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Technical Note

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Investigating the Properties of Folded Parchment – A Preliminary Study

Untersuchung der Eigenschaften von gefaltetem Pergament – eine Vorstudie

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Abstract: Parchment manuscripts form an important part of many historic collections. They are often found folded, with some displaying multiple fold patterns resulting from changing uses over their history. Parchment is a potentially fragile medium and folding can increase its susceptibility to damage, as well as hampering access and display. Treatment to address these issues may involve the relaxation of the folded structure, using humidification or a solvent such as propanol, and gentle pressing or stretching. However, this presents a dilemma – an inappropriately folded manuscript may be more prone to damage, but treatments require invasive interventions. This preliminary study has employed infrared spectroscopy and shrinkage temperature measurements to better understand the properties of folded parchment. It demonstrates that physicochemical changes can be detected at the fold and, to a lesser extent, in adjacent areas, compared to the bulk material, and that monitoring these changes allows the impact of different treatment methods to be assessed. This provides a basis for further research into the effect of both the original folding and of potential treatment methods, to inform conservation decisions and help ensure appropriate, effective, and sympathetic outcomes.

Keywords: folded parchment, humidification, shrinkage temperature, FTIR-spectroscopy

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Zusammenfassung: Pergamenthandschriften bilden einen wichtigen Teil vieler historischer Sammlungen. Sie werden oft gefaltet aufbewahrt, wobei sie auch mehrere Faltungen aufweisen können, die sich durch die unterschiedlichen Verwendungen im Laufe ihrer Geschichte ergaben. Pergament ist ein potenziell fragiles Medium, und die Faltung kann die Anfälligkeit für Schäden erhöhen sowie den Zugang und die Präsentation erschweren. Um diese Einschränkungen zu überwinden, kann man das Pergament befeuchten oder ein Lösungsmittel wie Propanol einbringen und es danach leicht beschweren oder spannen. Dies stellt jedoch ein Dilemma dar, denn wenngleich ein unsachgemäß gefaltetes Pergament anfälliger für Schäden ist, erfordert die Behandlung jedoch invasive Eingriffe. In dieser Vorstudie wurden die Eigenschaften von gefaltetem Pergament mittels Infrarotspektroskopie und Schrumpfungstemperaturmessungen untersucht. Erste Ergebnisse zeigen, dass physikalisch-chemische Veränderungen im Bereich der Faltungen und, in geringerem Ausmaß, auch in angrenzenden Bereichen stattgefunden haben. Eine genaue Charakterisierung dieser Veränderungen ermöglicht es, die Auswirkungen verschiedener Behandlungsmethoden besser abzuschätzen. Dies bietet die Grundlage für die weitere Erforschung der Auswirkungen sowohl der ursprünglichen Faltung als auch möglicher Behandlungsmethoden, und bietet eine Grundlage für konservatorische Entscheidungen.

Schlüsselworte: gefaltetes Pergament, Befeuchtung, Schrumpfungstemperatur, FTIR-Spektroskopie

1 Introduction

Parchment manuscripts form an important part of many historic library, archive, and museum collections. They are often found folded, either as an aspect of their original format or of their subsequent history; some exhibit multiple fold patterns indicative of changing uses. Once accessioned into a collection, folding may also result from storage choices, as a method of saving space, allowing items to be housed with associated objects or to accommodate existing storage furniture and facilities. To access, display or otherwise use such items, it is necessary to understand the nature of the material and the effects of folding on its physical and chemical properties.

Parchment has been used as a writing substrate since at least several centuries BC. It is formed from untanned animal skins which have been de-haired and de-fleshed, then scraped and dried under tension; during this stage, additional treatments may be applied to remove unwanted components such as fats and to smooth and stabilize the surface of the material. The effect of this processing is to remove the epidermis and the hypodermis, leaving the central skin layer, the dermis, which is principally composed of the protein collagen. Parchment is prone to physical, chemical, and microbiological deterioration, processes which often occur in combination. A particularly characteristic form of parchment degradation is gelatinisation, in which collagen denatures, with the triple helix structural elements of the protein dissociating to form a random coil structure. Gelatinisation is associated with exposure to water and is accelerated by heat and the effects of pre-existing damage through oxidisation and hydrolysis. Gelatinisation can be recognised in parchment through the presence of glossy or translucent regions in the material; these areas are mechanically weaker, more susceptible to chemical attack and at risk of separation in fluctuating environmental conditions due to their differing physical responses, thereby rendering the material as a whole vulnerable (Kennedy and Wess 2003; Larsen 2007; Maxwell, Wess, and Kennedy 2006; Ralston 2000; Robinet 2021).

As parchment is a potentially fragile medium, folding can induce damage through physical stresses both at the bulk (Figure 1) and microscopic (Figure 2) levels, ingraining of dirt and increased susceptibility to gelatinisation, and may

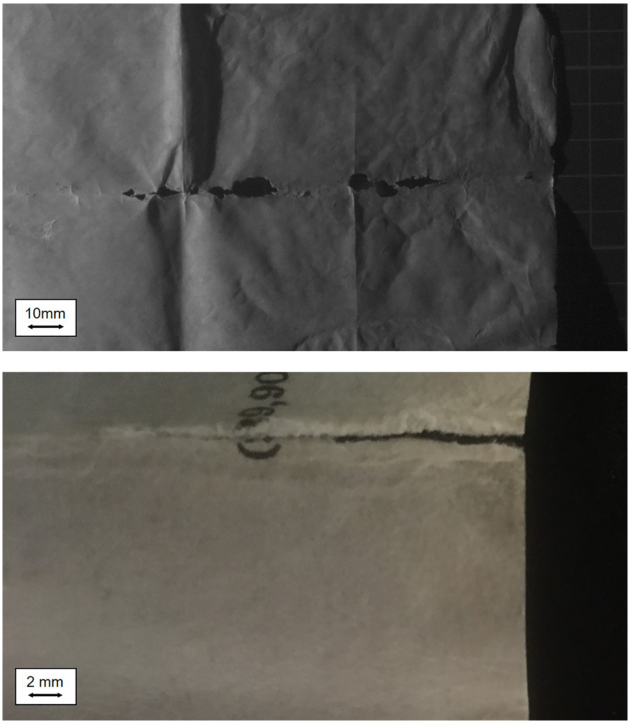

Figure 1: Splitting of a parchment document along the line of a fold.

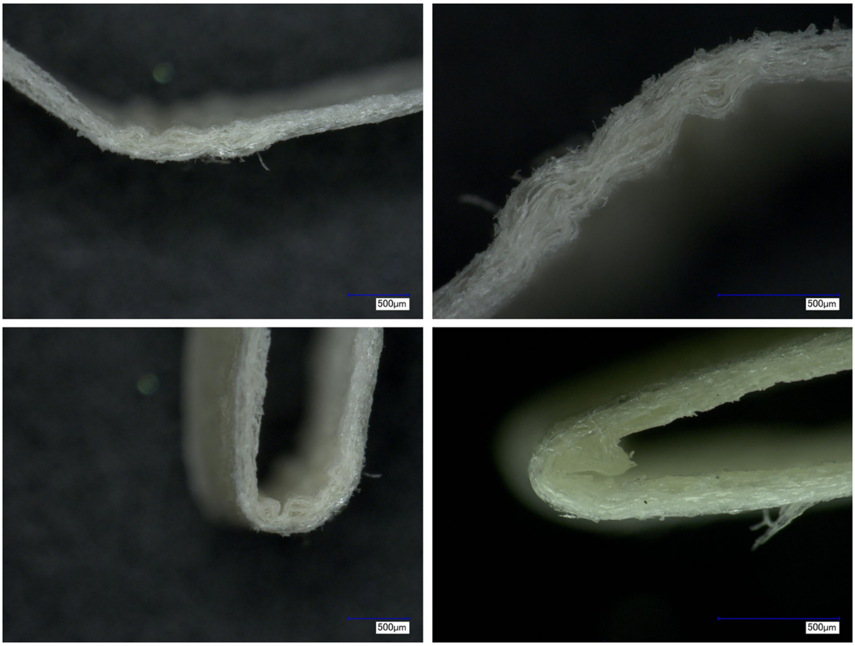

Figure 2: Evidence of delamination/defibrillation of parchment in the region of folds.

also loosen friable inks and pigments. Furthermore, if folded documents cannot be readily opened out, this will hamper their sympathetic handling and ability to be readily accessed, used, and displayed.

Treatment to address these issues may involve the careful relaxation of the folded structure, using methods such as humidification or the application of a solvent such as propanol, along with gentle pressing or stretching. Factors which would influence a decision to carry out this kind of treatment include facilitating the handling of the item, reducing physical stresses on the material, reducing the potential for loss of information, and enabling better access to extant information. However, this presents a dilemma – an inappropriately folded manuscript may be more prone to damage and more difficult to use, but treatments require invasive interventions which also introduce the risk of damage. Understanding effects of both the original folding and of different treatment methods will inform conservation decisions and help ensure appropriate, effective, and sympathetic outcomes. A range of analytical techniques can potentially provide insights into these properties (Badea et al. 2008; Bicchieri et al. 2011; Cappa et al. 2020a, 2020b; Derrick 1991; Dolgin, Bulatov, and Schechte 2009; Garside and Knight 2013; Giacometti et al. 2012; Haines 1987; Možir et al. 2014).

The work presented here represents a preliminary study into the use of analytical techniques to investigate the properties of folded parchment, and to determine if such an approach will then allow the effects of treatment methods to be studied. Mid infrared spectroscopy and shrinkage temperature measurements have been used to assess differences in physicochemical properties between folded and unfolded parchment, and these methods have then been used to study methods of relaxing folds in these materials. These initial investigations raise points for debate about current approaches and provide a basis for further research.

2 Method

The properties of a set of four naturally aged historic folded parchment documents were studied (Table 1). These items were acquired for the research, and largely consist of legal documents; they were chosen on the basis that they possessed fold structures which appeared to be largely contemporaneous with their original use, that they were non-accessioned so could be subjected to sampling and destructive testing, and that their dates of origin could be approximated (dates given in Table 1 are those recorded on the documents, and it is assumed that the material was used reasonably soon after manufacture). Analysis was carried out on sections (15 × 15 mm) cut carefully from the documents using a scalpel. For each document, samples were taken both from the regions of folds (selected such that the fold ran along the centre of the sample) and from the bulk material away from any fold. These areas were selected to avoid areas of obvious damage, staining or alteration (except for the fold, where relevant), as well as regions with overlapping folds or the presence of text, to minimise the impact of other factors on the measurements. Folded sections were selected such that the 'peak' of the fold was on the grain side of the parchment, for consistency. Multiple measurements were derived from each section, and for each document, at least three separate sections were used for each type of area (bulk material or fold), depending on the number of suitable regions that could be identified which fulfilled the criteria above.

The samples were examined via microscopy, then analysed using mid infrared (attenuated total reflectance) spectroscopy and shrinkage temperature measurements (Badea et al. 2008; Bicchieri et al. 2011; Cappa et al. 2020a, 2020b; Derrick 1991; Dolgin, Bulatov, and Schechte 2009; Haines 1987; Možir et al. 2014). The aim of these analyses was not to produce absolute data that indicate the condition of the parchment documents in a manner which would be comparable to other studies, but rather to detect differences in properties between folded regions and the bulk material in individual documents, to determine that such an approach was

Table 1: Parchment documents used for analysis and testing.

Property		Item			
Reference name		Indenture	Summerfield probate	Indictment	Second schedule
Figure		Figure 3(a)	–	–	Figure 3(b)
Date		1826	1829	1884	1887
Substrate description	Dimension ($h \times l$)	529 × 815 mm	520 × 683 mm	553 × 705 mm	554 × 690 mm
	Thickness	0.23 mm ($\sigma = 0.02$)	0.23 mm ($\sigma = 0.09$)	0.21 mm ($\sigma = 0.05$)	0.18 mm ($\sigma = 0.03$)
	Stiffness	Medium	Medium	Low	Low
	Surface treatment	Previous treatment (flattening and infill) may have changed surface aspect.	Lightly burnished	Burnish, slightly shiny and oily on the flesh side	Burnish, slightly shiny, oily surface on the flesh side
	Animal origin	Sheep	Sheep (?)	Sheep	Sheep
Parchment condition		Ingrained dirt across document (esp. right and bottom edges); folds may have been flattened during previous treatment; parchment infill to replace missing area; stains (dirt: top right corner, verso; ink: right bottom corner; wax/oil: middle of document)	Surface dirt at edges; some localised gelatinisation; stains at edge.	Surface dirt; ingrained dirt across verso (especially on exposed areas, in creases and folds); finger-marks.	Surface dirt; ingrained dirt across verso (especially on exposed areas, in creases and folds); finger-marks.

Table 1: (continued)

Property	**Item**			
Media description	Carbon black ink and stamps (left edge). Text on both sides.	Iron gall ink; carbon black printing ink; stamp on verso. Text on grain side.	Iron gall ink; carbon black printing ink; blue pen and red ink (rule lines); stamp & signature on verso. Text on grain side.	Iron gall ink; carbon black printing ink; blue pen and red ink (rule lines); stamp & signature on verso. Text on grain side.

Figure 3: Examples of parchment document used in this research: (a) ‘Indenture’ and (b) ‘Second schedule’.

viable. Thus, although the shrinkage temperature measurements were not carried out using the conventional method and sampling technique, using a micro hot table (as in, e.g., Cappa et al. 2020a, 2020b; Haines 1987), but rather with a simpler set-up that was available at the time, this was felt to be acceptable for a pilot study. Figure 4(a) indicates the sampling positions for these technique in the bulk of the material, and Figure 4(b) shows how these were applied to specimens taken from the region of a fold, to determine properties along and adjacent to the fold

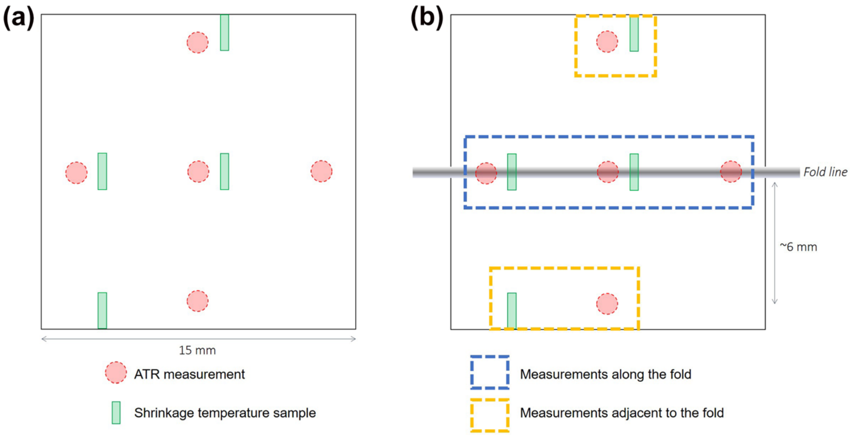

Figure 4: Sampling positions for ATR and shrinkage temperature measurements for specimens taken from parchment documents: (a) the bulk material; (b) material in the region of the fold (along and adjacent to the fold).

(approximately 6 mm distant); the sampling positions were chosen to also allow these samples to be used for a range of other analyses, if later considered appropriate.

2.1 Shrinkage Temperature

Shrinkage temperatures were measured using a modified melting point apparatus. Parchment samples of approximate size 2 × 0.5 mm were placed on a microscope coverslip on the heatable stage and covered with a single drop of purified water. The stage was then heated at a rate of 10 °C/min, with constant observation. The temperature at which the sample underwent distortion was measured. Between four and six measurements were taken for each area type for each document.

2.2 ATR Spectroscopy

Attenuated total reflectance Fourier-transform infrared (ATR FTIR) spectroscopy was carried out using a *PerkinElmer 'Spectrum 100'* spectrometer, fitted with a *'UATR'* ATR accessory (diamond crystal, single reflection). Spectra were subsequently investigated using *PerkinElmer 'Spectrum (v.10.02)'* software. Spectra were all recorded from the grain side of the material. The specimens were carefully scraped with a scalpel before analysis, to remove surface debris and any loose fibres or other material. Spectra were recorded over the range 4000–650 cm^{-1}, with a resolution of 4 cm^{-1} and 16 accumulations.

Changes in the relative characteristics of the amide I (C=O stretch) and amide II (N–H bend, C–N stretch) bands were investigated to give an indication of changes in the material, as follows (Derrick 1991): The wavenumber positions of the centres of the amide I and amide II bands were identified ($P_{amide.I}$ and $P_{amide.II}$), and the difference between them calculated ($P_{amide.I} - P_{amide.II}$); this is linked to protein denaturation, conversion of the relatively ordered collagen to disordered gelatine (with larger values indicating a greater degree of denaturation). The intensities of each of these bands above a baseline drawn from 1765 to 890 cm^{-1} were also measured ($I_{amide.I}$ and $I_{amide.II}$), and the ratio between them calculated ($I_{amide.I}/I_{amide.II}$); this is linked to protein hydrolysis (with larger values indicating a greater degree of hydrolysis). See Figure 5.

2.3 Humidification and Relaxation of Folds

A range of treatment methods for relaxing folded parchment were selected for investigation, based on treatment protocols identified by the conservators at the British Library (Singer and Hermans 1988; Wood 1995). These techniques included re-plasticisation using slow humidification (60% RH, one week), fast humidification (80% RH, 1.5 h) and isopropanol (applied as a spray) and applying gentle physical intervention with either uniform pressing or through the use of clips to

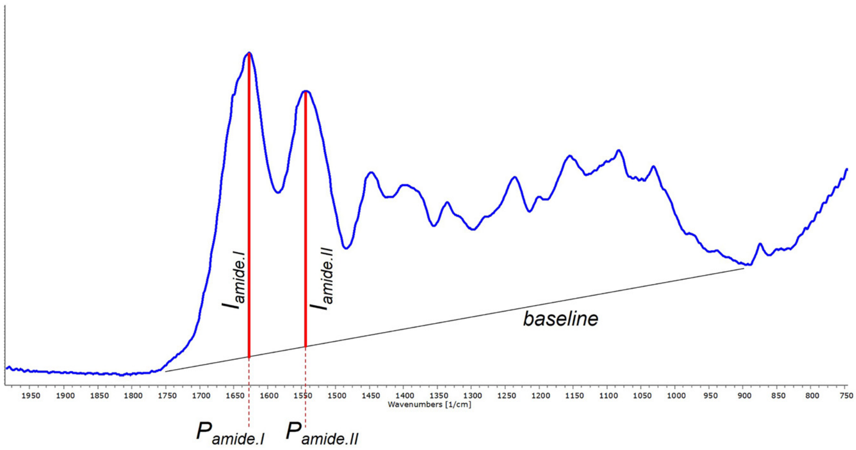

Figure 5: Derivation of parameters from mid infrared (ATR FTIR) spectra.

secure and tension the documents at their edges; in combination, this gave a total of six treatment regimes.

The effects of these treatment methods were assessed using the two techniques detailed above, with analysis carried out on sample before (i.e., untreated) and after treatment, as well as through condition assessment by a conservator. The sections selected for the 'before' and 'after' measurements were adjacent, to ensure that their original properties were as similar as possible.

3 Results and Discussion

3.1 Shrinkage Temperature

The average shrinkage temperature for the bulk material, and for material along and adjacent to the fold for each document is presented in Figure 6. It can be seen that in all four cases, the shrinkage temperature at the fold is lower than that of the bulk (by 4.3–6.6 °C, for these examples); a similar but smaller pattern is seen for measurements adjacent to the fold (by 1.2–2.7 °C). This suggests that the condition of the material along the line of the fold is impaired, and that even material has not been directly manipulated by the fold but is proximate to it has been weakened.

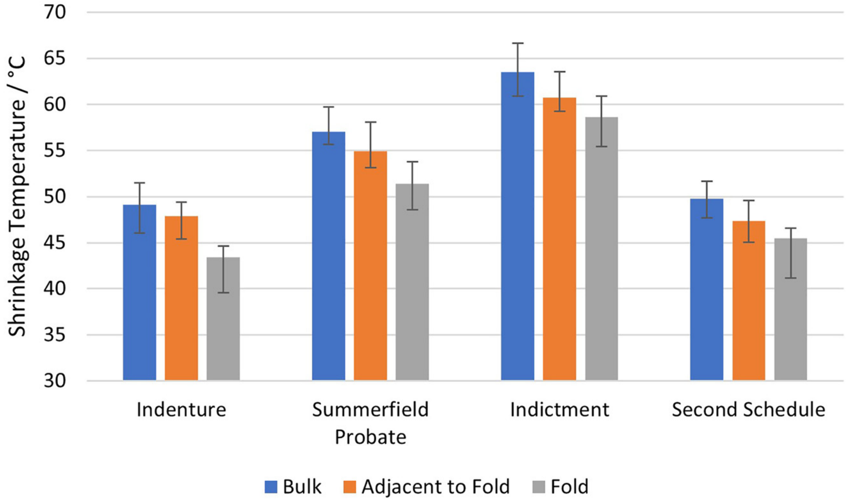

Figure 6: Average shrinkage temperatures for the bulk material, adjacent to the fold and on the fold, for the four documents (error bars represent the range of results).

3.2 ATR Spectroscopy

The ratio of intensities of the amide I and amide II bands ($I_{amide.I}/I_{amide.II}$) gave the clearest indication of a trend, as presented in Figure 7. This ratio has been linked to hydrolysis of parchment, with higher ratio values denoting greater degradation (Derrick 1991). From the data, it can be seen that in all cases the ratio derived from material at the fold is higher than that from the bulk material and an intermediate value is obtained from the region adjacent to the fold. This suggests that the parchment subjected to folding has undergone chemical deterioration (hydrolysis) to a greater extent than the document as a whole. This also corresponds to the trend observed with shrinkage temperature.

3.3 Humidification and Relaxation of Folds

Differences in shrinkage temperature and the FTIR-derived $I_{amide.I}/I_{amide.II}$ ratio before ('untreated') and after treatment were calculated. Results for the Summerfield Probate and the Indenture are shown in Figures 8 and 9; similar results were seen for the other samples. Conclusions about the suitability of different interventions have not been drawn, due to the small number of documents studied and the limited applicability of the method. However, the results from both techniques suggest that not only does parchment in the region of the fold tend to be in poorer

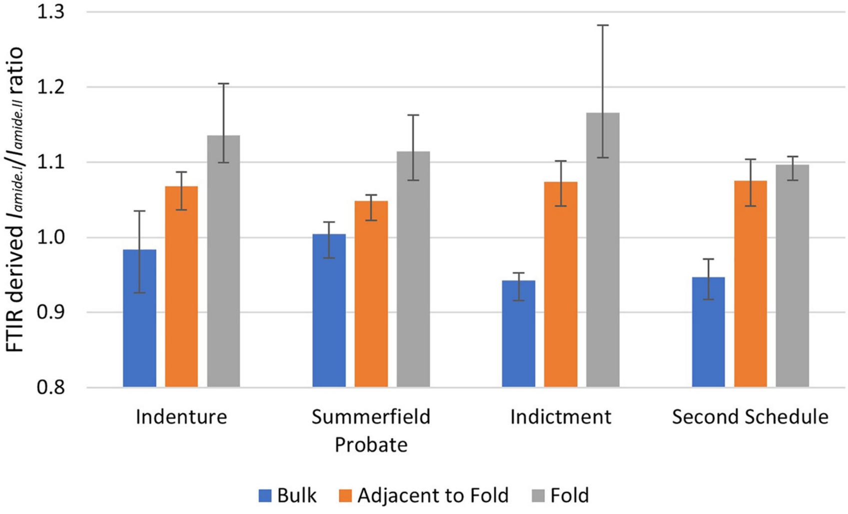

Figure 7: Average ATR FTIR derived $I_{amide.I}/I_{amide.II}$ ratios for the bulk material, adjacent to the fold and on the fold, for the four documents (error bars represent the range of results).

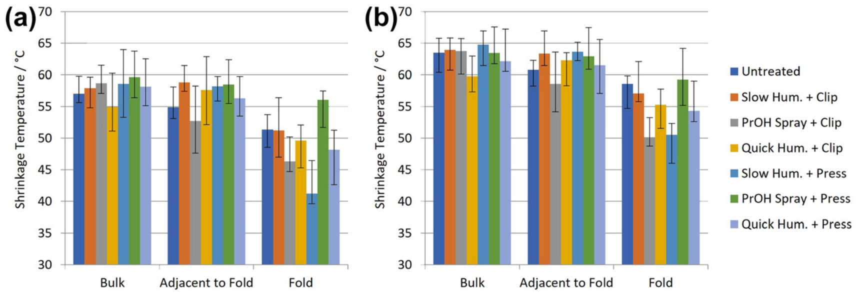

Figure 8: Change in shrinkage temperature after humidification treatments for (a) Summerfield Probate, and (b) Indenture (error bars represent the range of results).

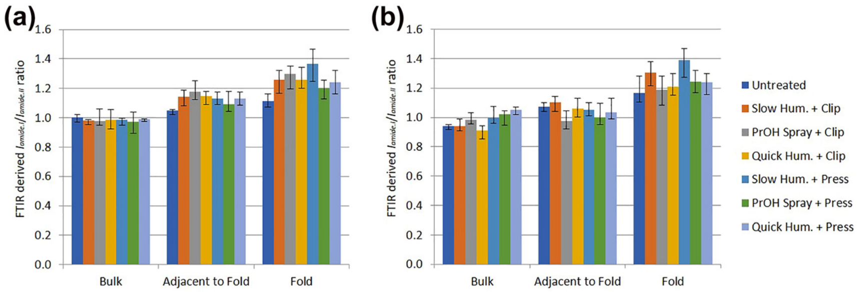

Figure 9: Change in ATR FTIR derived $I_{amide.I}/I_{amide.II}$ ratios after humidification treatments for (a) Summerfield Probate, and (b) Indenture (error bars represent the range of results).

condition, but also that it is more susceptible to further change when treated to relax the fold; furthermore the variability between different treatment methods, when measured in this way, is greater in the region of the fold, suggesting the behaviour of these areas is also more unpredictable. The results also support the broad agreement between the FTIR ratio and shrinkage temperature noted above, suggesting that a minimally invasive technique (e.g., FTIR) can provide useful information on these materials, which may help to inform conservation decisions.

4 Conclusion

This study suggests that both shrinkage temperature and $I_{amide.I}/I_{amide.II}$ intensity ratio measurements derived from ATR FTIR spectroscopy indicates that in the region of a fold, parchment tends to have undergone greater deterioration than the bulk material of the same document, and that this deterioration extends to a lesser extent to a distance of several millimetres from the fold. It also shows that such an approach can reveal information on the effect of treatment methods, which may be used to inform conservation decisions.

On the basis of this preliminary study, work is now being carried out to develop the research, in particular using a more robust method of shrinkage temperature measurement and a wider range of samples (including those which have other sources of physical stress, such as the presence of attached seals). The effects of folding on new parchment are also being investigated, to assess the rapidity with which measurable physicochemical changes occur in the material after folding. In addition, the use of FTIR mapping is being investigated to better understand changes in regions adjacent to the fold.

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