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Original article

White halos surrounding the Dead Sea scrolls

Yonah Maor[a], Pnina Shor[b], Zeev Aizenshtat[a,*]

[a] Institute of Chemistry, Casali Center, The Hebrew University, Edmond Safra Campus Givat Ram, Jerusalem 91904, Israel
[b] Israel Antiquities Authority, Dead Sea Scrolls Unit, Rockefeller Museum, Post Office Box 586, Jerusalem 91004, Israel

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ABSTRACT

The Dead Sea scrolls (DSS) are the most important archaeological find in Israel. Relatively well preserved in caves for 2000 years, additional damage has occurred since their removal in the 1950s. Among other issues, thousands of fragments were stored between glass plates, and over the years white "halos" formed around some of these fragments. Different theories about these "halos" have been proposed: the first, most obvious, option being salt migration. Since the salt content everywhere in the Dead Sea area (including aerosols) is extremely high, all of the scroll fragments would have collected large amounts of salt. Another theory, that the halos could be gelatin recrystallizing after being squeezed out of the degraded parchment, was more worrisome. If gelatin was squeezed out of the parchment, it would result directly in significant changes to the scrolls' physical properties. At the request of the Israel Antiquities Authority's (IAA) DSS conservation staff, we analyzed the powdery material with multiple methods: FTIR-ATR, Raman microscopy, XRD, ICP, and GC/MS. In addition to salt and minerals, our analysis found fatty acids (FA), but no gelatin, disproving that particular theory. By artificially aging modern parchment the phenomenon was recreated and the parchment samples were analyzed with destructive methods (electron microprobe, GC/MS) that could not be applied to the DSS in order to learn more about the process. The FAs are an important discovery not only for understanding the degradation process, but also as a source of information on the scrolls' production and treatment history – a source that can be analyzed even more accurately through destructive methods, without needing to touch the scrolls themselves.

1. Introduction

The DSS are manuscripts found in caves in the Judean Desert on the western shore of the Dead Sea. Most of the scrolls are dated to the end of Second Temple times 100 BCE – 70 CE, some are dated to earlier and later periods [1–3]. They have a great cultural significance because the collection includes the earliest known copies of every book of the Hebrew Bible (except for the book of Esther); along with non-biblical and sectarian compositions allow us a glimpse at a critical time in history when Christianity and Judaism were being formalized. The scrolls dated to the 2nd century CE are mostly historical documents. Approximately 80% of the collection is written on parchment while the remaining 20% are on papyrus, with one scroll on copper. The scrolls on papyrus are generally in better condition, although many times taped on both recto and verso. In the 1950s most of the scroll fragments were stored pressed between two glass plates and some of these fragments later developed white "halos". This paper describes the analysis and identification of that material and discusses the implications.

Parchment is made from animal skins, usually goat, sheep or calf. There is no known description of the methods of parchment manufacture at the time the scrolls were written. Modern parchment is produced by similar methods to those documented in the middle ages in Europe: hides are cured in salt then soaked in a lime bath (CaO), after which flesh and hair can be easily removed leaving only skin, the skin is then stretched on a frame to dry. It may be smoothed using a pumice stone, or chalk can be rubbed into the surface to whiten the parchment. Some modern manufacturers add enzymes to the parchment after the lime bath to soften the parchment. Historically this was accomplished using animal excrements or rotten vegetable matter; these could also be used for dehairing instead of a lime bath. The resulting parchment is mostly collagen. Skin also contains elastin, proteoglycans, glycosaminoglycans, glycoproteins and triglycerides. These are removed to a great extent during the parchment preparation [4]; for example, triglycerides undergo hydrolysis due to the highly basic conditions of the lime bath – the resulting glycerol and most of the freed fatty acids (FA) are washed away.

* Corresponding author.
E-mail addresses: yonah.maor@mail.huji.ac.il (Y. Maor), pnina@israntique.org.il (P. Shor), zeev.aizen@mail.huji.ac.il (Z. Aizenshtat).

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Fig. 1. (a) plate 740 – white "halos" around DSS fragments; (b) fragment 2 plate 740 – close up of a fragment with Sellotape® and "halo"; (c) residue on a plate after scroll fragments were removed.

In the 12th century the Rambam wrote a description of parchment manufacture according to Jewish tradition, using flour to process the skin after curing in salt and later lightly tanning the skin, particularly on the hair side which is the side used for writing Tora scrolls [5]. These methods are still used today. Flour is interpreted broadly, and ground barley is often used. Previous research on scrolls suggests the Dead Sea scrolls (DSS) were prepared by similar methods, and most samples analyzed had tannins on at least one side. The researchers did find enough variation in the samples to conclude several different methods were used. They also found lower levels of Ca than they were accustomed to seeing in European medieval and modern parchment. They concluded that the scroll parchment must have been made without a lime bath, using only the enzymatic method [6] (and many have since quoted this). We considered it would be surprising for people living in an area where lime was so easily obtainable, to use a much less effective method. When the parchment was prepared for our artificial aging experiments it was done in a lime bath, but washed thoroughly in clean water before drying. The result is parchment with less calcite than most of the scrolls we have analyzed.

During the first two decades from the discovery of the scrolls (circa 1950), a small team of scholars was given exclusive access to the scrolls. They were primarily concerned with studying the content of the scrolls, and apparently unaware of conservation issues. They made a number of misguided choices. Scrolls were unrolled by exposure to 75–100% relative humidity (RH), sometimes with glycerin added. Alcohol and ether were used to dry parchment [7]. Castor oil and other oils were smeared on scrolls to soften the parchment or to improve the legibility [8,9]. The scroll fragments were spread out over long tables in the "scrollery" for study. The room was not climate controlled, so there were large variations in temperature and humidity [10]. Samples were exposed to direct sun light from large windows, and since the windows were opened in the summer, also exposed to dust and pollution.

Most unfortunate was the scholars' choice for dealing with the small fragments. When they found pieces they believed fit together they taped them with Sellotape® (newly invented at the time). Associated fragments were then pressed between two glass plates for storage. As they completed more plates, they began stacking them in piles, thus subjecting the scroll fragments to a great amount of pressure. There were over 1000 plates in total.

The dedicated conservation lab, set-up by the IAA in 1991, has been transferring fragments to state of the art storage and trying to carefully remove the damaging pressure sensitive tape. Besides the obvious degradation of the fragments, an unidentified white powder collected around and slightly under some of the fragments stored between glass plates (Fig. 1). In the past this material was simply identified as "salt", i.e. sodium and potassium chloride stemming from the Dead Sea environment, leached out of the fragments [11]; however, our initial test found the powder had very low solubility in water, raising doubts about that identification. There was concern that this powder could be more directly related to the degradation of the parchment scrolls. As the parchment degraded, the gelatin (denatured collagen) formed may have squeezed out of the parchment and recrystallized on the glass plates around the fragments. If that were the case, the "halos" could be linked to changes in the physical properties of the parchment (stiffening, darkening etc.). Another theory was that the tape and other materials added to the scrolls after their discovery could be the cause of these "halos". Fig. 1b also demonstrates the extreme darkening of parchment due to Sellotape® use.

Free FAs and fatty acids salts are known to form "ghost images" on glass glazing over oil paintings and other fatty substances [12]; in that case the FAs are obviously present in much higher concentration, so their migration is not surprising. We had initially not considered this explanation as fat content in parchment is not very high. Testing of many historical parchments found great variation between samples, and difficulty measuring accurately, but FAs were always in the ppm range [13]. In the literature, only one other institute reported a similar occurrence (with papyrus). They identified the powder as mainly NaCl with plant hydrocarbons and traces of vegetable proteins; however, the organic analysis and results were not reported [14]. In our study, powder from several plates was analyzed by complimentary analytical methods, and artificial aging was used to recreate the phenomena and study the process.

2. Research aim

The aim of this research was to analyze and identify the material that collected around the DSS stored between glass plates (the white "halos"). Artificial aging was used to recreate the phenomenon in order to better understand that aging process. The ultimate goal was to clarify the significance of that material to the conservation of the DSS.

3. Materials and methods

3.1. The samples

3.1.1. Powder from DSS

DSS samples were provided by the scrolls conservation lab of the IAA. Glass plates that had been used to store both parchment

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