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NON-DESTRUCTIVE INVESTIGATION OF THE DEAD SEA SCROLLS

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ABSTRACT
The Dead Sea Scrolls belong to the most important cultural assets of mankind. Their long term preservation and study is a challenge that demands an interdisciplinary approach. As early as the 1950s natural scientists assisted the scholars in studying the scrolls. It was at this time that the first extensive study of the scroll material took place. It was found that most fragments were written not on leather but on parchment. In addition, a method for determining the age of the parchment was developed which is still of value today. In the 1990s the AMS-C14 method confirmed the palaeographic determination of the age of the manuscripts. The use of carbon ink throughout the scrolls is also consistent with the known scribal practices of that time. There are, however, manuscripts, and among them the famous Genesis Apocryphon Scroll, which exhibit ink corrosion, normally associated with iron-gall inks.

Today, 60 years after their discovery, a community of scientists from the Jewish National and University Library (JNUL), the Technical University of Berlin (TU Berlin), the Federal Institute for Materials Research and Testing (BAM) and Fritz-Haber-Institute of the MPG (FHI) set out to scientifically investigate the finds of Qumran using the most modern methods. The results of the study will be used to determine the provenance of the texts as well as to contribute to their long-term preservation. A considerable part of the non-destructive investigation is taking place in the Berlin State Library and at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung , BESSY II.

Preliminary investigations, performed at the BAM on some fragments, were used to evaluate the extent to which X-ray analytical methods can provide information regarding the geographical origin of the fragments and match the individual pieces. The interpretation of the measurement results is made more difficult by age and storage of the objects. It is believed that ageing processes as well as conservation methods have altered the samples in addition to the changes caused by environmental influences.

In collaboration with the TU Berlin, the samples from the parchments found in the caves near Qumran were tested by means of three-dimensional synchrotron based X-ray fluorescence analysis (3D-SyXRF). The aim of this non-destructive investigation was the identification of the inorganic material used in the manufacture of the parchments.

The XRF experiments are supported by the non-destructive analysis by means of synchrotron based infrared spectroscopy (SyFTIR) in collaboration with BESSY II as well as optical and electron microscopy in collaboration with Fritz-Haber-Institute (FHI).

INTRODUCTION
The collection generally known as Qumran scrolls or Dead Sea Scrolls (DSS) comprises some 900 highly fragmented manuscripts from the Second Temple period. They are written on parchment, papyrus and leather. A number of scrolls stored in clay vessels retained good condition through over two thousand years. Others found on the cave floors reached us in highly fragmented state. The mystery of their origin still puzzles the scholars. [Encyclopedia of the Dead Sea Scrolls.]

The major part of the fragments is written on parchment, thus placing parchment at the centre of our attention. In contrast to leather, animal skin used for parchment production is not tanned, but dried under tension after removal of the hair and fat. After a finishing, a fine, bright and extremely stable material is obtained, essentially consisting of collagen. Natural deterioration of parchment is caused by chemical changes due to oxidation, hydrolysis and gelatinisation of collagen chains, promoted by several biological and microbiological factors (bacteria, fungi etc.). These deterioration processes do not alter significantly the trace elements composition of the material. The scrolls history knows, however, additional deterioration agents.

In the first years after their discovery, text analysis and attribution of the fragments were the main concern of the scholars dealing with DSS and no special attention was paid to their preservation: castor oil was lavishly spread on the fragments to enhance the contrast; pieces were held together by scotch tape and/or squeezed between glass plates. Moreover, they were kept under conditions of pollution, light and constantly changing climatic environment. As a result the fragments started to degrade speedily. [N. Caldararo]

Later the restoration has become the main issue. However, in those days synthetic glues and consolidants found wide application. Furthermore, many techniques usually employed with well-preserved medieval parchment prove unsuitable in the case of the ancient highly degraded one. Unfortunately, the post-discovery history of the scrolls has not been documented properly. So today we are left to deal with the following issues: (i) identification of the previous treatment, (ii) proper assessment of the degradation state, (iii) removal of the effects due to previous "restoration", (iv) proper preservation and conservation techniques.

The alteration of the original material due to the extremely old age, storage in the caves and post-discovery treatment makes the provenance study extremely complicated. The determination of the original production site of parchment and ink is based on the trace elements originally incorporated during the production process. Analogue to the case of age determination by a radiocarbon method, contamination by non-original materials leads to a wrong provenance attribution. Thus, all foreign contributions must be recognized and filtered out. To achieve this aim we employ multi-instrument approach, i.e. we aim at an exhaustive characterization of the material by non-destructive methods. Invasive methods can hardly be used in the case of highly inhomogeneous materials, because of the extreme difficulty in choosing a representative sample shown in previous studies [W. S. Ginell].

We present here a case study of a Qumran parchment sample that has undergone a special treatment, which has altered significantly the original material. To identify the treatment we used X-ray fluorescence and infrared spectroscopy assisted by light and electronic microscopy.

RESULTS AND DISCUSSION

The case that we present here serves as an illustrative example of the methods applied to study the effects of the storage and post-discovery treatment on the origin identification. The samples shown in Fig.1 belonged originally to one piece of parchment discovered in the 50s in the Dead Sea area. Its precise discovery location is unknown because no documentation is associated with it.

The piece was divided into two parts, one kept as a reference and another subjected to Fuller's earth poulticing, a treatment usually employed for the removal of pressure sensitive tape residues and associated stains. This treatment consists in the application of an organic solvent (methyl-ethyl-ketone) in Fuller's earth compress to a tape-stained area. Fuller's earth controls directional evaporation of the solvent that carries the adhesive. It also serves as a mild bleacher and has been often used as a bleaching agent. The technique has many pros and contras, one of them being the uncertainty of the complete removal of the poultice material, Fuller's earth.

We have investigated the effects of the Fuller's earth by different methods addressing the following questions:

1. Is there a residue?
2. How does it affect the parchment?
3. How can we recognize it?
4. Does it affect the Cl/Br ratio, leading to an erroneous provenance determination?

The increase of weight of the sample from 35 mg to 47 mg upon the treatment is the first evidence of alteration and of the residue incorporation into the parchment. Fig. 1 shows light microscopic images of the parchment piece before (left side) and after the poulticing treatment (right side). The parchment was not cleaned after discovery and still carries the traces of its long sojourn in a cave. Despite that, the follicle pattern on the non-treated piece is clearly recognizable. It indicates that this parchment has been produced from a sheepskin. [M.L. Ryder]. However, the follicle pattern is completely lost in the right side picture indicating a strong alteration of the parchment surface.

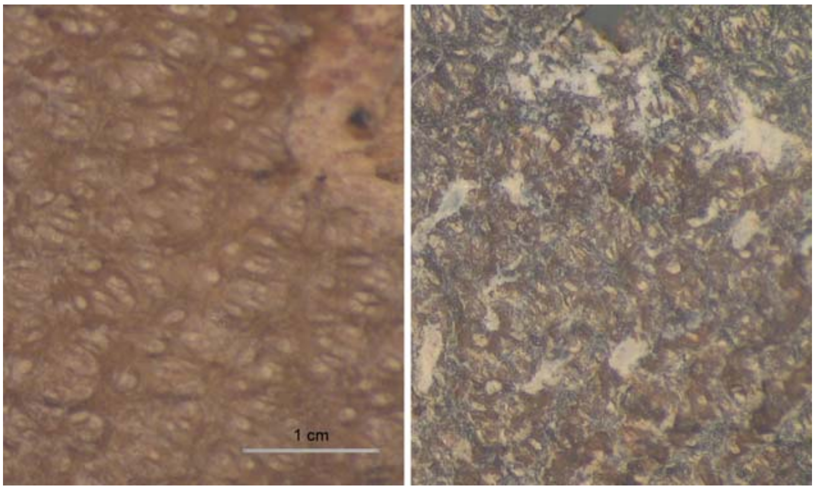

Fig.1 Stereo microscopic images of the Qumran fragment before (left) and after (right) Fuller's Earth poulticing.

The whitish islands appearing after the treatment, are often found on the scrolls after poulticing and have been previously interpreted as salt crystallization [A. Wallert]. An increased amount of Ca at these spots supports this interpretation. However the mechanism of crystallization that must have been caused by the treatment hasn't been clarified yet. Fuller's earth consists mainly of amorphous hydrous aluminum silicate (Al_2O_3 x $2SiO_2$ x XH_2O, X = 2 or 4) of a colloidal structure [Merck Index]. Different mineral additions characteristic of the local production have been reported [A. Porter]. Fig. 2 shows scanning electron micrographs of the parchment before and after the treatment. The left side image is characteristic of Qumran parchment covered with debris associated with the storage [I. Rabin et al.]. Under the debris the rests of fibrils can be detected. On the right side the surface seems to be coated or baked. The treated parchment completely lost its flexibility and became as hard as a stone.

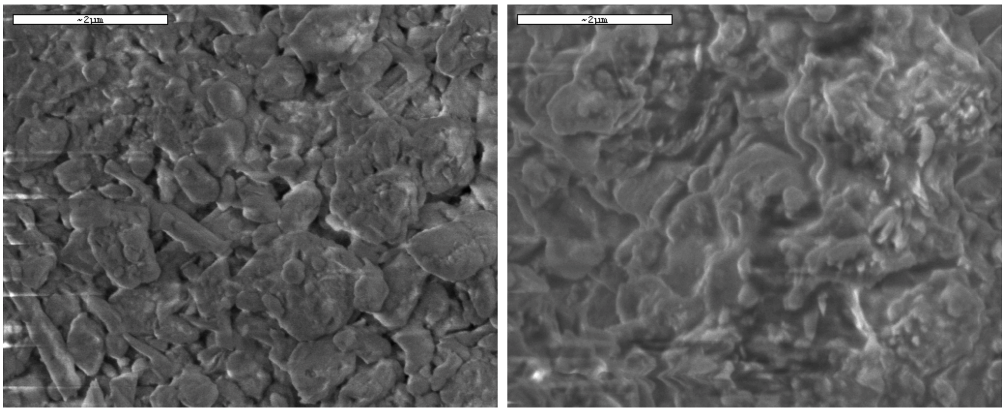

Fig. 2. SEM images of the Qumran parchment before (left) and after Fuller's Earth poulticing (right).

The alteration of the original parchment surface due to Fuller's Earth poulticing can be easily visualized with the help of microscopy. But other techniques are necessary to study and identify its effect on the parchment composition.

In the frame of the provenance research project, we are mapping parchment and inks composition to produce a Dead Sea Scrolls parchment/ink atlas that would allow attributing scrolls to definite geographical localities. The relative abundance of trace elements plays an especially important role in this study. As an example, the Dead Sea area is characterized by a specific Cl/Br ratio. Therefore the relative abundance of these elements measured in the analyzed fragments indicates whether they originate from the Dead Sea area or not.

For the correct handling of the results it is necessary to know whether the ratio can be altered by conservational practices. Analyses were carried out with the mobile energy dispersive micro-X-ray spectrometer ArtTAX(R) (Bruker AXS Microanalysis GmbH, formerly Röntec-GmbH, Berlin, Germany), described in detail elsewhere [H. Bronk et al., O. Hahn et al.]. This instrument is capable of detecting elements heavier than magnesium (Mg, z=12), i.e. covers the range of interest. All measurements were made using a 30 W low-power Mo tube, 50 kV, 600 µA, and with an acquisition time of 15 seconds (live time). For better statistics, at least ten single measurements were averaged for one data point within the scans along x- and y-coordinates. The data were then processed with the help of a model that takes the parchment matrix into consideration. The resulting two-dimensional elemental map of the sample under investigation serves as an indication of the homogeneity of the material. To distinguish between surface and bulk contributions we employ 3-dimensional XRF technique [B. Kanngießer et al.] that allows depicting the element distribution within a material.

Fig. 3a shows a portion of an x-coordinate profile of calcium and silicon in the Qumran samples under study (red solid lines). In accordance with the results from the microscopy investigation the unevenness of the curves reflects the deposits of the mineral residues from the storage in the caves. The profile changes drastically for the treated materials (black solid curves) indicating a novel deposition of the Ca and Si enriched substances. In fig. 3b we present the comparison of the concentration distributions for both samples. Besides the increased concentrations of Ca and Si, the amount of aluminum has grown almost one order of magnitude, thus pinpointing the foreign treatment material as Al-based. 3-D XRF analysis confirmed that the added material is mostly confined to the surface area.

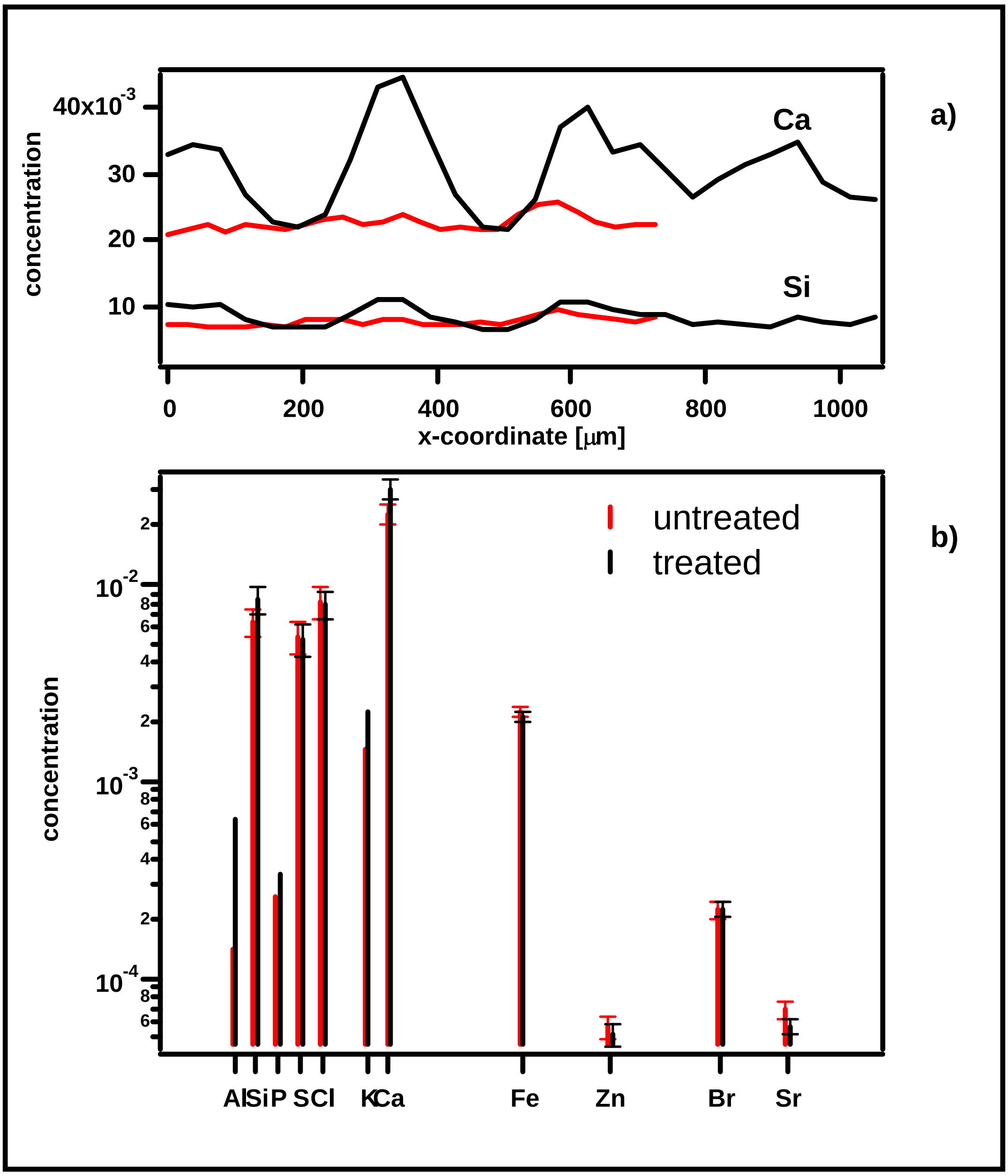

Fig. 3 (a) Ca and Si profile along a x-coordinate of the treated (black) and untreated (red) samples; (b) Concentration distribution of the elements of interest. Note the logarithmic scale of the y-axis. The red and black lines correspond with the untreated and treated samples, respectively.

The concentrations of chlorine and bromine were not changed by the treatment: the ratio of these elements (~37) clearly indicates their origin from the Dead Sea Area.

To detect possible chemical changes induced by the poulticing treatment we have characterized the parchment surface by means of infrared external reflection spectroscopy (IR-ERS). The sample surface has been illuminated by a broadband infrared light source. The light reflected specularly by the surface has been collected and Fourier-transformed to give wavelength resolved reflectance spectra. Upon further Kramers-Kronig transformation of these spectra, the absorption characteristic of the sample (pseudo-absorption spectra) was obtained [A. Masic et al.].

Fig. 4 displays pseudo-absorption spectra calculated from the reflectance output of three samples. The lower pair of spectra of a modern parchment shows Amide I and Amide II, the fingerprints of the intact collagen. The upper and the middle pair correspond to the Qumran sample untreated and poultice treated, respectively. In the spectral region studied, calcite and silicates identified on the ancient parchment surface can be interpreted as traces of the storage conditions and are in accord with microscopic picture. The intensity of the silicate and calcite bands is greatly increased on the side treated with Fuller's earth. This is consistent with the alumino-silicate coating revealed by the microscopy observations.

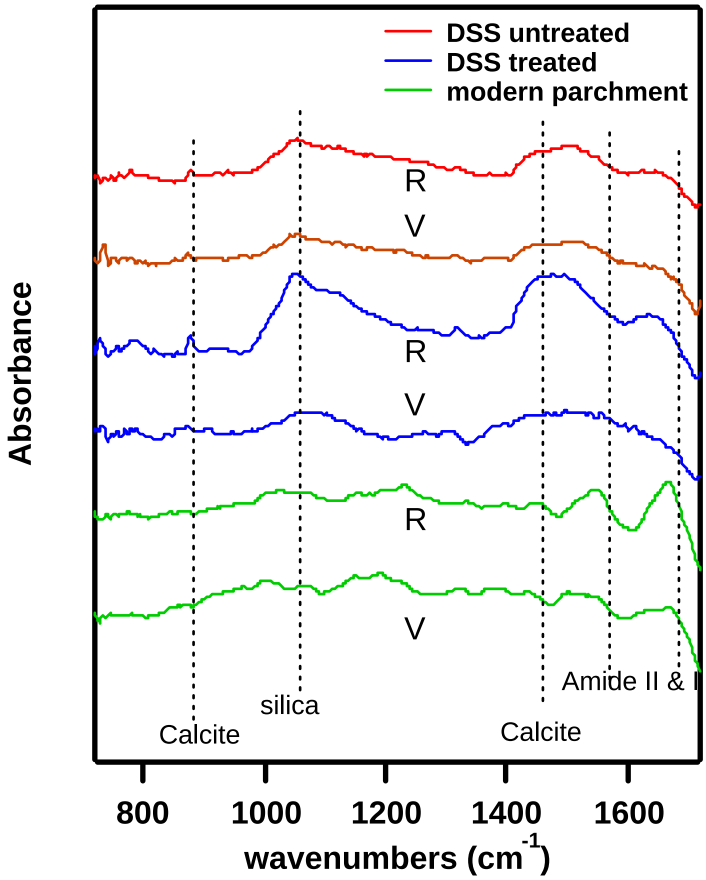

Fig. 4 Comparison of absorption spectra obtained from the reflectance measurement. Recto and verso sides of the parchment are marked with R and V, respectively.

Further IR-spectroscopy investigation of parchment treated with castor oil, British Museum Leather Dressing and Perspex glue have shown that these materials leave recognizable traces on parchment. None of them has been detected on the parchment samples investigated in this study.

CONCLUSIONS

In this work we have analyzed the effects of the conservation treatment employed to remove adhesive residues by means of poultice with organic solvent and Fuller's earth as the dry agent. With the help of microcopy we have shown that residue of the dry agent lead to irreversible changes of the parchment material. Despite the fact that Fuller's earth composition is very close to that of the storage residues from the caves near Qumran, IR-ERS and XRF methods were capable of identifying considerable quantities of the Fuller's earth on the parchment surface.

Fortunately, the conservational intervention had not affected the Cl/Br ratio necessary for the determination of the geographic origin of the parchment. This ratio (~ 37) indicates with high probability that parchment has been produced in the Dead Sea area.

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