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Original article

New results in Dead Sea Scrolls non-destructive characterisation. Evidence of different parchment manufacture in the fragments from Reed collection

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ABSTRACT

This work presents the non-destructive spectroscopic characterisation of original Dead Sea Scrolls (DSS) parchment fragments from Ronald Reed collection. The fragments are of paramount importance because they have never been subjected to any treatment of preservation and restoration, this allows to investigate the manufacturing method of real original Jewish parchments. The manufacture of "sacred" Jewish parchments, in fact, is traditionally supposed to use a superficial tannin treatment. To study the DSS fragments, it was necessary both to analyse mock-up samples, especially manufactured in order to reproduce ancient Oriental Jewish ritual parchments, and to compare the results with those obtained in the analysis of modern and ancient Western Jewish ritual parchments, in order to test the effectiveness of the selected spectroscopic techniques. Traditionally, the main difference between Oriental and Western traditional parchment preparation consisted in the dehairing method: enzymatic for Oriental and lime-based for Western. Moreover, a finishing treatment with tannin was supposed to be applied on ritual Jewish parchments. The need of reference samples derives from the knowledge that each parchment preparation, treatment and degradation can induce structural modifications that affect the spectral features. Fourier Transform Infrared Spectroscopy by Attenuated Total Reflection (ATR-FTIR), FT-Raman and m-Raman were used in this study. The experimental results allowed us to recognise, with different sensitivity, the presence of tannin by using m-Raman and IR spectroscopies and to prove that not all the archaeological samples were manufactured in the same way with vegetal extracts. Many salts (tschermigite, dolomite, calcite, gypsum and iron carbonate) were found on the surface of DSS fragments. They can derive from the degradation processes and storage environment before the discovery or from the manufacture. Moreover, the different sensitivities and instrumental characteristics of the used techniques permitted us to establish an analytical protocol, useful for further studies of similar materials.

1. Introduction

Ancient Jewish writings known today as Dead Sea Scrolls were discovered shortly after World War II in the caves of the Judean desert along the western shore of the Dead Sea. Dated to the end of the Second Temple period and the "time of the Christ" they have never stopped attracting attention of the scholars and the broad public. The larger part of the collection is written on a skin-based material that was rather soon associated with the skins that were specially prepared for writing and were mentioned in Talmud.

The scholars who worked on the collection were greatly interested in the precise dates of the compositions and they turned to Ronald Reed from Leeds University, an acknowledged expert in all matters concerning ancient leather and parchment. They hoped that the material itself might provide clues to dating, other than palaeography. In 1956, when the first contact was made, the idea of radiocarbon dating was just being born and could not be considered as a practical alternative. The archaeologists chose a representative collection of fragments bare of writing for the studies at the Leeds

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University. This first material study of the scrolls took several years and resulted in a number of scientific publications [1–3] and the very detailed doctoral thesis of Poole [4]. Using wet chemistry, light and electron microscopy and UV spectroscopy, the team concluded that the collection contained leather and parchment,whereby the latter was treated superficially with vegetable tannins, quite supporting the description available in Talmud. Years later, in his book on the ancient leather and parchment Reed revised his conclusions and reported that one variety of the parchment had never been tanned [5].

Today, the collection of the fragments studied by Reed and Poole is a part of the Reed Archive in the John Rylands University Library [6]. It was now made available to the authors of this paper for re-investigation using new techniques that have been developed since the first studies. The extreme importance of this collection relies on the fact that none of the fragments was subjected to series of consequent conservation treatments that considerable changed the original material.

2. Aim

The aim of this work was the non-destructive characterization of original DSS parchments from Reed collection by using molecular vibrational spectroscopies. Moreover, it seemed important to verify whether tannins application was a necessary step in the manufacture of "sacred" Jewish parchment, as traditionally supposed. Since tannins were applied in much smaller amounts than those required for leather tanning, their unequivocal recognition by non-destructive FTIR and Raman spectroscopies would lead to establish a scientific protocol for a non-destructive characterization of skin-based materials, both ancient Oriental Jewish ritual parchments and modern and antique Western Jewish parchments.

This work reports the results obtained in the analysis of some samples belonging to a larger number DSS fragments that were considered as representative of the whole investigated materials.

Before moving to the original DSS fragments, mock-up samples especially manufactured in order to reproduce ancient Oriental Jewish ritual parchments were analysed, as well as modern and ancient Western Jewish parchments, to test the effectiveness of the selected spectroscopic techniques.

3. Materials and methods

The most representative analyzed samples are briefly described below.

Mock-ups for the manufacturing method:

- GB1: goat parchment superficially treated with a 3% w/V solution of gum Arabic in water; 10 mL were applied on a $20 \times 20\,cm^2$ surface. The final amount of added gum Arabic was $0.75\,mg/cm^2$;
- GB2: goat parchment superficially treated with a 3% w/V solution of gum Raddiana (*Vachellia tortilis* sp.) in water; 10 mL were applied on a $20 \times 20\,cm^2$ surface. The final amount of added gum Raddiana was $0.75\,mg/cm^2$;
- GB3: goat parchment treated superficially with oak gall extract at 15% w/V concentration in water. The galls were washed, grated and cooked in a small amount of distilled water for 24 hours. The resulting liquid was filtered and set to the final volume. 5 mL were applied on a $20 \times 20\,cm^2$ surface. The final amount of added galls extract was $1.875\,mg/cm^2$;
- GB4: goat parchment treated superficially before with the oak gall extract and then with Gum Arabic, at the same amount and concentration used for GB1 and GB3 samples.

Modern and ancient Western Jewish sheep parchments:

- S1: modern ritual Jewish parchment manufactured with calcite and treated with oak gall extract on the surface at unknown concentration;
- S2: modern ritual Jewish parchment treated with alum and oak gall extract on the surface at unknown concentration;
- S3: ancient original ritual Jewish fragment of unknown manufacturing technique, 19th century;
- S4: ancient original ritual Jewish fragment of unknown manufacturing technique, 18th century.

S1 and S2 samples were specifically manufactured for the restoration of sacred parchment belonging to the Roman Jewish Community, courtesy of Rav. Amedeo Spagnoletto. Therefore, they can be regarded as examples of the Western preparation of sacred Jewish parchment.

Reed archive (R = Reed collection):

- R-4Q1 (Uninscribed fragment from Qumran, Cave 4);
- R-4Q2 (Uninscribed fragment from Qumran, Cave 4);
- R-4Q11 (Uninscribed fragment from Qumran, Cave 4);
- R-M9 (Uninscribed fragment from Cave Murabba'at);
- R-M10 (Uninscribed fragment from Cave Murabba'at);
- R-Q9 (Uninscribed fragment from unknown cave);
- R-A45 (Uninscribed fragment from Cave of Letters).

Two different and complementary vibrational techniques were used to investigate the samples, as described below.

3.1. Raman

Two kinds of Raman instruments were available, one to perform confocal μ-Raman, the other to collect FT-Raman spectra.

For confocal μ-Raman measurements a Renishaw In-Via Reflex Raman microscope was used, equipped with a Renishaw diode laser at 785 nm (output power 300 mW). In order to avoid sample degradation, neutral filters, when necessary, were applied. The backscattered light was dispersed by a 1200 line/mm grating and the Raman signal was detected by a Peltier cooled (203 K) deep depletion charge-coupled device (CCD, 578×384 pixel) optimized for near-infrared and ultraviolet. Nominal spectral resolution was about $3\,cm^{-1}$. The system, equipped with a Leica DMLM microscope to focus the laser on the sample and a colour video camera, allows for positioning the sample to select a specific region for the investigation.

Spectral acquisitions (5–10 accumulations, 50 s each) were performed with a $50\times$ objective. Under these conditions, the laser spot measures about $20\,\mu m^2$.

For FT-Raman measurements a Bruker FT Raman spectrophotometer RFS 100/S was used, equipped with Ge-diode detector cooled to liquid nitrogen temperature (77 K) and a near infrared [YAG:Nd] laser operating at 1064 nm. Measurements were carried out with the output power of 50–100 mW in the spectral range $100–3600\,cm^{-1}$ with a spectral resolution of $4\,cm^{-1}$, 4000 scans were co-added per spectrum.

3.2. Attenuated Total Reflection-Fourier Transform InfraRed (ATR-FTIR)

Infrared spectra were acquired with a Nexus Nicolet interferometer, equipped with a KBr beam splitter and extended with a ZnSe cell and a liquid nitrogen cooled MCT/A detector.

Measurements were performed in the $4000–650\,cm^{-1}$ range at a resolution of $8\,cm^{-1}$, averaging 300 acquisitions per sample.

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