Development of methodology using ATR-FTIR with PCA to determine groups which reflect species used in the making of historical Pacific barkcloth.

Margaret J. Smith[1]*, A.Sheila Holmes-Smith[2], Frances Lennard[1]

[1]Centre for Textile Conservation and Technical Art History, School of Culture and Creative Arts, University of Glasgow, Robertson Building, Glasgow, G11 6AQ, United Kingdom

[2]Department of Applied Science, School of Computing, Engineering and Built Environment, Glasgow Caledonian University, Cowcaddens Road, Glasgow, G4 0BA, United Kingdom

Email:

Margaret.Smith@glasgow.ac.uk

Frances.Lennard@glasgow.ac.uk

a.s.smith@gcu.ac.uk

*Corresponding author

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Development of non-destructive methodology using ATR-FTIR with PCA to differentiate between historical Pacific barkcloth.

Abstract

Barkcloths, non-woven textiles originating from the Pacific Islands, form part of many museum collections and date back to the 18th and 19th centuries. The ability to determine different plant species which have been used for producing barkcloth is required by art historians to help understand the origin and use of the cloths and by conservators for whom the species type may have an impact on textile durability, deterioration and hence conservation. However, to date the development of a non-destructive, robust analytical technique has been elusive. This article describes the use of Fourier transform infrared spectroscopy with attenuated total reflection (ATR - FTIR) and principal component analysis (PCA) to differentiation between historic barkcloths. Three distinct groups of historic cloths were identified using PCA of the FTIR region between 1200 and 1600 cm^{-1} where molecular vibrations associated with tannins and lignins are dominant. Analysis of contemporary cloths only identified *Pipturus albidus* cloth as different and highlighted the difficulties around producing a representative textile sample to mimic the historic cloths. While the methodology does not itself identify species, the use of historically well-provenanced samples allows cloths showing similarities to group together and is a significant aid to identification.

Keywords: Pacific barkcloth; ATR-FTIR; Multivariate analysis; Principal component analysis; species differentiation; microscopy.

1. Research aims

This research aimed to carry out a preliminary trial to determine if a new and reliable method combining spectroscopy and chemometrics could be developed to differentiate between historic Pacific Island barkcloth samples. The motivation for this work was driven by a lack of analytical methods within the heritage science literature on species identification for barkcloth samples, a preliminary requirement in preservation method development. To achieve this ATR-FTIR was employed along with multivariate analysis (MVA), specifically principal component analysis (PCA) and Hierarchical Cluster Analysis (HCA) to distinguish between historic barkcloth samples where the species used in their manufacture is unknown or where they have been labelled but the date or validity of the labelling may be in doubt. The innovation lies within the use of MVA to quantify the relationship between the historic barkcloth samples which ultimately would possibly allow art historians and conservators to identify selected characteristics, such as species which would lead to a better understanding of the origins of these barkcloth samples and hence their preservation.

Initially contemporary barkcloth samples of known species were investigated to ascertain if a model for historic cloths could be developed.

2. Introduction

Barkcloths, both plain and decorated, from the Pacific Islands form part of many museum collections worldwide and date back to the 18th and 19th centuries. Western explorers such as Captain James Cook and botanist Joseph Banks admired the beauty of barkcloth worn by the indigenous peoples they encountered in their travels [1] and brought examples of these cloths back from their voyages. Barkcloth is a non-woven cloth which is prepared by stripping the inner bark from young branches,

soaking the fibres in either freshwater or saltwater and then beating the bark to form cloths. These cloths are decorated with differing patterns associated with Pacific Island groups. Until the 19th century barkcloth was used as a textile for everyday clothing, bedding and soft furnishing as well as for ceremonial events. The practice in some islands disappeared with the introduction of imported woven textiles.

There are numerous historical and contemporary descriptions of making the cloths, often stating that they are made from *Broussonetia papyrifera* (BP), commonly called paper mulberry. In fact a number of species are used but BP is certainly the most prevalent, it has been known for almost 1,500 years as a plant whose bark can be used to make textiles [2]. Levetin and McMahon [1] describe the making in Polynesia, explaining the general term for such cloth is tapa (kapa in the Hawaiian Islands) and, typically, it is made from the inner bark of the paper mulberry. First, the bark is stripped from the tree in one piece. Next, the outer bark is scraped off. The inner bark of phloem, or bast fibres, is soaked to soften the fibres and remove impurities. For the finest cloth, fermentations alternate with soakings to further soften the fibres. The soaking in fresh or seawater is a process that is usually termed 'retting' and is a commonly used process in industry to remove the pectin, lignin and hemicellulose from bast fibres [4,5]. The barkcloth makers place strips of sodden inner bark on a hollowed log or anvil. Strips are overlapped so that, when beaten, they felt together to form a single large piece of cloth [1]. On some islands wooden beaters are marked with grooves which impress a pattern on the cloth. A comprehensive account of the making, materials and geographical origin of Polynesian barkcloth can be found in Larsen [3] where seventy-one ethnographic sources were reviewed to find cross-cultural variation in Polynesian bark cloth production. The data is compiled and the processes detailed through each production stage. Larson [3] reports that in Uvea, Futuna and Ponape the initial preparation of leeching of secondary compounds and colour through soaking of the bark is not recorded to have been carried out. In the Cook Islands, Austral Islands, Hawaii Islands and Rapa Nui the inner bark is removed from the outer bark and left in a stream or the ocean to allow the water to percolate through the fibres. In Mangareva, Samoan Islands, Tonga and Fiji and Viti Levu the outer bark is removed prior to soaking. The majority of historical collections record the cloths as being BP [3], though little or no analysis has been carried out on these cloths to confirm this. However accession records may not have taken into account the transfer of cloths between islands or indeed errors in recording origin due to lack of historical documentation and lack of specialist curatorial advice. There is some visual as well as morphological evidence [6] that cloths may be composed of two fibres.

Fig.1A and 1B show examples of contemporary samples from the Smithsonian Institution, Washington, DC and historic cloths from the Hunterian Museum, University of Glasgow, Glasgow, and from the Economic Botany Collection, Royal Botanic Gardens Kew, London.

To date there has been no straightforward, reliable method to identify the species used to make the cloths. Those methods used to date have primarily focused on morphology using microscopy, both light and scanning electron [7], and depend on comparisons of similar and dissimilar features. While these are often useful methods when executed by experts their weakness lies in the diagnostic features being robust enough for the analysis to be useful to a wider user group. The extreme action of the beating process often removes diagnostic features that would normally be present in more conventionally processed bast fibres. Scharff [6] reported that misidentification may occur if mixed fibres had been used in the cloth manufacture. DNA analysis has been used successfully to determine the species used in barkcloth making and also to determine provenance and authenticity [2,8]. The methodology reported uses around 1cm^2 of material which

may not be possible to obtain from museum objects where sampling opportunities are controlled by the condition of the cloth or the museum policies. Additionally access to such analysis may not be either financially or logistically feasible.

Inner bark, like wood, is composed of holocellulose which includes cellulose and hemicellulose together termed the carbohydrate fractions, lignin, pectin and a large number of extractives such as flavonoids and waxes. For the last few decades, wood scientists have used vibrational spectroscopy, especially Fourier transform infrared spectroscopy (FTIR) with attenuated total reflection (ATR-FTIR) to characterise the chemistry of wood components, their behaviour and ageing in various environments [9,10]. The combination of chemical analysis and statistics, chemometrics, is used to analyse the FTIR spectra in order to determine differences between hard and soft woods, to differentiate between species and to determine ageing. The variations in the spectrum where these changes can be detected mainly occur in the fingerprint region 1800-600cm^{-1}. Here small changes, not always visible from spectrum inspection can be teased out by the use of second derivatives and/or multivariate analysis [11, 12, 13, 14]. Hobro et al. [14] used ATR-FTIR to determine differences between walnut species and also the effects of steam on the wood. The spectra were subjected to partial least squares discriminant analysis. The validity of this type of spectroscopic analysis, especially in its application to qualitative analysis, has been confirmed by a number of studies. Poletto et al. [15] reported on the structural differences between four wood species using FTIR and comparing their findings to wet chemistry and thermogravimetric analysis to determine Klason lignin. FTIR has been employed to distinguish between hard and soft wood by comparing the differing proportions of cellulose, hemicellulose, lignin and extractives in the two wood types [16, 17, 18, 19]. It is also used to distinguish between species of new (fresh) wood. Rana et al. [20] used FTIR, chemical and histochemical methods to characterise differences between wood and lignin in five wood species from the family Dipterocarpaceae. Wang et al. [21] used FTIR, 2nd derivative IR and 2D-IR spectroscopy to determine between four species of *Dalbergia* which belong to the *Fabaceae* family. There have also been a number of studies which employed FTIR to determine the condition of historic and archaeological woods [9,10,22,23,24]. Pizzo et al. [10] used ATR-FTIR multivariate PLS analysis to determine differences in how wood had been preserved in waterlogged conditions and Traoré et al. [9] reported on the use of ATR-FTIR with PCA to highlight the differences in chemical composition between two archaeological woods.

Whilst the methodology was primarily developed for contemporary wood and its applications [10, 25] the small sample size and minimal sample preparation makes it an excellent choice for examination of wood based historic objects. Indeed ATR-FTIR allows for non-invasive analysis of flat objects such as textiles. To date there has been no straightforward, reliable method to identify the species used to make the cloths.

3. Material and methods

3.1 Information on the preparation of contemporary samples

The analysis focused on the four species: *Broussonetia papyrifera* (BP) (paper mulberry), *Artocarpus altilis* (AA) (breadfruit), Ficus prolixa (FP) (banyan) and *Pipturus albidus* (PA) (mamaki) sometimes called *Pipturus kauaiensis* (PK). Fig. 1A shows examples of contemporary samples from the Smithsonian Institution, Washington, DC. On visual inspection of the contemporary samples (2012-2015) it can be noted that samples made from BP and AA appear cream/light brown in colour while the FP and PA samples appear a much darker brown. The samples of contemporary barkcloth came

from the Pacific Islands and were prepared by community scholars who participated in a national history Research Experiences programme (2012-2015) at the National Museum of Natural History, Smithsonian Institution, Washington, DC (26). The number of samples was indicative of the number of cloths made from each species and so the largest number of samples were BP. The first three, BP, AA and FP all come from the family Moraceae and PA from the family Uriticaceae. Table 1 lists the 22 contemporary barkcloth samples used in the study. The differing preparation methods of these samples reflect the practice of the island or area in which they were made and so samples of the same species may appear slightly different due to the amount of retting, beating and finishing (polishing with shells or stones).

The conservators and contemporary makers of backcloth have noted that it is extremely difficult to produce a good quality sample of PA cloth using commonly used methodology i.e. stripping, soaking and beating [8,27].

3.2 Information on the historic cloths

The 15 historic cloths analysed came from three collections which are detailed in table 2. The dates shown appear on the collections' documentation and their accuracy has not been verified. The ABDU A4001 and A4006 were labelled at source as mamaki (sometimes labelled mamake) and the Economic Botany Collection (EBC) 42760 (AA) and 42760 (FP), breadfruit and banyan respectively. A number of the other cloths have been labelled retrospectively by curatorial staff and art historians.

In the main the cloths that were chosen for analysis were not painted or dyed as the methodology was dependant on measuring the molecular vibrations of the wood species only and not those present in the colorants used to decorate the cloths as these may affect the results. However, where it was clear based on light microscopy, that there was no dyeing and only surface painted decoration had been used samples from the underside of cloths were included. Fig. 1B shows examples of historic cloths from the Hunterian Museum, University of Glasgow, Glasgow, and from the EBC, Royal Botanic Gardens Kew, London.

3.3 Experimental Instrumentation

Stereomicroscopy was carried out on cloths to examine the fibres and the beaters marks of the cloths in detail. This was done using a Zeiss stereo-microscope (Stemi SV 11). The images shown here were not subjected to any further image processing.

Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR) was carried out using Perkin Elmer Spectrum One FTIR Spectrometer with Spectrum software version 5.0.1 and fitted with a Universal ATR Sampling Accessory. The ATR crystal used was a diamond/thallium-bromoiodide (C/KRS-5) with a penetration depth up to 2 µm ATR-FTIR is primarily a surface technique and the exposed diameter of the crystal was 1.33 mm resulting in a sample area of around 1.39 mm^2. 32 scan accumulations were used at a resolution of 4 cm^{-1}. Three replicates were measured from unsoiled regions of each cloth and the average spectrum calculated for use in subsequent analysis. The spectra were baseline corrected using a linear correction. All subsequent spectral processing and statistical analysis was carried out using the UnScrambler® X Version 10.5 software package. The averaged spectra were smoothed using the Savitzky-Golay polynomial with order 3 with the smoothed spectra examined to ensure that no important information was lost.

Principal Component Analysis (PCA) is a statistical method which reduces large data sets to a smaller number of components which describe the major differences between the samples. The region of the FT-IR spectra selected for analysis was 1200 cm^{-1} to 1800 cm^{-1} as this is the region

where the molecular vibrations associated with the tannins and flavones are predominant and excludes the large cellulose peak at ~1000 cm^{-1} which is common to all samples. Prior to PCA analysis the smoothed spectral data were corrected using the detrend method on Unscrambler® with a 2nd order polynomial. The detrend function removes any nonlinear trends from the data and corrects for any residual baseline curvature. The number of components for the PCA was evaluated by examining the total variance plot to determine the optimum number of components for each data set. Plots of the PC scores can reveal clustering of samples which have common features in their spectra. Interpretation of the scores plots is achieved by examination of the loadings plots in association with the second derivative spectra alongside the FTIR spectra of the samples.

Hierarchical clustering analysis (HCA) was performed to classify the cloths into clusters with the aim of understanding the closeness of the relationships between cloths by measuring the distance between samples. Here this was achieved by partitioning the data into three groups using complete linkage clustering and measuring the Euclidean squared distance between the groups. The results of this analysis are presented visually in a dendrogram.

4. Results and discussion

Stereomicroscopy alone can give a good indication of the fibres and their characteristics. Fig. 2 shows images of two cloths from the Hunterian collection E380-1 and E596-3 and the detail of these at two magnifications. There is some anecdotal evidence that cloths may be composed of two fibres [6] and this is also the conclusion drawn by these visual examinations. It is clear that E380-1 is composed of mixed fibres with the darker fibre presumably incorporated into the lighter wood during the beating process. However, E596-3 is a typical cream/white cloth made from only one species and in this case the striped effect is a slight variation in colour due to the beater's marks. But this is the limit of the information that stereomicroscopy can give when used to view a cloth.

From the contemporary barkcloth spectra (Fig.3A) it is clear that the spectrum for the mamaki cloth (PA T73) is different with clear peaks shown at 1603, 1315 and at 779 cm^{-1}. The peaks can be attributed to a combination of the C=C stretching of the aromatic ring [28, 29], C-O vibration in syringyl derivatives [30,31] and CH_2 bending and stretching [32] of the associated polysaccharides [25,3 ,34] respectively. Falcão and Araújo [34], stated that the intense band at 1325 cm^{-1} (O-H deformation vibration) that can overlap with a C-O-C stretching vibration around 1310 cm^{-1}, and the band at 762 cm^{-1} (sugar ring, breathing vibration) is consistent with the presence of hydrolysable tannins. Many of the differences observed for this spectrum may be attributed to mamaki cloth being more highly coloured than the other cloths suggesting a higher concentration of aromatic groups. This is confirmed by the high intensity of the peaks associated with C=C stretching of the aromatic ring at 1600 and 1450 cm^{-1}. Table 3 assigns the peaks identified.

Various attempts were made to try and find a suitable region within the ATR-FTIR spectra with which to perform PCA with each attempt failing to separate the contemporary cloths into distinct groups. The exceptions to this were the mamaki samples which were very different to the others and indeed were identified as outliers by the statistical analysis. Removing these points did not elucidate any distinct groupings for the other cloths. One of the reasons for this may be the difficulty in reproducing the retting process of the barkcloth which can be followed by the disappearance of the carbonyl (C=O) peak at around 1735 cm^{-1} which is associated with pectin and hemicellulose [4]. For the historical cloths there is little evidence of this stretch in the spectra (Fig.3B) [26,32] confirming that these cloths have been subjected to a retting process. This is in

contrast to that observed for the contemporary barkcloth samples (Fig. 3A) indicting that perhaps the manufacture of these reconstructions varied greatly and some methods did not fully remove these components. In addition, the age of the historic cloths may have also contributed to this decrease. The clear spectral differences between contemporary and historic cloth of the same species and the difficulty in recreating aged barkcloth have led to the conclusion that no useful information can be obtained by further statistical evaluation of the contemporary barkcloth samples.

Fig. 3B shows the ATR-FTIR spectra of the historic cloths. The main visual difference between the spectra is observed in the position of the spectral band between 1600 cm^{-1} and 1650 cm^{-1}. The changing spectral position is most likely due to changing intensities of spectral bands underneath the broad spectral peak at this position. Peaks in this region are associated with the C=O stretching of the flavones, O-H stretching and C=C stretching of the aromatic rings [28, 29, 32, 36, 37, 38, 39]. In all cloths the broad peak observed at ~1000 cm^{-1} is mainly due to cellulose and hemicellulose [32, 40]. Overall visual inspection of the ATR-FTIR spectra is insufficient to elucidate any appreciable differences between the barkcloth samples. Although changes to the peak positions in the 1800 - 1450 cm^{-1} spectral region are observed it was difficult to obtain any clear and consistent definition between the samples (Fig. 3B). Principal component analysis (PCA) was then employed to determine if differences between the samples could be highlighted within a statistical model [11, 37, 40].

Initially the number of principal components required to fit the data was determined from evaluation of the explained variance plot which suggested that 4 PCs were required to explain 97% of the variance in the data set. In fact 81% of the overall variance can be explained by the first 2 components. Fig. 4 shows the scores plot for the first two principal components obtained for PCA analysis of the historic cloths with 56% of the data described by PC1 and 25% by PC2 and no outliers identified. Inspection of the scores plot clearly shows that the data splits into 3 well identified groups where in each grouping we have an indication of the species of some cloths based on art historical and curatorial documentation. The group circled in blue are cloths containing mamaki fibre and the group circled in red are composed of either breadfruit or banyan based on our confidence in the labelling of these cloths at source. The final group outlined in green contains cloths which are thought to be paper mulberry based on curatorial labelling which we are confident is correct but has not been verified as having been labelled at source. Examination of the spectral loading line (Fig. 5) for PC1 and PC2 allows interpretation of the data when viewed along with the FTIR and the second order derivative spectra (Fig. 6). Fig. 6A shows the spectra for two cloths which separate along the PC1 score axis while Fig6B gives the spectra for two cloths which separate along the PC2 axis. The PC1 loadings plot (Fig. 5) has a maximum positive value at 1606 cm^{-1} which aligns with the broad peak in the FTIR spectra (Fig. 6Ai) which shows a clear difference for the spectra plotted suggesting that PC1 is separating cloths based on C=C stretching of the aromatic ring and the C=O stretching of polyphenol compounds both of which are observed in this region. The C=C stretching can be assigned to the tannins in the wood [41] and the C=O to the lignin and tannins which are composed of highly branched polyphenolic macromolecules. This can make determination of changes in lignin over time difficult to detect using FTIR alone. However, the differences in tannin content may be very useful in determining differences between the species as it is clear from visual examination that the amount of 'colour' present in the species of interest varies. It is likely that shifting of the peak position here is due to the changing intensities of the molecular vibrations identified in this region. The broad negative peak for the PC1 loading centred at 1482cm^{-1} does not

identify with a peak in the FTIR spectrum. However, close examination of the 2nd derivative (ringed in Fig. 6Aii) clearly shows differences in this region. In fact E591-4, which has positive score for PC1 has a positive peak in this region whereas 73329 has a negative peak and the negative score (Fig. 4). This spectral observation is as a result of subtle peak shifts in this region of the spectrum which the 2nd derivative is clearly sensitive to and does not correspond to an actual peak in the FTIR spectrum. However, there is clear evidence from Fig. 5 that the PCA analysis is sensitive to changes in this region.

From the loadings plot for PC2, an increase in the peak at 1518 cm^{-1} is correlated with a decrease in the peak observed at 1426 cm^{-1}. Given the positive value for the blue group this would suggest that this component is strongly influenced by the aromatic stretching in 1518 cm^{-1} region between the C=C of the benzene ring (table 3). This is also observed in the 2nd derivative spectra (Fig. 6Bii) where a negative peak is noted for E380-1 along with a positive score for PC2 (Fig. 4) and a positive peak in the 2nd derivative spectra alongside a negative score for E417-1. This may be consistent with the concentration of coloured aromatic components associated with cloths made from specific species. Overall score plots containing higher principal components did not reveal any further clear grouping for the historic cloths.

Therefore, by examination of the PC loadings plots alongside the 2nd derivative spectra it is possible to identify the differences in the FTIR spectra which are responsible for the groups identified in the PCA score plots in Fig. 4.

In order to further analyse the results obtained from PCA, HCA was performed with the dendrogram obtained given in Fig.7. The three clusters identified align perfectly with the groupings obtained in the PCA analysis. Interesting the cloths, E380-1 ABU4001, ABU4006 form a close linkage which also connects into the large group of cloths which are thought from historical records to be paper mulberry. This association could be due to the use of two species, including paper mulberry, in the preparation of these cloths and perhaps strengthens the visual evidence which suggested that these cloths form a striped pattern of two different coloured barks.

6. Conclusions

In this preliminary study of contemporary and historic bark cloth multivariate analysis of FTIR spectra in the 1200-1600 cm^{-1} region has been shown to be useful in grouping historical barkcloths originating from different species. PCA analysis identified three groups for the historical cloth with the loading plots highlighting where the differences between the FTIR spectra are predominant for each PC. In addition, employing HCA to analyse the data identified the cloths which have a close relationship to each other and showed a clear link between the cloths which are thought to be composed of mixed fibres. This shows the usefulness of this statistical technique to historic bark cloth analysis. This knowledge would add significant information to museum collection records both in terms of curatorial as well as conservation practice. An additional advantage of this technique is that a scientist with FTIR experience could reliably determine different grouping of barkcloth species using this methodology, it is not dependant on specialist knowledge of plant anatomy.

However, no useful information was obtained from the contemporary barkcloth samples to inform the model.

It should be noted that the presence of added colourants may affect the ability of FTIR, a vibrational spectroscopy technique, to differentiate between species' differences and cloths where pigments have been added need more careful analysis. Light microscopy of the cloths helps to

determine if and how colourants have been applied and is therefore a useful preliminary step before undertaking FTIR.

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Figure titles

Fig. 1A.

Contemporary barkcloth samples A) *Broussonetia papyrifera*, (B) *Artocarpus altilis*, (C) *Ficus prolixa* and D) *Pipturus albidus* .

Fig. 1B.

Historic cloths A) Hunterian Collection E417/1 (size 1010mm x 684mm), B) Royal Botanic Gardens Kew Economic Botany Collection 42760 labelled banyan and breadfruit (60mm x 55mm, 65mm x 45mm) C) Hunterian Collection E380-1 (size 185mm x 200mm)

Fig. 2.

Images and stereomicroscopy at two magnifications of E380/1-A, B and C and E596/3-D, E and F.

Fig. 3.

A.ATR-FTIR spectra of contemporary barkcloth samples 2071958 *Broussonetia papyrifera*, 2071958 *Artocarpus altilis*, 2071958 *Ficus prolixa* and T73 *Pipturus albidus* .

B. ATR-FTIR spectra of historic clothes Hunterian Collection E417/1, Royal Botanic Gardens Kew Economic Botany Collection AA 42760 and FP42760 and Hunterian Collection E380/1.

Fig.4.

PCA of historic barkcloths from four collections, PC1 v PC2 showing 3 groupings

Fig.5.

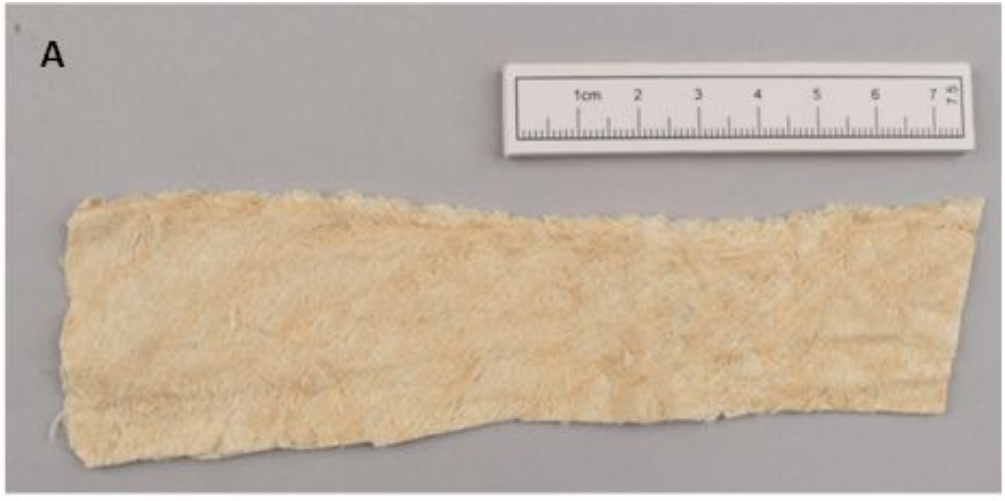
Loadings of PC1 and PC2.

Fig.6.

Spectra (i) and 2nd derivative (ii) 1800-1500cm^{-1}A. 73329 and E591/4 differentiated along PC1. B. E380/1 and E417/1 differentiated along PC2.

Fig.7.

Dendrogram showing three clusters identified.


A
1cm 2 3 4 5 6 7 7.5


C
1cm 2 3 4 5 6 7 7.5


B
1cm 2 3 4 5 6 7 7.5


D
1cm 2 3 4 5 6 7 7.5


A


B
Native cloth
manufactured from
bark of
KALOLA (KAKORI
(Banyan)
Native cloth from
BETA (Breadfruit
tree).
Roviana,
New Georgia

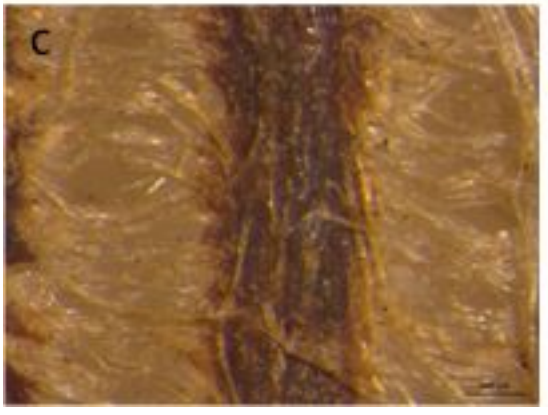

C

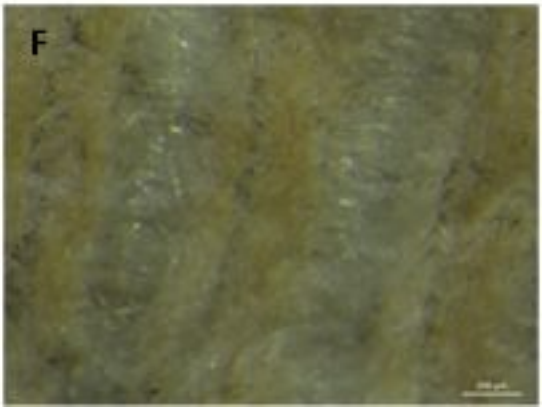

A

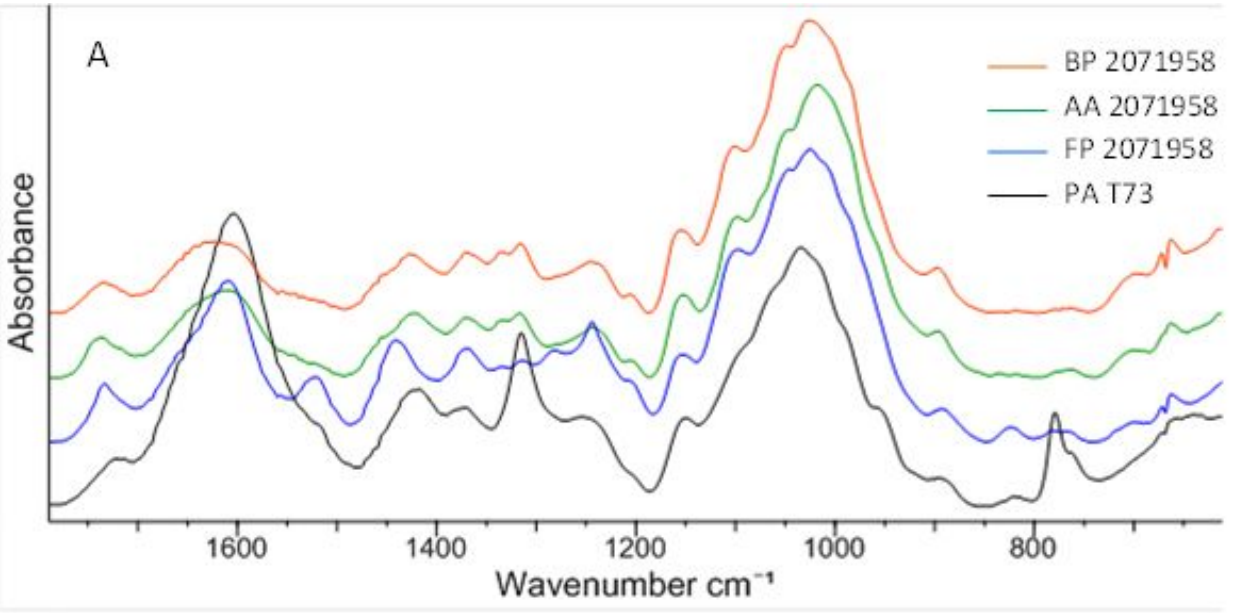

D

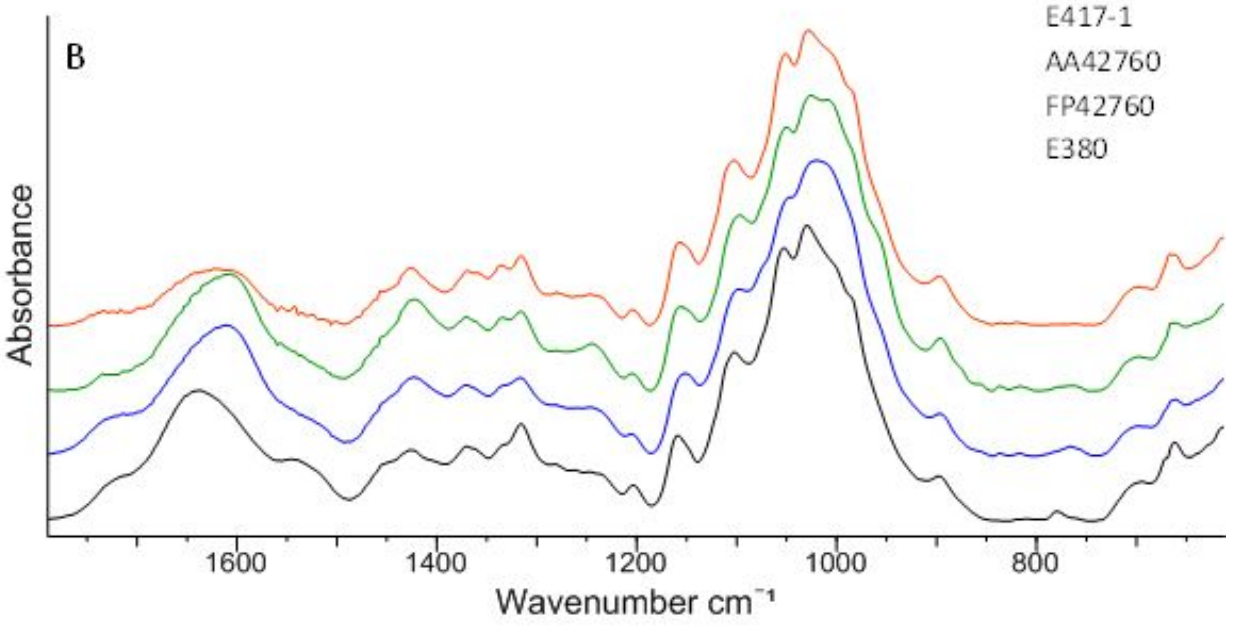

B

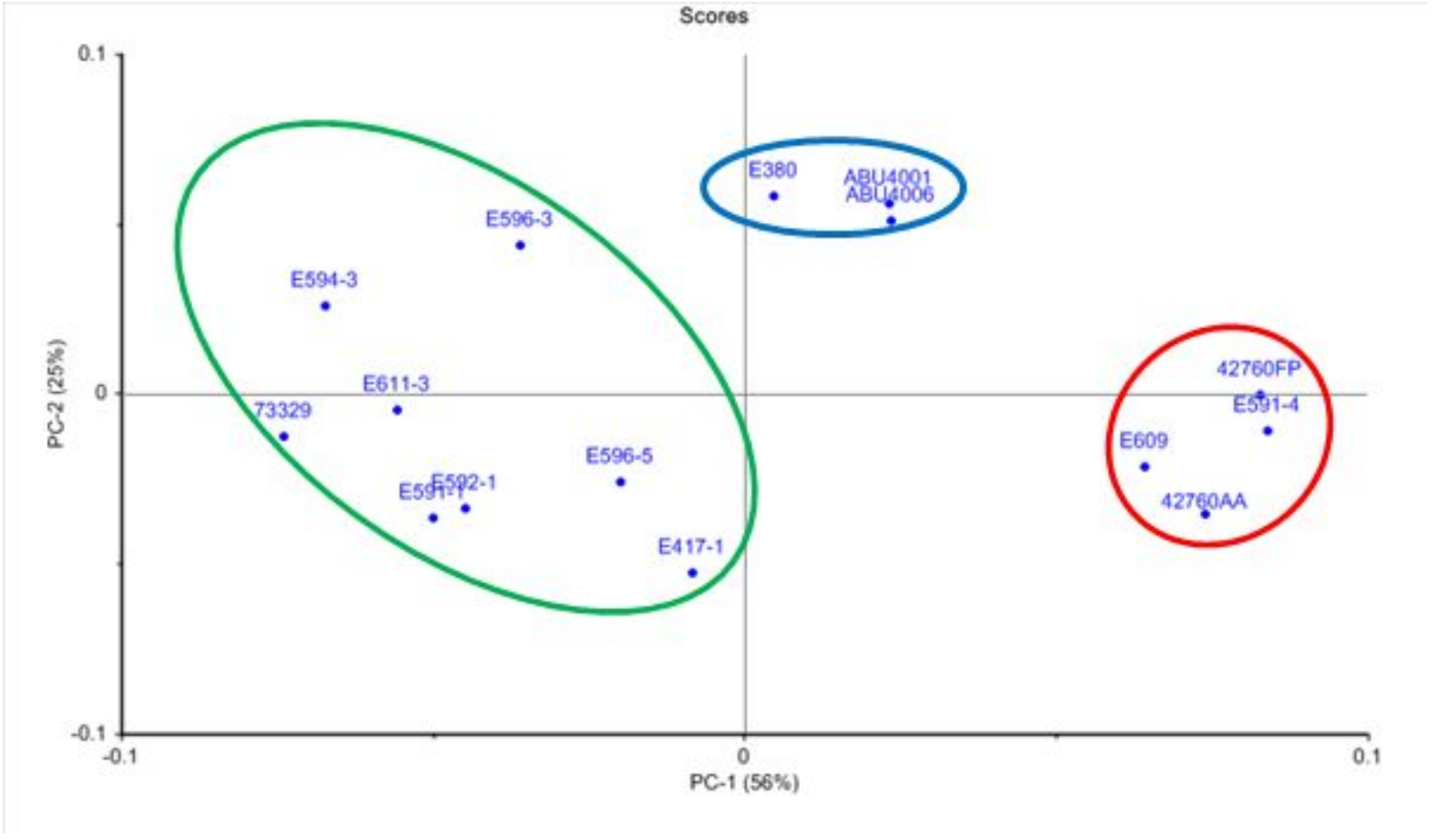

E

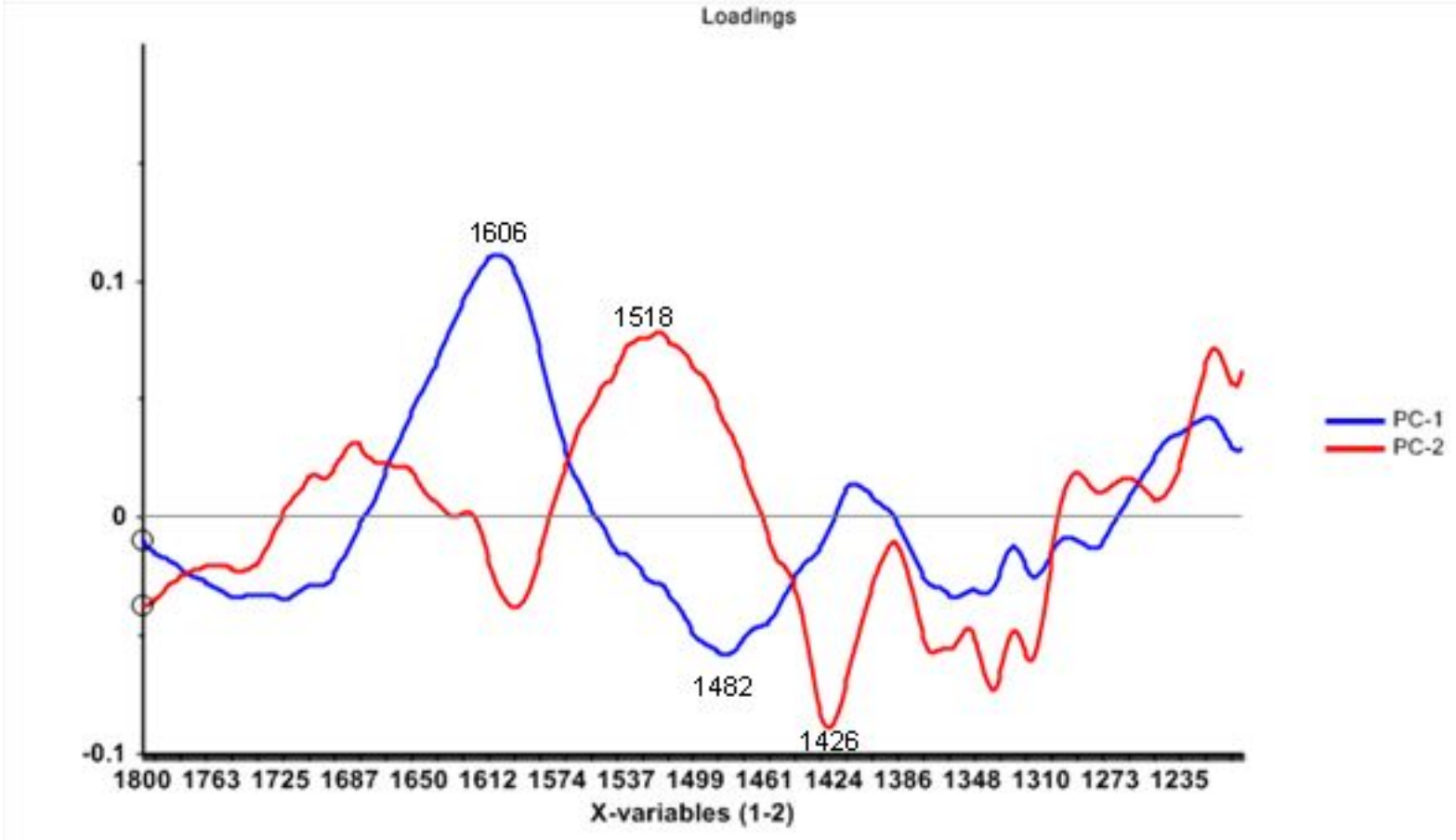

C

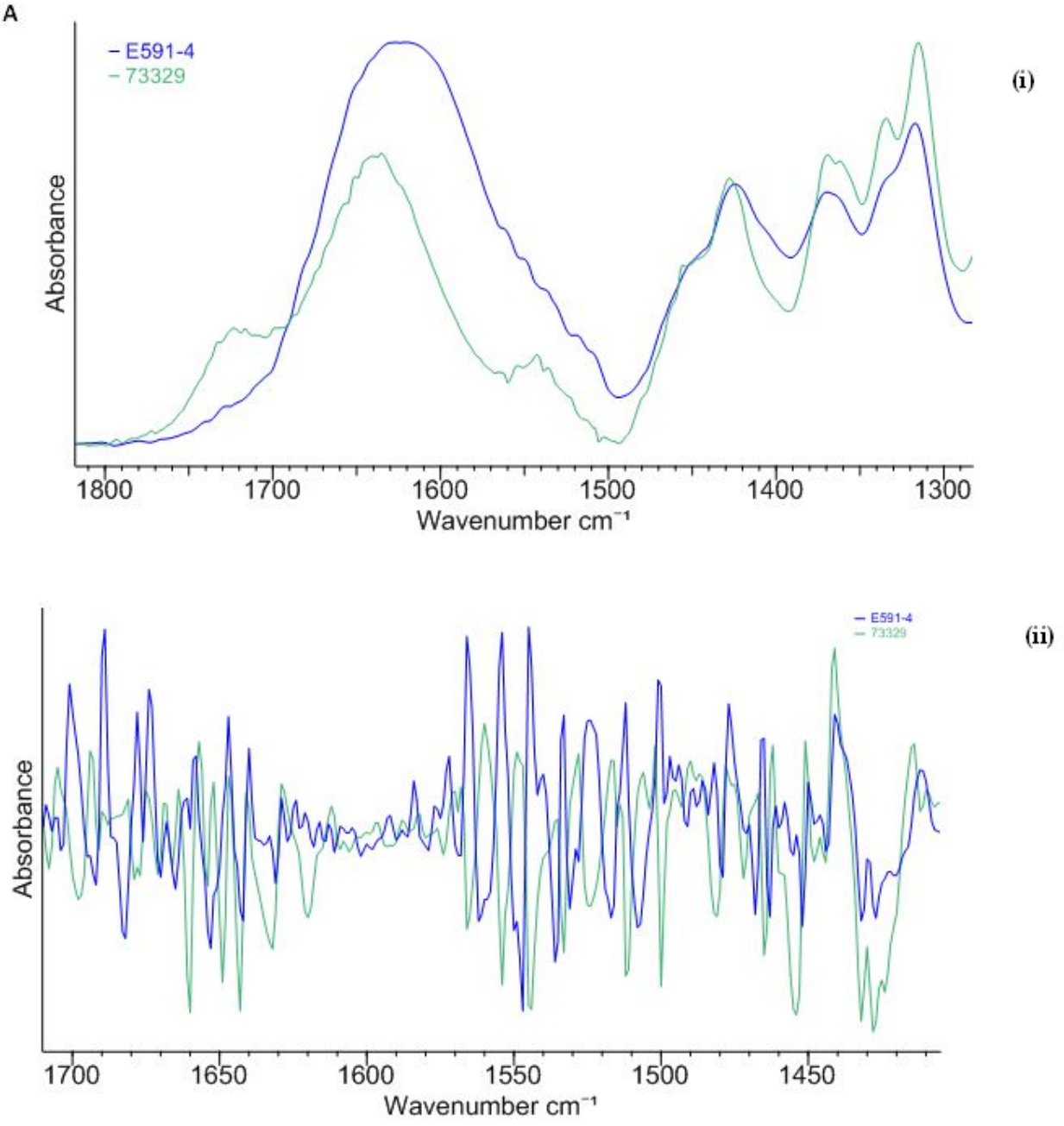

F


A
BP 2071958
AA 2071958
FP 2071958
PA T73
Absorbance
1600
1400
1200
1000
800
Wavenumber cm⁻¹

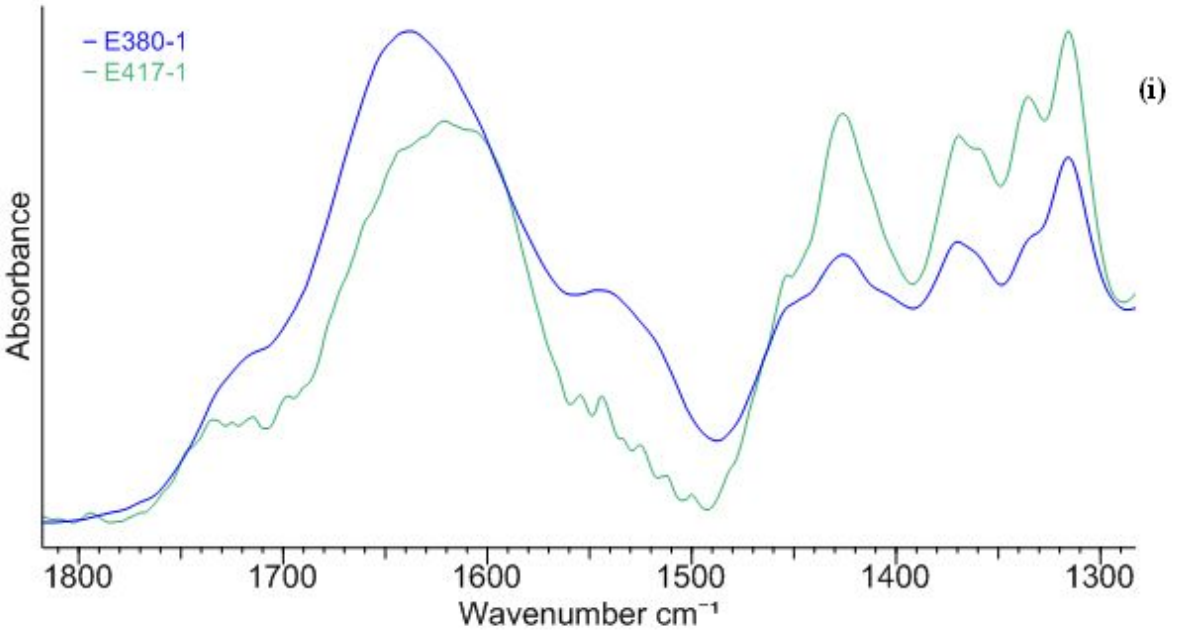

B
E417-1
AA42760
FP42760
E380
Absorbance
1600
1400
1200
1000
800
Wavenumber cm⁻¹


Scores
0.1
0
-0.1
-0.1
0
0.1
PC-2 (25%)
PC-1 (56%)
E380
ABU4001
ABU4006
E596-3
E594-3
E611-3
73329
E596-5
E592-1
E591-1
E417-1
42760FP
E591-4
E609
42760AA


Loadings
1606
1518
1482
1426
0.1
0
-0.1
1800 1763 1725 1687 1650 1612 1574 1537 1499 1461 1424 1386 1348 1310 1273 1235
X-variables (1-2)
PC-1
PC-2

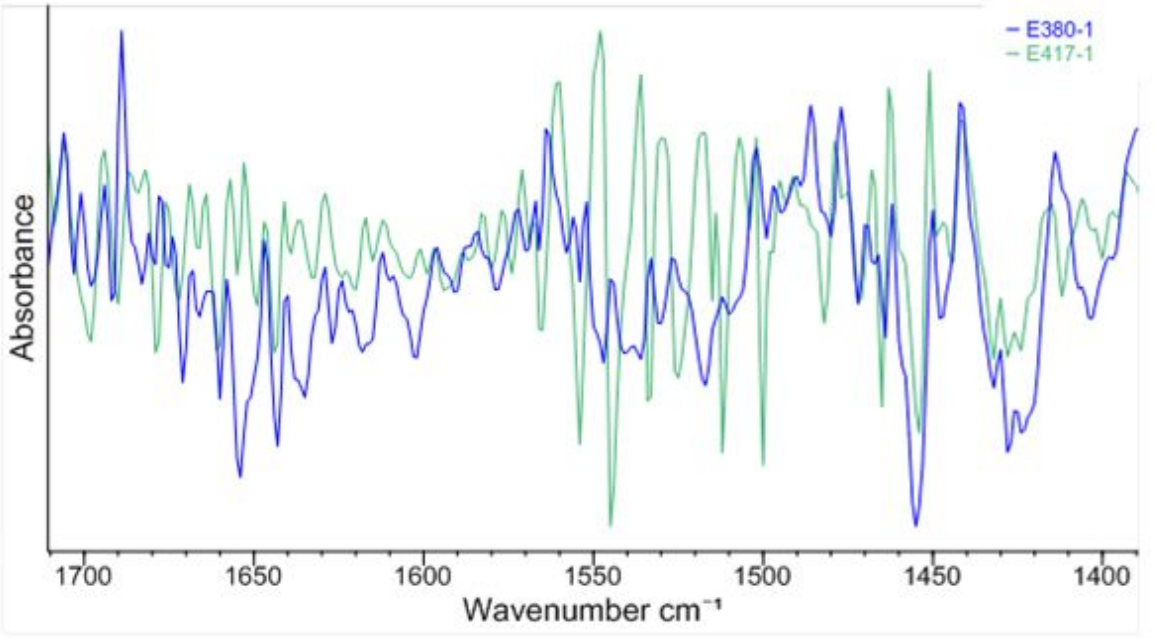

A
E591-4
73329
(i)
Absorbance
1800
1700
1600
1500
1400
1300
Wavenumber cm⁻¹
E591-4
73329
(ii)
Absorbance
1700
1650
1600
1550
1500
1450
Wavenumber cm⁻¹

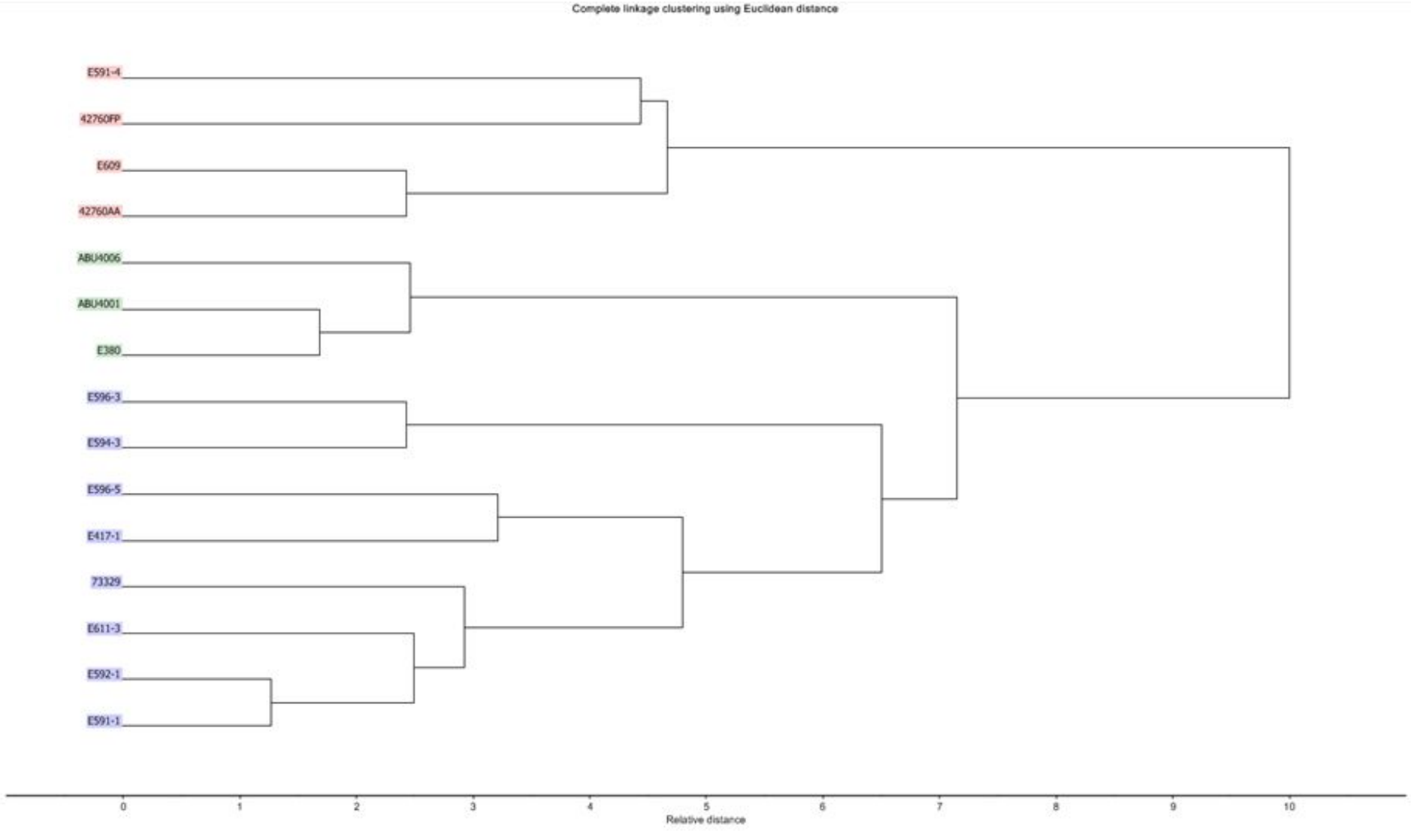
B


E380-1
E417-1
Absorbance
1800
1700
1600
1500
1400
1300
Wavenumber cm⁻¹

(i)

(ii)


E380-1
E417-1
Absorbance
1700
1650
1600
1550
1500
1450
1400
Wavenumber cm⁻¹


Complete linkage clustering using Euclidean distance
E591-4
42760FP
E609
42760AA
ABU4006
ABU4001
E380
E596-3
E594-3
E596-5
E417-1
73329
E611-3
E592-1
E591-1
0
1
2
3
4
5
6
7
8
9
10
Relative distance

Contemporary barkcloth samples	Accession number	Origin	Donation/ accession date
BP	2069806	American Samoa	2013
BP	2071953	Kingdom of Tonga	2015
BP	2071958	Marquesas Island	2014
BP	T15	Suitland, MD	2013
BP	T16	Suitland, MD	2013
BP	T74	Tonga	
BP	T75	Tonga	
BP	T77	Tonga	
BP	T80	Easter Island	2014
BP	T82	Easter Island	2014
BP	T83	Easter Island	2014
AA	2071958	Marquesas Island	2014
AA	T14	Hawaii	2012
AA	T19	Hawaii	2012
AA	T76		
AA	2069812	Cook Islands	2014
FP	2071958	Marquesas Island	2014
FP	2069812	Cook Islands	2014
PA	T21	Hawaii	2012
PA	T23	Hawaii	2012
PA	T73 (beaten)	Hawaii	
PA	T73 (more beaten)	Hawaii	

Table 1 Contemporary barkcloth samples supplied by Smithsonian National Museum of Natural History, Washington, DC, *Broussonetia papyrifera* BP; *Artocarpus altilis* AA; *Ficus prolixa*; Pipturus *albidus* PA.

Collection	Accession number	Origin (tentative)	Donation date
Hunterian Museum	E380-1	Hawaii	1826
	E417-1	Samoa	1783
	E591-1	Tahiti (attribution)	1809
	E591-4	Polynesia	1809
	E592-1	Samoa (attribution)	1689
	E594-3	Tahiti (attribution)	NA
	E596-5	Tahiti (attribution)	NA
	E596-3	Tahiti (attribution)	NA
	E609	Tahiti (attribution)	NA
	E611-3	Hawaii (attribution)	NA
Economic Botany Collection	42760 (AA)	Solomon Islands	1929
	42760 (FP)	Solomon Islands	1929
	73329	Tahiti	1874
University of Aberdeen Museums	ABDUA4001	Hawaii	NA
	ABDUA4006	Hawaii	NA

Table 2 Historic barkcloths (Not available NA)

Wavenumber Range (cm^{-1})	Band and Assignment	References
1740 -1720	Xylan C=O and hemicellulose C=O stretch unconjugated ketones, carbonyls and in ester groups (frequently of carbohydrate origin) and aliphatic groups (xylan)	[28, 30, 39, 35]
1650 - 1635	Water associated with lignin or cellulose and conjugated C-O C=O stretching in flavones	[28, 29, 32, 36]
1630 - 1610	Assigned to tannins C=C associated with aromatic bond of condensed tannins C=O stretching in flavones C=O stretching flavonoids (extractives)	[4, 37, 38, 39, 41]
1610 - 1590	C=C stretching of aromatic ring	[28, 29]
1520 - 1500	Aromatic skeletal vibration plus C=O stretch Aromatic skeletal vibration C=C characteristic of lignin C-C stretch bands within ring skeleton	[15, 20]
1450	C=C associated with aromatic bond of condensed tannins	[38]
1420 - 1430	Aromatic skeletal vibrations, C-H plane deformation of cellulose C-H deformation in lignin and carbohydrates CH_2 scissoring in lignin and carbohydrates	[32, 43, 44]
1375	C-H in plane deformations for polysaccharides	[40]
1330 - 1310	C-O vibration in syringyl derivatives Condensation of guaicyl unit, syringyl unit and CH_2 bending, stretching	[30, 31] [32]
1270 - 1260	Guaicyl ring and C-O stretch lignin and xylan	[38]
1230 - 1220	C-O-C stretching in phenol-ether bonds of lignin Syringyl ring and C-O stretch in lignin and xylan	[32] [39]
1175 - 1155	C-O-C antisymmetric bridge stretching vibration in cellulose and hemicellulose C-O-C stretching in pyranose rings, C=O stretching in aliphatic groups	[32, 40]
1140	Aromatic C–H in-plane deformation; typical for G units,	[28, 29]
1030	C-O deforming in secondary alcohols and aliphatic ethers	[32]
900 - 895	Cellulose , C-H stretching out of plane of aromatic rings	[32]
850 - 835	Aromatic C-H out-of-plane deformation (extractives and lignin)	[39]
820 – 775	Vibrations of the C-H bonds in benzene rings Vibrations of galactans	[27, 33, 34]

Table 3 Characteristic infrared bands for wood.

Table 1 Contemporary barkcloth samples supplied by Smithsonian National Museum of Natural History, Washington, DC, *Broussonetia papyrifera* BP; *Artocarpus altilis* AA; *Ficus prolixa*; *Pipturus albidus* PA.

Table 2 Historic barkcloths (Not available NA)

Table 3 Characteristic infrared bands for wood