige and power of certain social entities, but also as an expression of gender identity [1, 29, 36–43]. However, until now the color materiality is poorly understood, i.e., regarding the materials and immaterial knowledges involved in the making of textiles. The interpretation of their materiality requires an interdisciplinary approach and the implementation of various analytical techniques.

A review of the available published literature shows that analytical studies applied to historic Andean textiles are still scarce [3, 44–73], more so for colonial and republican periods [47]. For the pre-Columbian period, studies usually involve the analysis of a few samples, commonly reds or blues, with little information about other colors or shade variations [3, 48–55, 57–67, 70]. Further colors like yellow, green, white, or brown are less studied [49, 50, 53, 56, 64, 66, 67, 69, 70]. Only a few of them have widened the analyses of the dyes and focused on the mordants [50, 51, 54, 67, 68, 70]. Some

investigations have approached the painted textiles, a rarely addressed subject [71, 72]. From an analytical perspective, they applied chromatographic or spectroscopic techniques including gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography with diode array detectors (HPLC-DAD) and/or mass spectrometry (HPLC-MS), direct analysis in real time mass spectrometry (DART-MS), which albeit sensitive are destructive methods [3, 48–50, 53, 54, 56–60, 62–64, 66, 70]. Analysis by surface-enhanced Raman spectroscopy (SERS) was applied in just five publications to analyze archaeological textiles from Peru and northern Chile [55, 61, 65, 69, 73]. Finally, the available literature shows a particular emphasis on the analysis of polychrome textiles from the Paracas and Nazca cultures (700 BC–800AD), on South–Central Perú [51–53, 59–61, 66, 67, 70]. For northern Chile, only three studies have been published addressing the physicochemical analysis of textile dyes: one related to textiles from San Pedro de Atacama, almost 500 km to the south of our study region, and the others for Arica, 270 km to the north [63, 69, 73]. Other results were just announced at a conference and are still unpublished [55]. In general, those studies and others have demonstrated the use of indigo from plants of the genera *Indigofera* spp., *between others*, for the blue shades, carminic acid obtained from cochineal (*Dactylopius coccus coccus*), purpurin and alizarin from plants of the Rubiaceae family (*Galium* spp. or *Rebunium* spp.) for the reds and other plants mixed in complex recipes with several dyes and mordants to obtain other colors and tones [13–22, 55, 67, 74, 75].

The identification of the fibers and the colorant raw materials used for dyeing constitutes one of the ways for achieving a better understanding of textile technology and production [10, 51, 66–68, 70]. Although several analyses are available, more knowledge of the technological processes involved can be reached through the combination of multiple analytical techniques. HPLC and other chromatographic techniques are preferred for the identification of textile dyes [74, 76–78], but every textile garment or ornament is unique; hence we must prioritize the use of non-destructive or micro-analytical techniques. In sum, we present the analysis of dyed fibers from different textiles from the Atacama Desert in northern Chile, specifically from the Tarapacá region (Fig. 1). Each sample was first observed by optical microscopy. The fibers were identified by Fourier-transform infrared spectroscopy (FTIR). Then colorimetry was used for preliminary identification of colors. Finally, dye identifications were performed by fiber-optics reflectance spectroscopy (FORS) and surface-enhanced raman spectroscopy (SERS).



Materials and methods

Archaeological samples

The analyzed textiles belong to two important cemeteries from the Tarapacá region, ascribed to two different periods of the pre-Columbian chronological sequence of the Atacama Desert in northern Chile: Tarapacá-40 and Pica-8 (Fig. 1).

Tarapacá-40 is located in the desert, about 60 km from the Pacific coast; the site corresponds to an extensive cemetery, placed at the north slope of the Tarapacá ravine (Fig. 1). Excavations began in the 1960s and continued until the 2000s [79–83], and now its collections are deposited in different institutions (museums and universities) throughout the country [84]. ¹⁴C-AMS dating of different burial contexts from the site allowed proposing it was occupied during the Formative period (ca. 1.110–1.100 B.C.- 410–550 A.D.) [26, 83]. The cemetery's configuration is associated with the occupation of its contemporary village Caserones-1, composed of more than 350 structures [81, 82, 85, 86]. This period is characterized by the consolidation of the villages with more sedentary dwellers and a food-producing economy [87]. Previous textiles studies from Tarapacá-40 have focused on the collections available on museums from northern Chile [26, 41, 79]. In the present study, a total of 163 textiles from this cemetery were considered: five samples were taken from five textiles, including two blankets, two headdresses, and a bracelet (Fig. 2a–e; Table 1).

Pica-8 is a vast cemetery located in the Pica oasis, at the south from Tarapacá valley and 90 km from the Pacific coast (Fig. 1). The site was excavated in the 1960s [88–91], and as in the case of Tarapacá-40, the collections are also dispersed in several institutions [84]. Dating studies placed the occupation in the Late Intermediate Period (ca. 769–969 to 1301–1414 A.D. [92]. Pica-8 belongs to the Pica-Tarapacá cultural complex, a set of communities settled in the driest area of the Atacama Desert, which for living exploited several resources from other ecological regions and at the same time articulated the exchange of resources with other neighboring cultural traditions. Deep social differences and inequalities, with a higher economic specialization, are characteristics of this considered society of the Late Intermediate period [91]. Textile analyses from this same cemetery were also previously published [28, 93]. During our project, a group of 258 textiles were considered, and a total of 17 samples were collected from eight textiles (Fig. 2f–m). The textile pieces correspond to seven tunics and a loincloth (Table 1).

Sampling was performed at the Collection Deposit of the Anthropology Department of Universidad de Chile after a process of dry cleaning and repackaging in new boxes to replace previous and original plastic bags from

the excavation. The study included a material-technical analysis and an assessment of their state of conservation, which in turn contributed to the identification of functional and typological characteristics. The first description of textiles fibers, techniques and colors was carried out. Colors were preliminarily reported using the Munsell Table. Quantitative colorimetric measurements were also performed with a CR-10 colorimeter (Konica Minolta) to complete the Munsell description. Samples consist of a textile fiber fragment of less than 2 cm of length. At the laboratory, optical microscopy analyses were performed using a B-600TiFL microscope (Optika) to acquire morphological information of the yarns and fibers of the archaeological textiles, the state of conservation, the color and possible salt adhered coming from the sand and the original archaeological context (Fig. 3). Infrared reflectance spectra of the archaeological textiles were preliminarily acquired using a Bruker Alpha FTIR spectrometer equipped with an external attenuated total reflection module (ATR-FTIR) to confirm the origin of the fiber before FORS and SERS analysis.

Fiber-optics reflectance spectroscopy

A portable FieldSpect-4 (ASD Inc., Colorado, USA) available at LANCIC Laboratory in Mexico was used to acquire visible, NIR and shortwave near-infrared (SWNIR) reflectance and absorbance ($\log[1/R]$) spectra. This technique is not available in Chile until now. A non-contact probe was used, which is placed at 8 cm from the sample. A D65 illuminant provides illumination over the whole spectral range. The analysis area is about 3 mm in diameter and spectra were obtained with a 0.2 s integration time. In absorbance mode, data is processed with the Kubelka–Munk theory [94, 95]. Calibration was performed using a certified reflectance standard (AS-02035-000CSTM-SRM-990–362, ASD Inc).

For analysis purposes, the visible and NIR regions are presented together in a zone named visible-near infrared (VNIR). VNIR ranges from 300 to 1000 nm and SWNIR ranges from 1000 to 2500 nm. Inflection points in all spectra were determined using the first derivative of the spectrum, generated using the Origin Software (Origin-Lab Corporation, Northampton, USA).

SERS analysis

A washing protocol was developed to avoid particles adhered to the surface of the fiber from interfering with the dye-substrate interaction during SERS analysis. Textile samples of approximately 5 mm were placed in vials containing 0.01% v/v solutions of Triton™ X-100, a mild non-ionic detergent, and then stirred in a vortex. After washing, the samples were repeatedly rinsed with water under vortex stirring to remove the detergent. The



Fig. 2 Textiles analyzed in the present studies from Tarapacá-40 (2a to 2e) and Pica-8 (2f to 2 m)

Table 1 Description of textiles and synthesis of colorimetry, FT-IR, FORS and Raman analysis including archaeological context information for each textile studied






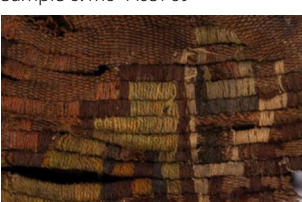
Details of textiles analysed	Site and period	Description	Color	FT-IR	FORS	Raman
Sample 1: M1- A05842 	Tarapacá-40 Context: SM'-T22 Formative period (Fig. 2a)	Blanket	Red orange Munsell 10R 5/10 L* a* b* 31.8 22.9 22	Proteinaceous fiber	Anthraquinone insect	No Result
Sample 2: M2- A04024 	Tarapacá-40 Context: SM-T22 Formative Period (Fig. 2b)	Headdress	Red orange Munsell 10YR 5/8 L* a* b* 35 31.6 23.3	Proteinaceous fiber	Anthraquinone insect	No Result
Sample 3: M4- A05823 	Tarapacá-40 Context: SM'-T52 Formative period (Fig. 2c)	Headdress	Red orange Munsell 10R 5/12 L* a* b* 31.5 27.5 23	Proteinaceous fiber	Anthraquinone, possible cochineal	Anthraquinone
Sample 4: M5- A05909 	Tarapacá-40 Context: SM'-T75 Formative period (Fig. 2d)	Bracelet	Brown Munsell 7.5R 4/8 L* a* b* 21.3 24 11.1	Proteinaceous fiber	Anthraquinone, possible cochineal	Carminic acid
Sample 5: M19- A05859 	Tarapacá-40 Context: SL-T8(δ) Formative period (Fig. 2e)	Blanket	Red Munsell 7.5R/4.8 L* a* b* 22.2 20.4 11.8	Proteinaceous fiber	Posible alizarin	Anthraquinone
Sample 6: M6- A05769 	Pica-8 Context: Sector A, Tumb 15 Late Intermediate period (Fig. 2f)	Tunic	Green Munsell 5GY 5/2 L* a* b* 39.4 – 0.1 10.8	Proteinaceous fiber	–	Indigoide

Table 1 (continued)










Details of textiles analysed	Site and period	Description	Color	FT-IR	FORS	Raman
Sample 7: M8- A05765 	Pica-8 Context unknown Late Intermediate period (Fig. 2g)	Tunic	Blue Munsell 2.5B 4/2 L* a* b* Not measured	Proteina- ceous fiber	–	Indigoide
Sample 8: M9- 05,765 	Pica-8 Context unknown Late Intermediate period (Fig. 2g)	Tunic	Green Munsell 10Y 4/4 L* a* b* 31.3 2.7 16.4	Proteina- ceous fiber	–	Indigoide
Sample 9: M10- A05765 	Pica-8 Context unknown Late Intermediate period (Fig. 2g)	Tunic	Green Munsell 5GY 2.5/1 L* a* b* 33.4 6.9 14.7	Proteina- ceous fiber	–	Indigoide
Sample 10: M11- A05751 	Pica-8 Context unknown Late Intermediate period (Fig. 2h)	Loincloth	Red Orange Munsell 2.5 YR 4/8 L* a* b* 33.7 21.2 18.9	Proteina- ceous fiber	–	Carminic acid
Sample 11: M12- A05751 	Pica-8 Context unknown Late Intermediate period (Fig. 2h)	Loincloth	Green Munsell 7.7GY 3/2 L* a* b* 30.6 3.2 9.6	Proteina- ceous fiber	–	Indigo
Sample 12: M13- A05751 	Pica-8 Context unknown Late Intermediate period Figure 2h)	Loincloth	Green Munsell 2,5GY 6/2 L* a* b* 45.0 1.0 19.1	Proteina- ceous fiber	Indigoide	Indigoide

Table 1 (continued)

Details of textiles analysed	Site and period	Description	Color	FT-IR	FORS	Raman
Sample 13: M14- A05749 	Pica-8 Context: Sector D, Tumb 1 Late Intermediate period (Fig. 2i)	Tunic	Red Munsell 10R 4/6 L* a* b* 24.5 24.4 11.1	Proteina- ceous fiber	Alizarin	Alizarin
Sample 14: M17- A03844 	Pica-8 Context: SF, T1 Late Intermediate period (Fig. 2j)	Tunic	Red Munsell 10R 4/6 L* a* b* 23.3 16.1 11.0	Proteina- ceous fiber	–	Carminic acid
Sample 15: M18- A03844 	Pica-8 Context: SF, T1 Late Intermediate period (Fig. 2j)	Tunic	Blue Munsell 7.5GY 3/2 L* a* b* 18.9 -1.3 2.2	Proteina- ceous fiber	–	Indigo
Sample 16: M22- A05743 	Pica-8 Context: SI, T2 Late Intermediate period (Fig. 2k)	Tunic	Brown Munsell: 5YR 3/2 L* a* b* 24.4 4.1 6.2	Proteina- ceous fiber	–	No Result
Sample 17: M23- A05743 	Pica-8 Context: SI, T2 Late Intermediate Period (Fig. 2k)	Tunic	Green Munsell 2.5GY 3/2 L* a* b* 22.2 0.7 4.2	Proteina- ceous fiber	–	Indigo
Sample 18: M27- A05768 	Pica-8 Context unknown Late Intermediate period Figure 2l)	Tunic	Green Munsell: 10GY 4/2 Colorimetría L* a* b* -	Proteina- ceous fiber	Indigoide	Indigoide

Table 1 (continued)

Details of textiles analysed	Site and period	Description	Color	FT-IR	FORS	Raman
Sample 19: M28- A05768 	Pica-8 Context unknown Late Intermediate period (Fig. 2l)	Tunic	Yellow Munsell: 10R 3/2 Colorimetría L* a* b* -	Proteinaceous fiber	–	Indigo
Sample 20: M29- A05685 	Pica-8 Context: SD, T56 Late Intermediate period (Fig. 2m)	Tunic	Brown Munsell: 10R 4/8, Colorimetría L* a* b* -	Proteinaceous fiber	Alizarin	Anthraquinone
Sample 21: M30- A05685 	Pica-8 Context: SD, T56 Late Intermediate period (Fig. 2m)	Tunic	Yellow Munsell: 10R 4/8 Colorimetría L* a* b* -	Proteinaceous fiber	–	Alizarin
Sample 22: M31- A05685 	Pica-8 Context: SD, T56 Late Intermediate period (Fig. 2m)	Tunic	Brown Munsell: 5YR 2.5/1 Colorimetría L* a* b* -	Proteinaceous fiber	–	No Result

effectiveness of the washing procedure was verified by optical microscopy and scanning electron microscopy (data not shown).

Gold nanoparticle substrates for microSERS measurements were prepared by chemical reduction with sodium citrate using the method described previously [96, 97]. In particular, 0.1 mL of HAuCl_4 solution (4%, w/v) is added to 40 mL of triple-distilled water, then 1 mL of trisodium citrate solution (1%, w/v) is added dropwise with stirring. The resulting mixture is boiled for 5 min.

SERS spectra of samples were recorded with a Raman Renishaw InVia Reflex apparatus, equipped with the 532, 633, and 785 nm laser lines, a Leica microscope, and an electrically cooled CCD detector. The instrument was calibrated using the 520 cm^{-1} line of a Si wafer and a $50\times$ objective. Its resolution was set to 4 cm^{-1} and 1–10 scans of 10–50 s each were averaged. Spectra were recorded in the $200\text{--}1800\text{ cm}^{-1}$ region. The laser

power was set between 10 and 100 mW. Spectral scanning conditions were chosen to avoid sample degradation and photodecomposition and the 785 nm laser line was used. Data were collected and plotted using the programs WIRE 3.4, GRAMS 9.0, and OriginLab Pro 2016.

Results of colors characterization

All analyses performed on fiber samples present similar characteristics and correspond to animal keratin (data not shown). FTIR results confirmed that all the fibers are of proteinaceous origin [98, 99], likely animals from the Camelidae subfamily (*Lama* spp. or *Vicugna* spp.) as previously interpreted by macroscopic identification [28, 41]. The colorimetric analysis revealed the use of a wide range of colors and hue variations: red, red–orange, yellow, brown, green, and blue, combined with naturally colored fibers (Table 1), highlighting the great polychromy of textiles from the Tarapacá region.

FORS analysis of the fibers suggested the presence of anthraquinones of both vegetal and animal origin for the red fibers, as well as indigo on the green ones. The FORS spectral features of alizarin and cochineal, among other red dyes, have been previously reported [100–103]. Alizarin and other similar red dyes from vegetable origin show apparent absorption maxima at 505–510 and 540 nm, while for cochineal those are red shifted towards 520–525 and 555–560 nm, leading to differentiating both anthraquinones (Fig. 4a, b). In our case, those apparent absorbance maxima are barely present on the spectra of the red samples, probably due to the combination of two factors: the degradation of the dye over time and the small sample size. The non-contact FORS probe used has an analysis area of 3 mm in diameter and the fibers studied are only about 1 mm thick, hence, part of the signal acquired originated on the sample support, instead of the fiber itself. However, the first derivative of the reflectance has proven to be more sensitive for the identification of madder and cochineal-based dyes [100], due to the presence of inflection points at 496–503 nm and 533–545 nm for cochineal, while for alizarin they are at 486–490 nm and 520–524 nm. Although we are only referring to alizarin, it is worth pointing out that purpurin is often found in the same vegetable sources and the FORS spectra of both dyes are similar [103]. Therefore, by this analytical technique we would only be able to distinguish plant-based anthraquinone dyestuffs from the anthraquinones with animal origin.

With the information from the reflectance and the first derivative spectra, it can be suggested that cochineal was used to dye the Samples 1 and 2, while a plant from the genus *Galium* spp. or *Relbunium* spp. is the source of the plant-based dye present on Sample 4 (Fig. 4a, b, respectively; Table 1). However, other animal-based anthraquinone dyes, such as kermes or Armenian cochineal, cannot be discriminated from the American cochineal by FORS alone [102, 103] and the assumption that the animal-based anthraquinone dye found on the analyzed fibers is in fact cochineal is supported by historical context, since this is the only red anthraquinone of animal origin found on previous studies on the Andean area for pre-Columbian collections [15, 17, 18, 21] and that was still used during colonial times [105, 106].

In the case of the green samples (Samples 12 and 18), FORS results suggest the presence of indigo (Fig. 4c), from the apparent absorption maxima at 648 nm and the inflection point at 717 nm, in agreement with the spectra of indigo references and the results of FORS analysis of Mexican codices [107] and polychrome ceilings [108].

SERS has proven to be a powerful technique for the analysis of colorants in textiles [61, 65, 109–113]. Most of these works used silver nanoparticles, while gold nanoparticles are equally useful [114, 115]. In our analyses, the best results were obtained using gold nanoparticles and a 785 nm excitation laser. The optical microscopy images of the fibers, covered with nanoparticles and later dried, showed that the textile samples have an adherence to the nanoparticles

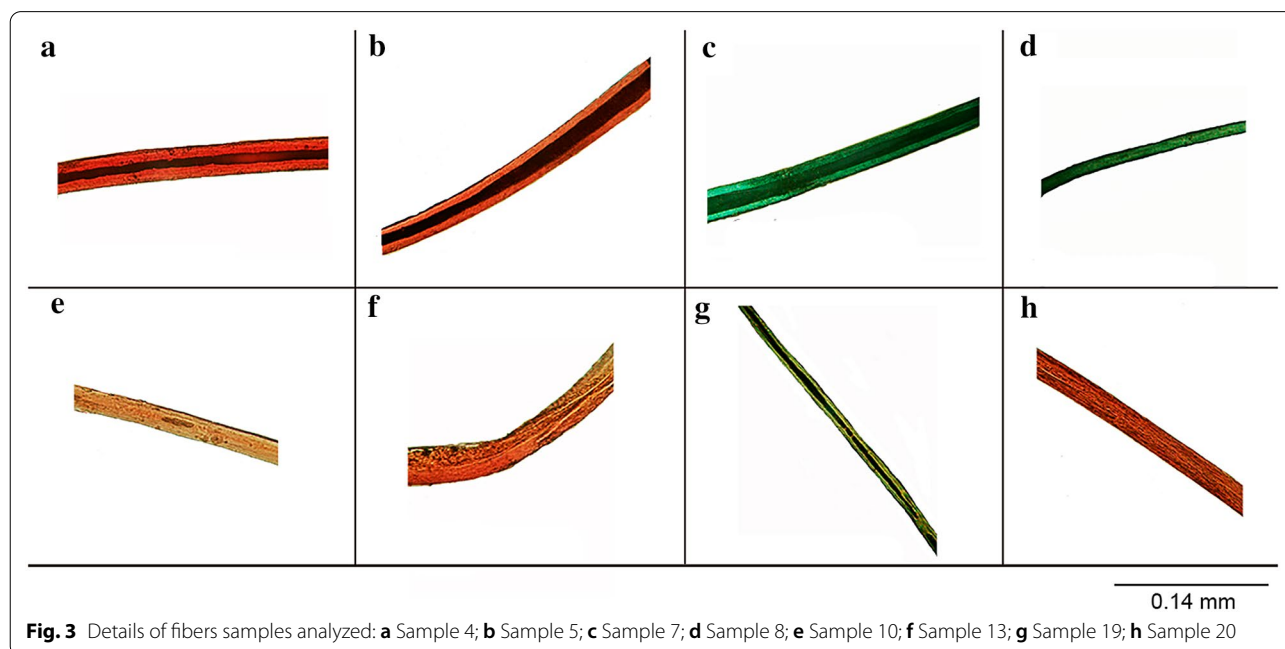


Fig. 3 Details of fibers samples analyzed: **a** Sample 4; **b** Sample 5; **c** Sample 7; **d** Sample 8; **e** Sample 10; **f** Sample 13; **g** Sample 19; **h** Sample 20

as previously described [112]. In our case, using fibers already washed with Triton™ X-100, we observed areas with agglomerates of the nanoparticles, while others showed a thin and uniform layer of AuNPs. The latter led to better-defined spectra, with a high signal-to-noise ratio, while photodegradation was avoided.

Alizarin, carminic acid and indigo were identified on the samples (Table 1). In the case of alizarin, Cañamares and collaborators carried out a complete theoretical analysis and SERS experiments [116], while the results reported by Chen and co-authors were registered after the extraction of the dye from the textile by acid hydrolysis [110]. In our case, the spectra were acquired directly from the dye adhered to the fiber.

The SERS measurement obtained for Sample 13 (Fig. 5a) shows a complex spectrum of the dye-mordant-fiber (DMF) molecular system where groups of bands are consistent with signals reported for alizarin [117, 118]. The SERS spectra provide additional information regarding shifts in wavenumbers, changes on their relative intensities are fundamentally the presence of new bands that cannot be observed when analyzing isolated molecules. These spectral features may be related to a certain arrangement and orientation of the dyes due to the interaction between NPs/fibers or NPs/dyed fibers. According to SERS selection rules, the intensity increases or decreases when the α_{zz} component of the polarizability of the analyzed vibrational mode is parallel or perpendicular to the excitation beam, respectively. Band shifts are related to the electronic redistribution in the vicinity of the atoms involved in the interaction. This concept supports the chemical or charge transfer contribution to the mechanism of enhancement of the Raman signals [119].

The spectral changes discussed above are present in the spectrum of Fig. 5a (see spectra (a) in Additional file 1: Appendix A). The weak band around 1647 cm^{-1} can be attributed to the coupled $\nu\text{CO}/\nu\text{CC}$ vibrational modes. The coupled vibrational mode $\text{ip}\delta\text{CH}_3/\text{ip}\delta\text{COH}/\nu\text{CC}$ is observed at 1475 cm^{-1} as a shoulder and with medium intensity, although it has been described before as a high-intensity mode [116, 117]. This difference may be because this molecular moiety is vibrating inclined in relation to the surface.

A commonly reported high-intensity characteristic band is present at 1258 cm^{-1} [120, 121]. It is associated with coupled $\nu(\text{CO})/\nu(\text{CC})/\delta(\text{CCC})$ modes and is included among a group of high-intensity bands in the $1460\text{--}1200\text{ cm}^{-1}$ interval. The signal at 1078 cm^{-1} , attributed to a CC stretching in proteins, is not reported

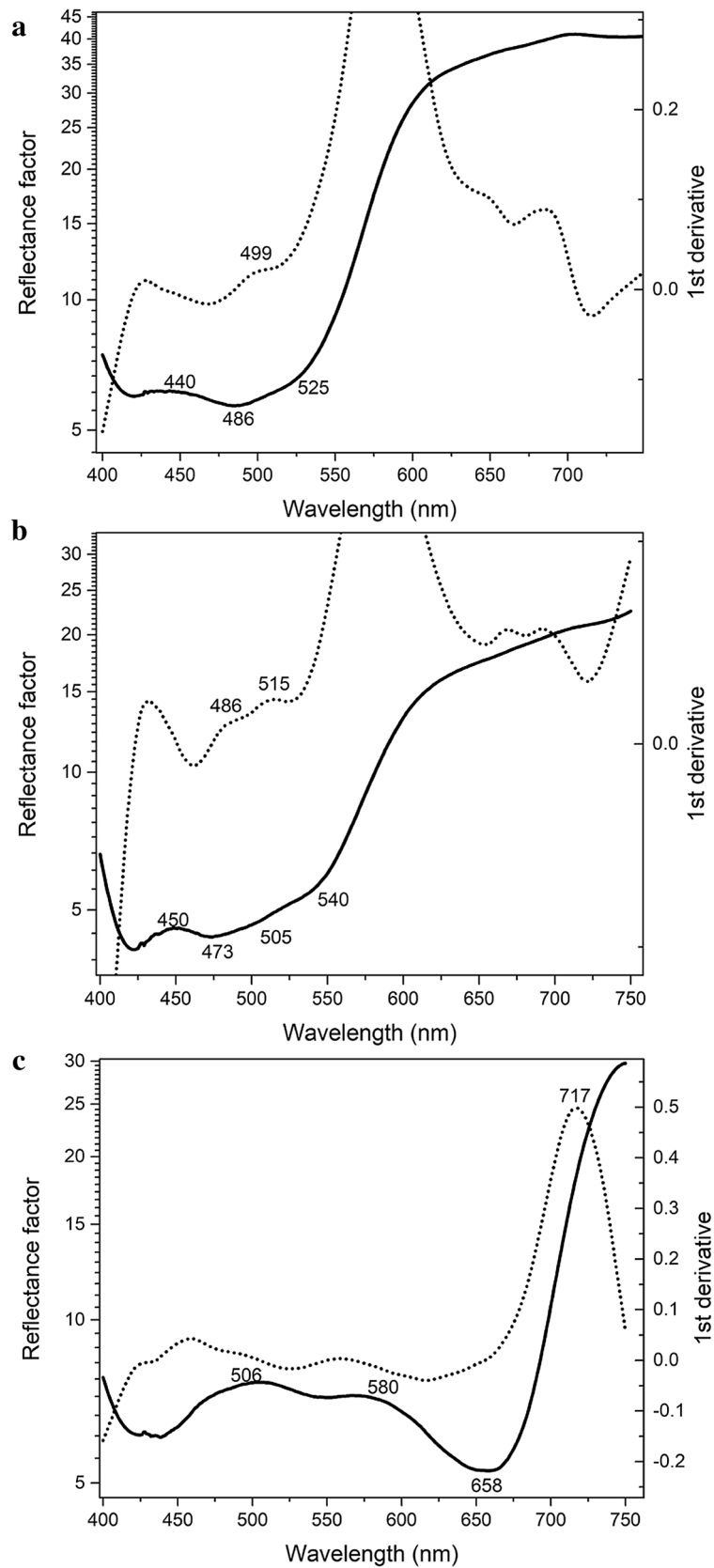
for alizarin [116–118]. Owing to our experience in the vibrational analysis of proteins and according to the literature [122–125], this band may be related to the protein structure of the animal fiber. Vibrations of the peptide backbone in proteins are usually associated with three main regions of the Raman spectrum [126]. We expect to find the vibrations of the backbone skeletal stretch region at $870\text{--}1150\text{ cm}^{-1}$, which arose from the $\text{C}\alpha\text{-C}$, $\text{C}\alpha\text{-C}\beta$, and $\text{C}\alpha\text{-N}$ stretching coordinates. The extended amide III region, expected at $1230\text{--}1340\text{ cm}^{-1}$, is mainly involved in the in-phase combination of the N–H in-plane deformation with the $\text{C}\alpha\text{-N}$ stretch, with mixing among the N–H and the $\text{C}\alpha\text{-H}$ deformations. Finally, the C=O stretch gives rise to the amide I region in the range of $\sim 1630\text{--}1700\text{ cm}^{-1}$ [126]. In our case, some amino acid bands were also observed in the spectrum of the DMF complex, as is the case for the proline bands at 956 or 858 cm^{-1} . A complete vibrational assignment is given in Table 2.

The SERS vibrational analysis of carminic acid was performed based on our own SERS data and those reported for the pure dye, isolated from cultural heritage samples or as part of a more complex molecular system [116, 118, 127]. As in the case of alizarin, Cañamares et al. carried out a complete theoretical and experimental analysis using analytical grade carminic acid [116], while the results published by Pozzi et al. account for the effect of sample pretreatment with vapours of hydrofluoric acid, before the SERS analysis [111].

Cochineal was identified in Sample 4 and its SERS spectra (Fig. 5b) show bands of both carminic acid and protein [116, 118, 127] (see spectra (b) in Additional file 1: Appendix A). The intense band at 1582 cm^{-1} is attributed to νCC of an aromatic ring, while Cañamares et al. found this band to be of medium intensity and assigned it to a coupled $\nu(\text{CC})/\delta(\text{COH})/\delta(\text{CH})$ mode. As discussed for alizarin, the differences in the intensity may be related to the orientation of this vibrational mode, parallel to the excitation beam. It is also described that this signal is accompanied by the bands at 1472 and 1322 cm^{-1} , associated with modes $\text{ip}\delta\text{CH}_3/\text{ip}\delta\text{COH}/\nu\text{CC}$ and $\delta\text{COH}/\delta\text{CC}$, respectively. The band at 1322 cm^{-1} is particularly interesting since it has been reported as a strong band by Garrido et al. [128], while Cañamares and collaborators reported it as a medium intensity band [116]. In both cases is broadband that encloses a group of bands in the $1380\text{--}1300\text{ cm}^{-1}$ interval. Moreover, this band could be influenced by the amide III vibration described for proteins [123, 124]. Bands near 1397 , 1076 , 956 and

(See figure on next page.)

Fig. 4 FORS spectrum: **a** Sample 1: anthraquinone, **b** Sample 13: anthraquinone, and **c** Sample 18: indigo



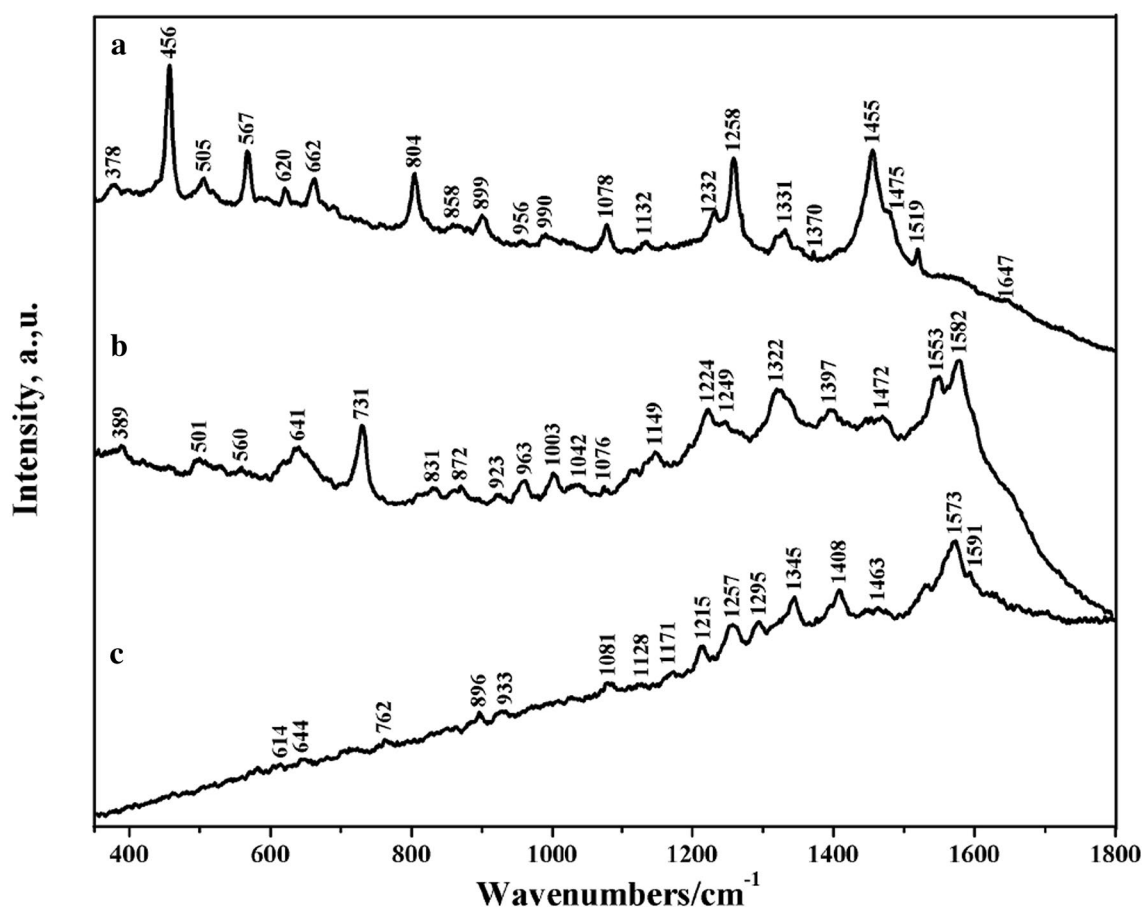


Fig. 5 SERS spectrum: **a** Samples 13: alizarin, **b** Sample 4: carminic acid, and **c** Sample 11: indigo

858 cm^{-1} suggest the presence of the proteinic structure of the animal fiber, as reported before by our group in the study of isolated proteins or as part of a complex matrix [122–124]. Other bands that can be attributed to the dye are located at 505 and 456 cm^{-1} . A complete vibrational assignment is given in Table 2.

In some cases, we were not able to differentiate alizarin from carminic acid, because a band group can be present in the spectral region 1200–1600 associated to anthraquinone structure present in both molecules [116]. This overlapping of the spectrum can be associated with changes in pH and the similarity of both dyes' structures.

For the vibrational analysis of indigo, found in Sample 11 (Fig. 5c), we used our SERS data and the results obtained from other researchers [61, 104, 129–131] (see spectra (c) in Additional file 1: Appendix A). A strong band is observed at 1573 cm^{-1} (ring stretching mode), with a shoulder at 1591 cm^{-1} related with ν_{CC} , ν_{CO} and in-plane NH deformations (δ_{NH}) modes (Fig. 6c). The bands at 1345 and 896 cm^{-1} can be assigned to coupled vibrations involving the stretching and bending

vibrations of the six-member ring. C-H deformations are responsible for the bands at 1463 and 1257 cm^{-1} , and the five- and six-member ring vibrations produce bands at 762 and 644 cm^{-1} . A complete vibrational assignment is given in Table 2.

The SERS spectra of sample 19 suggested the presence of indigo (Table 1). Despite being usually associated with blue or green hues, some indigo derivatives give yellow tones. This is the case of leucoindigo, whose Raman and SERS spectra have already been reported by Fiedler et al. [132] and Celis et al. [69], respectively. Both studies show the characteristic band of indigo, centered at 1573 cm^{-1} , along with other vibrational signals common to indigo and leucoindigo. Although leucoindigo is easily oxidised when exposed to air, Celis and co-authors suggest the formation of a metal complex as a possible explanation of its stability in the dyed threads [69]. In the case of Maya mural painting, Vandenebeele et al. [133] reported the presence of indigo in blue, green and yellow fragments. This was later addressed by Domenech et al. in 2013 [134], whose main findings pointed to the

presence of dehydroindigo, another yellow derivative of indigo. Recently, the same group revisited the subject and discussed evidence that supports their previous results [135].

Discussion

All colors identified in our study suffered numerous alterations during the years, which undoubtedly modified their original hue and shade. The variation in shade, saturation, and shine in the same and/or different yarn can also be related to the degradation of the dye, since all the analyzed textiles belong to burial contexts (Table 1), where they were used as mortuary clothing and/or deposited as burial offerings. Several variations on the shade (Sample 22) and color saturation for a single yarn (Sample 10) can be attributed to changes that took place after the chemical interaction of the dye with the body fluids, during the decomposition of the buried individual. However, we cannot rule out the occurrence of different initial preparations for dyeing, associated with the use of varied aqueous media and/or the inclusion of mordants looking for better fixation of the color on the fibers [10, 54, 66–68, 70]. Thus, the observed differences can be the consequence of technological factors inherent to the dyeing process (fermentation time, length of the exposure of the yarn to the mordants, temperature and humidity during the process, among others), which yield numerous alternatives and combinations amid them, as well as provoked by external agents and factors following the use of the textiles as burial offerings.

We were able to demonstrate the usefulness and expeditiousness of the simultaneous application of different analytical techniques to the study of Andean textiles. FORS was just recently applied to textiles from this region [65] but has proven very suitable for preliminary characterization of the dyes if the proper references are available. In our case, the analysis was hampered by the fact that they were performed on small fragments of the dyed fibers, after sampling. When possible, it is always advisable to carry out the FORS measurements directly on the textile, using the non-contact probe. In this way, one may take advantage of both the portability and non-destructive character of the technique and acquire multiple spectra from different areas of the same textile, looking for more precise identification of the dyes present. On the contrary, SERS is a potent tool for the characterization of textile dyes on small fragments of fibers and with relatively short analysis times, for a big number of samples. At this stage, we decided not to pursue the identification of mordants, in part, due to a cleaning and fumigation protocol applied to the textiles in 2015, which could interfere with the results. Also as indicated by Wallert and Boytner, soil and body remain can

Table 2 SERS bands (cm⁻¹) in the range 350–1800 cm⁻¹ of alizarin, carminic acid and indigo identified in Samples 13, 4 and 11, respectively and the most probable bands assignment

Sample 13	Sample 4	Sample 11	Assignment
1647vw			uCO/ uCC
		1591sh	uCC/ uCO/ ipδNH
	1582vs	1573s	uCC ring
1519w	1553		uCC ring
1475sh	1472w	1463w	ipδCH ₃ /ipδCOH/uCC; δCH
1455vs			uCC/δCOH/ δCH
1370vw	1397w		uCC/δCH
		1345m	u(CC)/δ(CCC)
1331vw			uCC
	1322s		δCOH/δCC; Amide III
		1295w	ring6 str., def
1258vs		1257m	uCO/ uCC/ δCCC; ρC _{Hiph, asym} /uCN/ uCC _{ring6} /uCC _{ring5}
	1249w		δCH
1232w	1224m	1215w	δCH/δCCC; δCH
1163vw		1171w	uCC/δCH
	1149w		uCC/uCN; δCH
1132m		1128w	δNCH Pro
1078vw	1076w	1081mw	uCC/δCOH; uCC prot
	1042w		uCN Pro
	1003		Breathing ring Phe
956vw	963m		ρCC/δCCC; skeletal Pro
	923w	933w	uC-COO ⁻
858vw	872w	896vw	ρCH ₃ /δCCC; uCC ring Pro
804s	831		uCC skel
		762vw	uCC ring
	731vs		ρ(CH ₃)/δCCC
662m	641s	644vw	γCO/ γCH/γCOH/τ(CCCC); NCC def
620 mw		614vw	SkelVibration
567m	560w		Skel Vibration
505w	501w		Skel Vibration
456 s			Skel Vibration
378mw	389w		Skel Vibration

Band description: w weak, vw very weak, m medium, mw medium weak, s strong, vs very strong. str., stretching, def., deformation, ip in plane, op out plane, breath. breathing, skel. Skeletal, ring6 six-member rings, ring5 five-member rings, prot. protein, sh shoulder, Pro proline, Phe phenylalanine

Vibrational modes description: v stretching, δ in the plane bending, γ out plane bending, ρ rocking, τ torsion

contaminate textile, and results obtained by elemental analysis for example can be ambiguous [54].

In general terms, FORS and SERS allowed the identification of red, orange, yellow, blue, and green dyes. For a set of samples, the identification of alizarin using both techniques were very precise, while for others, although the FORS signals are very weak, it was possible to identify the presence of alizarin or carminic acid (Table 1:

Samples 3 and 20). For this second group of samples, the dyes identification by SERS is troublesome, due to the complexity of the spectra acquired. Some of the SERS bands observed can be assigned to alizarin or carminic acid, indistinctly, as opposed to FORS. However, the observed bands are characteristic of anthraquinones, the common molecular structure of both alizarin and carminic acid (Table 1: Sample 4).

Our colorimetric, FORS and SERS results show that the different colors and their shade variations can be achieved from natural extracts, both from animal and vegetal origin. For the reds and its varied shades, including a few orange and brown fibers, we detected the use of anthraquinones from animal origin, carminic acid, from an extract of the cochineal insect (*Dactylopius coccus coccus*), as well as alizarin, commonly found on the roots of a plant from the family of Rubiaceae, *Galium* spp. or *Relbunium* spp., depending on the taxonomic classification, used [14, 18, 21, 66]. In the blue, green and one yellow (Sample 19) samples, we found indigo or indigo-like molecules, known as indigoids, obtained from indigo-producing plants [13, 16, 18, 21, 66]. However, we cannot discard that other dyes were mixed with indigo to modify hue and shade as observed in Paracas textiles [53, 66].

Finally, the results reached for textiles from the Tarapacá region associated with the Formative period allowed detecting the use of carminic acid and alizarin, dyestuffs that will continue to be used during Later Intermediate period (Table 1). In chronological terms, it is interesting to confirm that the same dye technology was preserved for almost 2400 years. It is also interesting to observe that the same colorants can be used for different types of textile garments and ornaments. When comparing our results with previous molecular identification of red dyes in neighboring regions, we found that in the north in southern Peru purpurin from a plant from *Relbunium* species and carminic acid from cochineal were reported for the Late Intermediate period (1000–1450 A.D.) [54]. The use of cochineal (carminic acid) was also recently reported in Formative textiles from Arica locality to the north of Tarapacá region studied, but without more precision to archaeological context [73]; while only purpurin was identified at San Pedro de Atacama to the eastern south, for the Middle (600–1000 A.D.) and Late Intermediate periods (1000–1450 A.D.) [63]. In the case of the Tarapacá region, only alizarin and carminic acid have been continuously used for a long time. If this can be confirmed we could identify some specific and different knowledge concerning the dye manufacturing process and dyeing cultural tradition, as each region demonstrates the use of different dye molecules (carminic acid, alizarin and purpurin) probably from different plant origins.

The local origin of dyeing plants

Niemeyer and Agüero [63] suggested that the *Relbunium* spp. found in the San Pedro de Atacama textiles came from northwest Argentina, based on the strong trade relationship between the localities in the area. Nevertheless, the authors did not consider the possibility that the raw materials may also have its origin on the Pacific coast, where specimens of *R. corymbosum* have been registered, locally identified as *G. corymbosum* [21, 136–138], as well as other *Galium* species, principally *G. corymbosum* and *G. aparine* (distributed along the whole coastline of northern Chile), *G. diffusoramosum* (Taltal) and *G. hypocarpium* (Paposo) [137–145].

In relation to indigo, for its part, the main sources in South America are plants from the genus *Indigofera* (Fabaceae), *Eupatorium* (Asteraceae) and *Yangua* (Bignoniaceae), of which only the first two are found near our study area [21]. Although *Indigofera* species are typically found in Perú and Northwestern of Argentina [21, 146], there are also records of *I. suffruticosa* specimens in the Azapa Valley, near Arica, as well as in the Chaca area on the Vitor ravine, to the north of Tarapacá region [147, 148]. Specimens of *I. truxillensis* have also been found in regions north of Arica, and Tarapacá [140, 149]. Meanwhile, the only native *Eupatorium* species in the Atacama Desert are *E. glechonophylla* (also known as *Ageratina glechonophylla*) and *E. salvia*. The first is distributed in the coast (0–200 m.a.s.l.) from Antofagasta to the south, almost 400 km of distance from Tarapacá locality [137], mainly in Paposo locality [136]. *E. salvia* is also found along the coast further to the south, with a northernmost limit in the Coquimbo region, more than 1000 km to the south of our region study [137].

Considering this phytogeographical distribution of dye plants in the Atacama Desert, Niemeyer and Agüero's proposal should be re-evaluated. Because it is a fact that pre-Colombian communities in the Atacama coast were in close contact with this inland oasis, as well as with other groups that inhabited the inland valleys territories since remote times [150–155]. The traditional Andean model has placed in a prominent position the trade with foreign regions and the products and technologies from abroad, from territories beyond the Andes mountain to the east, while to the coastal gatherer-hunters have been assigned a passive role in the regional economies. In that sense, given the abundance of plants of *Galium* species along the northern Chile coastline, this could have been also a possible source of direct supply or by an exchange of dyestuffs, for the textile production. This possible hypothetical link with the coast becomes even more plausible when we consider that several vegetable sources of indigo are also found on the littoral, including *E. glechonophylla* and *A.*

glechonophylla. Also, we cannot forget that brominated indigo can be extracted from an extremely popular marine mollusc from the coast of the Atacama Desert, the *Concholepas concholepas* [21], a potential animal source of dye supply that has not yet been considered in archaeological studies of the region. Further efforts for the elaboration of local references are absolutely needed.

Archaeological studies on textile dyes in the Atacama Desert have also scarcely considered the available ethnohistorical and ethnographic information, looking rather for substances and species popular in other neighbouring regions. This trend generates a hiatus in local information, since not all Andean or South American communities opted for the same technical solutions when it came to coloring their fabrics.

As an example, for the San Pedro de Atacama area, the naturalist Rodolfo Philippi pointed out in 1854 that “for the blue, you can use añil [or indigo], for the red grana, for the yellow and indigenous plant, called fique, which I have not seen. Grana is a kind of cochineal that is brought from the Otra Banda provinces [Northwestern Argentina], mainly from Santiago del Estero” [156]. In an ethnographic study from the mid-twenty century, Grete Mostny and co-workers recorded that the people from Peine village used alum as a mordant for dyeing textiles, and the color came from different local plants, such as *monte verde*, *chilca* and *mocaraca* for the green, *tícara* for the brown, *algarrobo* for mustard hues and *sacha-uva* for purples [157]. Munizaga and Gunckel, in a similar contemporary study, carried out at the Socaire village, also acknowledged the use of *tícara* (*Krameria iluca*), *romasa* (*Rumex patientia*) and *monte verde* for dyeing yellow textiles [158]. Finally, Villagrán and Castro, on a research with an extensive geographic scale, identified the use of *molle* (*Schinus molle*), *algarrobo* (*Prosopis alba*), *monte verde* (*Krameria lappacea*), *pingopingo* (*Ephedra andina*), *kopa* (*Artemisia kopa*), *Siput’olas* or *pulikás* (*Parastrephia* species, including *P. lepidophylla*, *P. quadrangularis* and *P. teretiuscula*) and male *tíkara* (*Ambrosia artemisoides*) for dyeing purposes, each one of them with a particular color and shade, depending on their preparation and combination [159]. We need to broaden our knowledge about the use of local plants to produce dyes, to later generate useful references for chemical analysis as it has been done in different regions of the Central Andes [17–21, 160].

Conclusions

The results presented here show that the textiles from Tarapacá-40 and Pica-8 cemeteries from the Atacama Desert were dyed with substances that until now were

not found near the localities. Its closest supply is, on the other hand, at approximately 100 km, both on the Pacific coast and in the valleys to the north and Northwestern Argentina to the southeast. However, the local populations of the Pica and Tarapacá valleys lived in close social and economic ties with those inhabitants settled in the supply areas of these plants and insects with dyeing potentials [87, 91]. Thus, the color technology from the Tarapacá pre-Columbian textiles must have depended above all on an extensive social network and the association with different and distant communities. Extra local relations constructed not just for dyes procurement, but also for the other raw materials needed such as fibers. The identification of cotton was also confirmed in our preliminary recognition of the complete textile collection studied. Unfortunately, the advancement of regional archaeology does not yet make it possible to confirm how and where textiles were produced and how dyed fibers were obtained. At this moment, we cannot precise if they obtained only the dyestuffs and completed locally the process of dyeing fibers, or balls of dyed yarns and they wove the different textile garments, or finally, they obtained the complete woven textile pieces by exchange from other localities.

In addition, archaeological studies dealing with textile dyes in the Atacama Desert have paid little attention to the available ethnohistorical and ethnographic information, looking instead for substances and species popular in neighboring regions. This has led to a lack of information about local dyeing technologies since not all the Andean or South American communities had probably chosen the same technical solutions when it comes to textile dyeing. The brief ethnohistoric and ethnographic review presented in the discussion section demonstrates the local availability of a wide variety of plants with dyeing capabilities in the Atacama Desert. However, very few of them have been studied to identify chemical markers that can be traced to pre-Columbian objects. Meanwhile, archaeology continues to look for the most popular dyeing plants used outside the region.

Considering these shortcomings concerning the reference samples, the textiles from the Tarapacá region are an excellent evidence of deep knowledge regarding dyes and dyeing techniques, about botanical and insect species available for these purposes, as well as a particular dexterity for the construction of complex polychrome textiles, conceived before the fabrication. The number and size of the textiles deposited as offerings, their shapes, and designs points to the existence of specialists, committed not only to the fabrication of the textiles but also to the previous stages of acquisition and conditioning of the fibers, in addition to the procurement and

elaboration of the materials used to prepare the solutions or dyestuffs where the fibers were immersed.

So, to conclude, these results need to be complemented and reviewed regarding the production processes: on the one side to precise the nature of the fiber raw materials and their possible provenance (wool, cotton, etc.) and hence their domestication and exploitation; and on the other side, the nature and localization of the vegetable and animal resources from where the dyes were extracted and produced. This paper constitutes just a first approach to this topic in the Atacama Desert.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-021-00538-9>.

Additional file 1: Appendix A. SERS spectrum: (a) Sample 30: alizarin, (b) Sample 17: acid carminic, and (c) Sample 12: indigo.

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Authors' contributions

MS: conceptualization, investigation, in situ analyses, formal analysis, writing original draft, editing, funding acquisition, project administration; CL: investigation, in situ analysis, funding acquisition, project administration; JC-V: laboratory analyses, formal analysis, visualization, writing; EC-G: formal analysis, visualization, writing original draft, editing; SG: in situ analyses, laboratory analyses; MAM-R: in situ analyses, laboratory analyses; BB: investigation, formal analysis, writing original draft; JLRS: investigation, supervision, editing original draft, funding acquisition, project administration; All authors read and approved the final manuscript.

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Availability of data and materials

Data is available by contacting the corresponding author. After reviewers' comments supplementary data (Supplementary Material-Appendix A) is included in this final version.

Declarations

Competing interests

The authors declare that they have no competing interests.

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