Dyes used in pre-Hispanic textiles from the Middle and Late Intermediate periods of San Pedro de Atacama (northern Chile): new insights into patterns of exchange and mobility

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Abstract

Pre-Hispanic Andean textiles constitute the longest continuous textile record in the world, their structure and design being one of the most significant markers of group identity in Andean populations. Since the Late Formative Period (ca. 100–400 AD), the region around San Pedro de Atacama (SPA) in the Atacama desert of northern Chile has been part of a complex and extensive network of interacting polities through which raw materials, agricultural products, goods, people and ideas circulated in the South-Central Andes. The archaeological record in SPA abounds with textiles from various cultures that participated in such network. A study of these textiles would allow intercultural as well as diachronical comparisons. Numerous studies on textiles found in SPA have focused on their technological and iconographic features. This work addresses the identification of the organic dyes employed in the manufacture of 38 textiles found in funerary contexts in SPA from the Middle (ca. 400–1000 A.D.) and the Late Intermediate periods (ca. 1000–1450 A.D.), using high performance liquid chromatography with a diode array detector (HPLC-DAD). Purpurin and not alizarin was found in all red dyed fibers and indigotin (IND) and indirubin (INR) in all blue dyed fibers. Natural sources of these dyes are exogenous to SPA; their importation into SPA lasted for nearly a millennium. A positive correlation was found between [IND]/[INR] concentration ratio and the altitude of the place where the fiber was presumably dyed. Overall, the results indicate that finished garments and also raw dyes and ready-to-use dyed fibers were imported into SPA from neighboring regions and that foreign weavers were possibly active at SPA.

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1. Introduction

Pre-Hispanic Andean textiles constitute the longest continuous textile record in the world (Cardon, 2007). Characteristics of textile structure and design provide one of the most significant markers to group identity in Andean populations, as shown by archaeological, ethnohistorical and ethnographical studies (Aguero et al., 1997, 1999, 2000; Cassman, 2000; Murra, 1962; Oakland Rodman, 1992; Wallace, 1975). The South Central Andes (Fig. 1) has been the area of development of a number of long-lasting pre-Hispanic societies. One such society occupied the region around San Pedro de Atacama (SPA) in the Atacama desert of northern Chile. As early as the Late Formative Period (ca. 100–400 AD), SPA had become part of a complex and extensive network of interacting polities through which raw materials, agricultural products, goods, people and ideas circulated in the South-Central Andes including the extreme north of Chile, the Pacific coast, the Bolivian altiplano and Northwestern Argentina (Berenguer, 2004; Berenguer and Dauelsberg, 1989; Llagostera, 1996, 2006; Núñez, 1996; Salazar et al., 2014; Tarragó, 2006). The archaeological record in SPA includes textiles from various cultures that participated in such network. Some of these textiles rank among the finest produced in the South Central Andes, with exquisite craftsmanship, unique designs and brilliant colors, and appear in a very good state of preservation on account of the extreme aridity of the region (Berenguer, 2004; Blanchette et al., 1990). A study of textiles from SPA would thus allow intercultural as well as diachronical comparisons.
Numerous studies on textiles found in SPA have focused on their technological and iconographic features (Agüero et al., 1997, 1999, 2000; Lindberg, 1963, 1967; Oakland, 1986a, 1986b, 1994; Oakland Rodman, 1992; Oakland Rodman and Cassman, 1995; Uribe and Agüero, 2001, 2004, 2005), and have led to their classification into styles, e.g., Tiwanaku, Bolivian Oriental valleys (BOV), La Aguada from Northwestern Argentina, and SPA (local) styles (Agüero, 2000, 2003, 2012). In this work, we have extended stylistic studies of SPA textiles to encompass raw materials used in their manufacture, thus subscribing the broader concept of style discussed by Chilton (2002), which considers the complete operative chain leading to the finished product, including the materials employed. The ample availability of fiber from camelids in SPA led us to focus the study on the dyes employed. The predominant colors in SPA textiles are shades of yellow, red and blue. Yellow shades usually arise from the use of carotenoid and flavonoid containing plant extracts. These two families of compounds are of widespread occurrence in plants; distinctive composition profiles in different plant species could be of potential diagnostic value to identify the plants of origin, provided that comparable chemical analyses of plant reference materials were available (Ferreira et al., 2004; Zhang et al., 2008). Unfortunately, this condition is not met by potential sources of yellow dyestuffs in South America. In contradistinction, dyes with shades of reds and blues come from a limited number of sources in pre-Hispanic South America (Cardon, 2007); hence, the identification of the dyes can lead in a straightforward manner to a small set of putative and related plant sources. In the present work, we have analyzed red and blue dyed fibers from pre-Hispanic textiles found in SPA. The dyes were extracted from the fibers and high performance liquid chromatography with diode array detection (HPLC-DAD) was used to separate the components of the organic extract and identify them by comparison of their retention times and UV—visible spectra with those of standard compounds. This methodology has been extensively applied in the study of organic dyes used in textiles (Degano et al., 2009; Rosenberg, 2008), including some from pre-Hispanic cultures of Peru (Degano and Colombini, 2009; Saito et al., 2003; Sousa et al., 2008; Wouters and Rosario-Chirinos, 1992).

2. Materials and methods

2.1. Objects studied

The basis for this study was a set of textiles from cemeteries at the different oases (or ayllus) of San Pedro de Atacama: Catarpe, Coyote, Quitor, Solcor and Solor. All textiles inventoried and stored in the textile deposit of the Museo R.P. Gustavo Le Paige s.j. were individually examined. From the ca. 550 textiles in the deposit, the 38 textiles chosen were all those which simultaneously contained well preserved red and blue dyed fibers and could be ascribed to the Middle or the Late Intermediate periods. Within the group selected, several forms of textiles were present (bags, embroidered basket, headbands, ritual cloth, mantles, tunics and fragments thereof), both in local and foreign styles (Table 1; Fig. 2).

2.2. Local and foreign textiles from SPA

Several studies form the basis upon which textiles have been assigned to styles (see for example: Agüero, 1998; Agüero et al., 1997, 1999; Cases, 1997; Conklin and Conklin, 1996–97; Llagostera, 1995; Oakland, 1986a, 1986b, 1991; Oakland Rodman, 1992; Rydén, 1956; Strömberg, 1956; Uribe and Agüero, 2001, 2004). In general, the style and hence presumed place of manufacture of the textiles was assigned on the basis of iconographical and technological features, contextual evidence of the tomb where they were found, and assignment to cultural period. Thus: i) Tiwanaku style textiles are weft faced and decorated with interlocked tapestry showing figures which have their referents in the Tiwanaku lithic sculpture; or are decorated with embroideries in cross knit loop stitch in side selvedges and openings creating similar icons, or warp faced decorated with stripes with the use of one continuous weft (Oakland, 1986a); ii) La Aguada style baskets (“tipas”) were made using an intercrossed and wrapped technique (Llagostera, 1995:11,13) with iconography depicting a feline or individuals throwing darts while tunics show iconography depicting a feline and a 2-headed snake, similar to those found in Aguada engraved ceramics and in a petroglyph in Catamarca, Northwestern Argentina (Llagostera, 1995:20); iii) SPA local style is characterized by rectangular warps with mords with satin stitch embroideries in side selvedges and openings. The stripes can be decorated by floating and transposed warps, always using multiple wefts. These attributes are shared with textiles from the El Loa region and Northwestern Argentina (Agüero, 1998, 2000, 2003, 2012; Agüero et al., 1997, 1999; Oakland Rodman, 1992; Uribe and Agüero, 2001, 2004); and iv) Bolivian Oriental valleys style shows similar iconographic designs as those of SPA style, using multiple wefts and transposed warps, and sometimes discontinuous warps and wefts. Additionally, while textiles woven at SPA used only camelid fibers, BOV textiles used mainly cotton, generally mixed with camelid fiber and even other local plant fibers.

2.3. Chronology of textiles from SPA

Chronology was determined mainly through correlation with the style of pottery occurring in the tomb where the textile was found (Agüero et al., 1997, 1999; Berenguer et al., 1986; Stovel, 2013; Tarragó, 1968, 1989) or based on dates for other contexts from the same archaeological site where the textile was found (Torres-Rouff and Hubbe, 2013); in the case of a few textiles, dates were available for elements of their funerary context (see Appendix).
Table 1

Textiles analyzed by high performance liquid chromatography with diode array detection (HPLC-DAD).

<table>
<thead>
<tr>
<th>Object</th>
<th>Site</th>
<th>Tomb/Mummy</th>
<th>Period</th>
<th>Style</th>
<th>Mean [IND]/[INR]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tunic</td>
<td>Quitor 2</td>
<td>T1983:15;#8</td>
<td>M</td>
<td>La Aguada</td>
<td>4.6</td>
</tr>
<tr>
<td>Embroidered basket</td>
<td>Solcor 3</td>
<td>T113</td>
<td>M</td>
<td>La Aguada</td>
<td>14.0</td>
</tr>
<tr>
<td>Bag (bolsa mizque)</td>
<td>Solcor 3</td>
<td>T112:#3900A</td>
<td>M</td>
<td>BOV</td>
<td>0.47</td>
</tr>
<tr>
<td>Bag (bolsa chuspa)</td>
<td>Quitor 2</td>
<td>T65:2:#13979</td>
<td>M</td>
<td>BOV</td>
<td>3.1</td>
</tr>
<tr>
<td>Bag</td>
<td>Solcor 3</td>
<td>T112:#3902</td>
<td>M</td>
<td>BOV</td>
<td>16.5</td>
</tr>
<tr>
<td>Bag</td>
<td>Solcor 3</td>
<td>T112:#3901</td>
<td>M</td>
<td>BOV</td>
<td>20.9</td>
</tr>
<tr>
<td>Tunic</td>
<td>Solcor 3</td>
<td>T132, tunic 1 (exterior)</td>
<td>M</td>
<td>Local (low)</td>
<td>3.1</td>
</tr>
<tr>
<td>Bag (talega)</td>
<td>Catarpe 2</td>
<td>1828:#13947</td>
<td>LI</td>
<td>Local (low)</td>
<td>7.4</td>
</tr>
<tr>
<td>Tunic</td>
<td>Solcor 3</td>
<td>T20:#57a1</td>
<td>M</td>
<td>Local (low)</td>
<td>8.9</td>
</tr>
<tr>
<td>Tunic</td>
<td>Quitor 1</td>
<td>M1187C</td>
<td>LI</td>
<td>Local (low)</td>
<td>12.4</td>
</tr>
<tr>
<td>Fragmented tunic</td>
<td>Coyo Oriente</td>
<td>4012-1</td>
<td>M</td>
<td>Local (low)</td>
<td>17.0</td>
</tr>
<tr>
<td>Tunic</td>
<td>Coyo Oriente</td>
<td>5382:#7 tunic 2</td>
<td>M</td>
<td>Local (low)</td>
<td>20.4</td>
</tr>
<tr>
<td>Tunic</td>
<td>Quitor 2</td>
<td>T3427-1</td>
<td>LI</td>
<td>Local (low)</td>
<td>21.3</td>
</tr>
<tr>
<td>Fragmented tunic</td>
<td>Quitor 1</td>
<td>T3438</td>
<td>LI</td>
<td>Local (low)</td>
<td>22.1</td>
</tr>
<tr>
<td>Tunic</td>
<td>Solcor 3</td>
<td>1983-27</td>
<td>M</td>
<td>Local (low)</td>
<td>22.7</td>
</tr>
<tr>
<td>Fragmented tunic</td>
<td>Coyo Oriente</td>
<td>4185-89</td>
<td>M</td>
<td>Local copy of Tiwanaku (low)</td>
<td>23.7</td>
</tr>
<tr>
<td>Tunic</td>
<td>Solcor 3</td>
<td>T107; tunic 2</td>
<td>M</td>
<td>Local (low)</td>
<td>24.7</td>
</tr>
<tr>
<td>Tunic</td>
<td>Solcor 3</td>
<td>T107; tunic 3</td>
<td>M</td>
<td>Local (low)</td>
<td>24.9</td>
</tr>
<tr>
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<td>Coyo Oriente</td>
<td>3978-1</td>
<td>M</td>
<td>Local (low)</td>
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<tr>
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<td>Quitor 1</td>
<td>M1187D,#21529</td>
<td>LI</td>
<td>Local (high)</td>
<td>43.3</td>
</tr>
<tr>
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<td>Coyo Oriente</td>
<td>4012-8</td>
<td>M</td>
<td>Local (high)</td>
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</tr>
<tr>
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<td>M1187B</td>
<td>LI</td>
<td>Local (high)</td>
<td>58.6</td>
</tr>
<tr>
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<td>Coyo Oriente</td>
<td>20, body 1;#57</td>
<td>M</td>
<td>Local (high)</td>
<td>73.4</td>
</tr>
<tr>
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<td>Coyo Oriente</td>
<td>4012-4</td>
<td>M</td>
<td>Local (high)</td>
<td>92.3</td>
</tr>
<tr>
<td>Headband</td>
<td>Solcor 4</td>
<td>T132 (5),8671</td>
<td>M</td>
<td>Tiwanaku</td>
<td>95.3</td>
</tr>
<tr>
<td>Bag</td>
<td>Quitor 2</td>
<td>T2467</td>
<td>M</td>
<td>Tiwanaku + BOV</td>
<td>3.6</td>
</tr>
<tr>
<td>Mantle</td>
<td>Coyo Oriente</td>
<td>4084-86.1</td>
<td>M</td>
<td>Tiwanaku</td>
<td>33.7</td>
</tr>
<tr>
<td>Ritual cloth (inkuna)</td>
<td>Coyo Oriente</td>
<td>T5347-1</td>
<td>M</td>
<td>Tiwanaku</td>
<td>34.4</td>
</tr>
<tr>
<td>Fragmented tunic or mantle</td>
<td>Coyo Oriente</td>
<td>3935</td>
<td>M</td>
<td>Tiwanaku</td>
<td>38.5</td>
</tr>
<tr>
<td>Mantle</td>
<td>Solcor 3</td>
<td>T109:#13149</td>
<td>M</td>
<td>Tiwanaku</td>
<td>38.9</td>
</tr>
<tr>
<td>Headband</td>
<td>Solcor 3</td>
<td>T2511;#13959</td>
<td>M</td>
<td>Tiwanaku</td>
<td>40.5</td>
</tr>
<tr>
<td>Bag</td>
<td>Quitor 2</td>
<td>T20:#1356</td>
<td>M</td>
<td>Tiwanaku + BOV</td>
<td>42.1</td>
</tr>
<tr>
<td>Tunic</td>
<td>Coyo Oriente</td>
<td>5382,1</td>
<td>M</td>
<td>Tiwanaku</td>
<td>43.6</td>
</tr>
<tr>
<td>Bag (bolsa chuspa)</td>
<td>Quitor 2</td>
<td>T65;#3</td>
<td>M</td>
<td>Tiwanaku</td>
<td>63.4</td>
</tr>
<tr>
<td>Bag</td>
<td>Solcor 3</td>
<td>T113:#8475</td>
<td>M</td>
<td>Tiwanaku</td>
<td>127.5</td>
</tr>
<tr>
<td>Mantle</td>
<td>Coyo Oriente</td>
<td>4012-13</td>
<td>M</td>
<td>Tiwanaku</td>
<td>228.5</td>
</tr>
<tr>
<td>Fragmented tunic</td>
<td>Solcor 3</td>
<td>T107; tunic 1</td>
<td>M</td>
<td>Tiwanaku</td>
<td>255.6</td>
</tr>
</tbody>
</table>

a BOV: Bolivian oriental valleys.
b Presumably fibers were dyed at SPA or BOV and textile was woven at SPA — see Discussion.
c Presumably fibers were dyed at SPA — see Discussion.
d Presumably fibers were dyed at SPA or BOV — See Discussion.
e Presumably fibers were dyed at Tiwanaku — See Discussion.

2.4. Chemical analysis of textiles

Numerous HPLC-DAD methods have been developed to identify dyes in textiles (Degano et al., 2009; Rosenberg, 2008). Mordant dyes such as anthraquinones are commonly extracted using acidic methanol (Degano and Colombini, 2009) while indigo dyes are conveniently extracted using high-donor number aprotic solvents such as dimethylsulfoxide (DMSO) (Koren and Verhecken-Lammens, 2013). Red dyed fibers (ca. 1–10 mg) were separated from the textile, cut into small pieces (<2-mm long) and extracted in a sealed tube with 200 µL 30% HCl and 200 µL methanol for 20 min at 60 °C under sonication; the extracts were then filtered (Millipore, PTFE, 0.2 mm, 4 mm-diameter), evaporated to dryness and reconstituted in 30 µL of methanol prior to analysis. Extracts (20 µL) were injected into the column (Merck LiChrospher 100, RP18 – 5 µm, length: 125 mm, diameter: 4 mm) of a high performance liquid chromatograph (Shimadzu LC-20AD) coupled to a diode-array detector (Shimadzu SPD-M20A). Blue dyed fibers (ca. 0.5–5 mg) cut into small pieces (<2-mm long) were ground using a pellet pestle (Sigma Aldrich), and extracted with 150 µL DMSO for 20 min at 65 °C under sonication, and further for 10 min at 135 °C in a block heater (Rocker, Taiwan). The samples were filtered (Millipore, PTFE, 0.2 µm, 4 mm-diameter) and 20 µL of the filtrates directly injected into the HPLC column, as described above. In both cases, the initial elution solvent consisted of 20–80 mixture of solvent A (acetonitrile with 0.1% trifluoroacetic acid) and solvent B (water with 0.1% trifluoroacetic acid); during a 45-min linear gradient, the composition of the mixture changed to pure solvent A. Solvent flow was 0.5 mL/min and column temperature 30 °C.

Identification of compounds in the eluates was based on comparisons of retention times (Rt) and UV–visible spectra with those of the standards purpurin, alizarin, carminic acid, indigo (IND) and indirubin (INR), all from Sigma-Aldrich (Fig. 3). Chromatograms of the red fibers were obtained at 430 nm (λmax for alizarin) and at 480 nm (λmax for purpurin and carminic acid), and chromatograms for blue fibers were obtained at 540 nm (λmax for INR) and 600 nm (λmax for IND). Areas under the peaks with maxima at these wavelengths were used to quantitate INR and IND, respectively. These wavelengths were used instead of the frequently used 275 nm because: i) most organic compounds have strong absorption at 275 nm and potential impurities may distort the measured areas, ii) they provide, over and above the retention time, an element of selectivity to the analysis, and iii) since the absorption coefficient of INR (the compound present in the lowest proportion in extracts of blue fibers) at 540 nm is higher than at 600 nm, the chances of trustworthily quantifying it are enhanced. Full UV–Vis spectra (200–700 nm; resolution: 1.4 nm) were recorded for
peaks at the retention times of standards in the chromatograms of the fiber extracts (Fig. 4).

Quantification of IND and INR in blued dyed fibers was achieved by determining $\frac{IND_{600\text{nm}}}{INR_{540\text{nm}}}$ ratios — i.e., the ratio between the area under the chromatographic peak for IND measured at 600 nm and the area under the chromatographic peak for INR measured at 540 nm — and extrapolating the concentration ratio $[\text{IND}] / [\text{INR}]$ from a calibration line made using pure compounds.

Fig. 2. Illustrations showing different types and styles of textiles analyzed. A: Headband Tiwanaku style from Solcor 3, T132 (5), #8671; B: Mantle Tiwanaku style from Solcor 3, T109, #13149; C: Embroidered basket La Aguada style from Solcor 3, T113; D: Headband mixed Tiwanaku/Bolivian Oriental valleys styles from Solcor 3, T20, #1356; E: Bag with mixed Tiwanaku/Bolivian Oriental valleys from Quitor 6, T2467; F: Tunic Tiwanaku style from Coyo Oriente, T5382.1; G: Tunic fragments local style from Coyo Oriente, T4185-89; H: Ritual cloth Tiwanaku style from Coyo Oriente, T5347-1. Photographs by Carolina Agüero.

Fig. 3. Structures of dyes mentioned in the text and some of their precursors. Alizarin, purpurin and carminic acid are frequently found in extracts of red dyed fibers, while indigotin and indirubin are frequently found in extracts of blue dyed fibers.
The calibration line was constructed as follows: i) DMSO solutions were prepared which contained measured quantities of IND and INR in ratios and concentrations close to the range found in the fiber extracts ([IND]/[INR] = 1.2 to 234; peak areas in extracts ranged from 33,500 for INR540nm to 16.8 million for IND600nm and in standard solutions from 30,000 to 18.7 million, respectively); ii) these solutions were submitted to the same analytical procedure as the fibers, iii) IND600nm/INR540nm ratios were determined, and iv) a regression line through the origin was calculated with initial [IND]/[INR] ratios vs. experimental IND600nm/INR540nm ratios.

Fiber analyses were performed at least in duplicate. The reproducibility of the method was tested with three textiles with low, medium and high mean [IND]/[INR] ratios (7.4, 38.9 and 92.3; see Table 1).

3. Results

All red dyed fibers showed the presence of purpurine at Rt = 33.59 ± 0.88 min (mean ± SD) and the absence of alizarin and carminic acid (Table 1, Fig. 4-A and 4-B). All blue dyed fibers showed the simultaneous presence of INR at Rt = 35.21 ± 0.86 min and IND at Rt = 37.00 ± 0.73 min (Table 1, Fig. 4-C and 4-D).

The calibration line determined was [IND]/[INR] = 1.74 × IND600nm/INR540nm (R² = 0.99; N = 15). Standard errors of the replicated analyses of tissue fibers with low, medium and high [IND]/[INR] ratios were 16.3, 19.2 and 22.0% of the mean, respectively.

A positive and highly significant correlation (Pearson correlation: r = 0.488, N = 38, P = 0.0019) was found between mean [IND]/[INR] values and altitude where the fibers were presumed to have been dyed. The altitudes used in the correlation were: 3900 m.a.s.l. for Tiwanaku style textiles (except for headband from Solcor 3, T132 (5), 8671 and bag from Quitor 6, T2467, which were presumed to have been dyed at SPA and SPA or BOV, respectively, as discussed below); 2650 m.a.s.l. for local SPA textiles, 1500 m.a.s.l. for La Aguada textiles, and 2650 m.a.s.l. for BOV style textiles (presumed to have been dyed at SPA since they were woven at SPA with camelid fibers, which were used only sparingly in textiles woven in the BOV — see section 2.2). Within the set of textiles woven at SPA, two subsets could be discerned, one with low (<27) and one with high (>43) [IND]/[INR] ratios (Table 1). Statistical comparisons were performed between the two subsets of locally woven textiles and the Tiwanaku style textiles. Significant differences were found between textile types (Kruskal–Wallis ANOVA: H = 26.473, df = 2, P < 0.001); Dunn post-hoc tests showed significant differences (p < 0.05) between local style with low [IND]/[INR] ratio and Tiwanaku (Q = 4.259) and between local style with low [IND]/[INR] ratio and local style with high [IND]/[INR] ratio (Q = 4.020), and non-significant differences (P > 0.05) between local style with high [IND]/[INR] ratio and Tiwanaku (Q = 0.530) (Fig. 5).

4. Discussion

4.1. Red dyes

The main sources of red dyes in the Central Andes during pre-Hispanic times were the cochineal insect Dactylopius coccus...
(Hemiptera: Coccoidea: Dactylopiidae) and plants of genera *Galium* and *Relbunium*, both belonging to the family Rubiaceae (Cardon, 2007). Anthraquinone dyes in extracts of plants from these genera are reliable chemotaxonomical markers; thus, species of the genus *Galium* contain alizarin but not purpurin and species of the genus *Relbunium* contain purpurin but not alizarin (Dutra Moresi and Wouters, 1997; Schappe, 1986; Thomson, 1971). Hence, the likely source of red dyes used in textiles which showed the presence of purpurin and the absence of alizarin are plants belonging to the genus *Relbunium*. In South America, 20 species of *Relbunium* are distributed along the Andes from Guyana to southern Peru, western and southeastern Bolivia, and northwestern Argentina, northeastern Argentina and southeastern Brazil, and southern Chile (Dempster, 1990). With the possible exception of *R. corymbosum*, which has been collected once in the coast south of Antofagasta and once in the western slopes of the Andes opposite Arica (northern Chile), *Relbunium* does not grow in northern Chile, indicating that the red dye used in locally manufactured textiles came from sources exogenous to SPA. The most abundant and widely distributed species of *Relbunium* in South America are *R. corymbosum* and *R. hypocarpium*, whose distributions include western and southeastern Bolivia and northwestern Argentina. Given the demonstrated interactions between these two regions and SPA during the periods of manufacture of the textiles studied (Stovel, 2008), these two *Relbunium* species are the likely sources of the red dye found in SPA textiles (Roquero, 2008).

It is interesting to note that the same source of red dye was apparently used for nearly a millennium of cultural development at SPA. This situation contrasts with that prevailing in Peru, where *Relbunium*-derived dyes were used predominantly during the Late Formative and Early Middle periods (1100 B.C.–600 A.D., in Paracas and Nasca cultures), and were gradually substituted by cochineal while (Stovel, 2008); thus, Northwestern Argentina could have been the preferred area to access the plant-based red dye used in the first textiles dyed at SPA.

During the Middle period, Tiwanaku textiles were dyed with both plant and insect dyes; the absence in SPA of Tiwanaku style textiles dyed with cochineal during such period is intriguing. Given that some of the areas of the Pacific coast and adjacent highlands where cochineal thrives were under Tiwanaku influence during the Middle period, the dye used in Tiwanaku textiles most likely came from such areas; its further exportation to SPA using the caravan route which, surrounding the Uyuni salt lake linked Tiwanaku with SPA, seems uncompetitive in relation to plant-derived red dyes imported via the shorter and more direct route linking SPA with Northwestern Argentina. An alternative direct route for importation of cochineal from the coast of Peru, although possible, has not received support through other materialities.

Even though this interpretation needs future testing, it is interesting to consider that it suggests that certain materials were brought from specific areas in spite of the fact that SPA interacted with other polities which also had access to the same raw materials. In this regard, cultural options and values seem to be at play in the configuration of Andean exchange (see Nielsen, 2007; Salazar et al., 2014). In fact, the interplay between local availability of raw materials, traffic routes, interregional social connections and local processes of group identity formation were probably responsible for the organization, reproduction and transformation of the multiple interacting spheres simultaneously operating at SPA during the Middle and Late Intermediate periods.

4.2. Blue dyes

Indigo was present in all blue textile samples studied. Main sources of indigo in South America are plants of the genera *Indigofera* (Fabaceae), *Eupatorium* (Asteraceae) and *Yangua* (Bignoniaceae); the only species of these genera which are native to Chile are *Eupatorium glechonophyllum* and *E. salvia* (Martiorena and Quezada, 1985), but neither species grows in the region around SPA; hence, the blue dye used in the textiles analyzed also came from sources exogenous to SPA.

Dyeing with indigo, in spite of being a highly complex chemical–biochemical technology, has been mastered and performed by numerous ancient civilizations of Asia, the Middle East, Europe, Africa and the Americas (Balfour-Paul, 2006: 11ff). Although a wide variety of traditional recipes have been developed by different cultures (Cardon, 2007), two basic dyeing processes can be distinguished which use either leaves or purified dye obtained from leaf extracts (the so called indigo “balls” or “cakes”), respectively (Cardon, 2007: 240ff). As of last century, synthetic dye has also been used.

In the first process, the fibers are soaked in the plant extract and are then aerated, exposing them to atmospheric oxygen, whereby the blue indigo dye is produced in situ, on the fiber. Chemically, the process involves the enzymatic hydrolysis of the colorless glycosidic precursor naturally present in the plant, indican or isatans depending on the species, to produce the colorless aglycone, indoxyl, a compound which suffers oxidative condensation upon exposure to air to give IND. In oxygen-rich environments, indoxyl may be further oxidized to isatin, whose condensation with indoxyl gives INR (Clark et al., 1993; Maugard et al., 2001; Muroganandan and Bhattacharya, 2008; Fig. 3); in fact, high INR amounts may be obtained by manufacturing processes favoring the oxidation of indoxyl to isatin (Eastaugh et al., 2008). Hence, provided the oxidation to indoxyl is the rate-limiting step in the production of INR, a higher relative yield of INR may be obtained through technological differences in the dyeing process favoring the oxidation of indoxyl to isatin (Garcia-Macias and John, 2004; Kohama et al., 2005; Wouters and Rosario-Chirinos, 1992).
In the second process, the dyeing vat is produced by dissolving the indigo cake with the help of natural antioxidants and/or a reducing agent in basic medium (traditionally, reducing bacteria fed with various natural sources of nutrients or, in modern times thiourea dioxide) whereby a colorless form of the dye is produced; the fibers are soaked in this vat and are then aerated, whereby the reduction process is reversed and the blue indigo dye is produced in situ, on the fiber. Chemically, the reduction of indigo produces leuco-indigo which is later reoxidized to indigo by atmospheric oxygen when the fibers are aerated (Fig. 3).

Little is known of the method used for dyeing with indigo in pre-Hispanic America. However, it seems likely that the first of the processes described was used since ecocasts such as indigo cakes have never been found in archaeological sites in spite of their high chemical stability.

The analysis of textiles showed the presence of both IND and INR (Fig. 4-C and 4-D); their concentration ratio, [IND]/[INR], showed satisfactory levels of analytical reproducibility and a large dispersion within each of the groups (styles) of textiles analyzed. This dispersion can be accounted for by several factors, such as: i) differences in the dyeing process; for example, different textiles may have been dyed using extracts from plants belonging to different populations, and collected at different times and places of the year; hence with different composition of co-adyuvant substances and/or leading to different pH in the dyeing vat (Kohama et al., 2005); ii) processing by different artisans in a time when methods for accurately measuring and dosing the components of a dyeing vat were either inaccurate or not available; iii) dyeing under different environmental conditions such as temperature, humidity, etc. thus affecting the reactions producing the dyes and bonding the dyes to the tissue fibers; and iv) although indigo is a rather stable molecule when protected from light and kept in a dry environment (Sousa et al., 2008), differential thermal or photodecomposition of the dyes may have occurred while the fiber was dyed, or the textile was manufactured, used, deposited, excavated, cleaned, stored, exhibited or analyzed.

It is apparent from the data in Table 1 that the [IND]/[INR] ratio is highest for most Tiwanaku style textiles, whose fibers were presumably dyed at the high altitude altiplano, and lowest for La Aguada, BOV and some SPA textiles, whose fibers were presumably dyed at lower altitudes. In fact, a positive and significant correlation was found between [IND]/[INR] values and altitude where the fibers were presumed to have been dyed. On the basis of the nature of the dyeing process and the chemistry involved, and notwithstanding the possible sources of variations noted above, we hypothesize that dyeing a fiber at lower altitude (higher oxygen availability) leads to the production of more INR relative to IND and hence to the incorporation in the fiber of a higher proportion of INR; thus, a lower [IND]/[INR] ratio will be obtained when fibers are dyed at lower than at higher altitude.

This hypothesis was tested with the scanty data available in the literature. Sousa et al. (2008) reported the percentages of IND and INR found in 17 samples of blue fibers (one datum was excluded because INR was not found in the fiber) from 11 textiles of the Paracas Necropolis and Nasca cultures of southern Peru and encompassing the period from 200 B.C. to 300 A.D. (some textiles are specified as Paracas/Nasca) from the Boston Museum of Fine Arts; these quantities can be directly transformed into [IND]/[INR] ratios. Two sets of textiles could be clearly discerned (and statistically proven to be different: one-way ANOVA, H = 7.0, d.f. = 1, P = 0.008) with mean [IND]/[INR] ratios of 4.5 (N = 14) and 30.6 (N = 3), respectively. These sets may be associated with fibers dyed near the coast and lower valleys, and upper valleys of central Peru, respectively, the main regions occupied by these cultures (Proulx, 2008).

IND and INR were also reported in blue-dyed fibers from tombs of the Necropolis of Ancón (1040–1260 A.D.) and corresponding to the transition from Wari to Chancay cultures in the central coast of Peru (Degani and Colombini, 2009). The results reported are not straightforward to convert into [IND]/[INR] ratios because only chromatograms at 275 nm are shown in the paper. If absorption coefficients at 275 nm were similar for both dyes, a mean [IND]/[INR] ratio of 2.5 (range = 1.3–4.5, N = 3) may be estimated by measuring the areas under the peaks in the figure of the paper, consistent with fibers dyed at locations near the coast.

IND has been found in extracts made from blue fibers (Pawlak et al., 2006; Puchalska et al., 2004), sometimes accompanied by INR (e.g., Karapanagiotis et al., 2011; Liu et al., 2011; Nowik et al., 2005; Vander Berghe et al., 2009; Zhang et al., 2008); however, very seldom are these two compounds quantified. For example, Koren (2008) reported a high IND/INR ratio in a textile from the Judean desert outside Jerusalem, Abdel-Kareem et al. (2010) reported an IND/INR ratio of 1 in a Coptic textile, and Sanz et al. (2011) studied Chinese textiles of two shades of blue and found mean IND/INR ratios of ca. 9 and 1. The causative factors of these widely different IND/INR ratios have not been addressed; it is not unlikely that dyeing techniques and dyeing environment are major factors affecting them (Garcia-Macias and John, 2004; Kohama et al., 2005).

The two subsets of textiles woven at SPA distinguished on the basis of their [IND]/[INR] ratios (Fig. 5) suggests that imports to SPA may have included fibers dyed in the northern highlands which were locally used to weave textiles in the local and BOV styles, as well as raw dyeing materials which were used to dye fibers locally; both types of imports were taking place during both the Middle and Late Intermediate periods (Table 1), consistent with the known patterns of diachronic interaction of SPA with neighboring areas (Llagostera, 1996; Stovel, 2008).

Some of the textiles analyzed deserve further comment. The Tiwanaku style headband from the Solcor 3 tomb T132(5) #8671 (Fig. 2-A) gave an [IND]/[INR] value of 1.7, outside the range found in textiles presumably dyed at the Tiwanaku highlands. Various anthropological studies have shown that during the Middle period the human biological diversity at SPA increased (Knudson, 2007; Nado et al., 2012; Torres-Rouff and Knudson, 2007; Torres-Rouff et al., 2014; Varela and Cicclovo, 2009), in part due to immigrants from Tiwanaku (Torres-Rouff et al., 2014); some of these immigrants may have been weavers who brought from Tiwanaku the skills and instruments to produce Tiwanaku style textiles at SPA with locally dyed fibers. Alternatively, local artisans could have copied foreign styles in locally-produced textiles, similarly to what has been observed in other materialities (Salazar et al., 2014: 146–147).

Along similar lines of reasoning, the Coyo Oriente tunic 4185–89 textile (Fig. 2-G) represents a particularly interesting case. Oakland (1986b:106–108) assigned it to the Tiwanaku style but suggested the likelihood that it was of provincial manufacture mainly based on the low quality yarn (unevenly spun and plied with large variations in diameter), the low yarn counts, and the variations within motifs, both in design and in color, and their asymmetrical distribution (see however Uribe and Agüero, 2001:400). Consistent with this view, the comparatively low IND/INR of 23.7 suggests the use of fiber dyed (and possibly spun) at low altitude and hence the involvement of weavers not living in Tiwanaku. Again, this textile may have been woven by weavers among the population of Tiwanaku origin settled in SPA (Knudson and Torres-Rouff, 2014) or by local artisans copying elements of the Tiwanaku style in the textiles they manufactured; in either case, the artisans were unable to reproduce the exquisite craftsmanship exhibited by original Tiwanaku tunics.

The bag covering the skull of the individual in tomb T 2467 from Quitor 6 (Fig. 2-E) exhibits a mixture of styles, partly BOV and partly...
connections for some objects, and certain others for other types of available. Thus, interaction networks seem not to have been limited to distinguish between these hypotheses.

Finally, there are some Tiwanaku style textiles whose IND/INR ratios are in-between the two ranges defined for the local SPA style textiles, i.e., 27 < IND/INR < 43. It seems most parsimonious that these textiles were dyed at a high altitude, albeit using a different technological process than those showing very high IND/INR ratios (60–260) because of the unlikeliness that the center of the Tiwanaku state imported raw materials used in the manufacture of emblemic objects such as textiles.

In summary, the results presented add the raw material dimension to the study of SPA textiles and confirm and complement with new evidence the textile styles that have been proposed for SPA. The use of exogenous raw materials for the local manufacture of goods at SPA is not restricted to textiles; for example, the raw material for many snuff trays manufactured in a local style at SPA (Horta, 2014) was foreign wood (Niemeyer, 2013; Niemeyer et al., 2013; Riquelme-Toro and Niemeyer, 2015). This underlines the importance of an exchange of goods which took advantage of technological process than those showing very high IND/INR ratios (60–260) because of the unlikeliness that the center of the Tiwanaku state imported raw materials used in the manufacture of emblemic objects such as textiles.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jas.2015.02.003.

References


