Bio- and Material Cultures at Qumran

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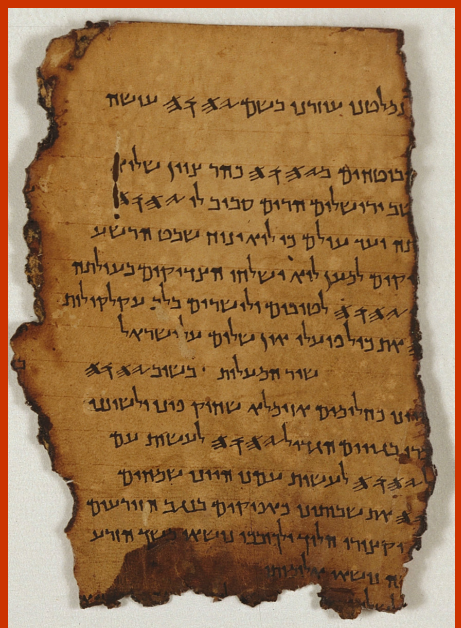
Edited by Jan Gunneweg, Charles Greenblatt and Annemie Adriaens



COST Action G8

BIO- AND MATERIAL CULTURES AT QUMRAN

Papers from a COST Action G8 working group meeting held in Jerusalem, Israel on 22-23 May 2005

Edited by Jan Gunneweg, Charles Greenblatt and Annemie Adriaens

Cover illustrations

Upper Central:
Caves 4 and 5, next to Wadi Qumran, where parchment and papyrus fragments have been found of approximately different 600 scrolls. (Photo: Gunneweg)

Left down:
Fragment of linen with blue embroidery that was found in Cave 11 and served as a wrap for a scroll. The piece measures 1.5x1.5 cm. (Photo: Gunneweg)

Mid down:
A typical scroll jar with lid found in Cave 1 at Qumran. Height about 57 cm. (Photo: Gunneweg)

Right down:
A Hebrew written text of a scroll of Book I of Kings, the so-called Q11b page that was found in Cave 11 (Photo: Tsila Sagiv, Courtesy Israel Antiquities Authority)

Table of Contents

Section III Conservation

Preface

The *Bio- and Material Cultures Qumran Meeting, 2005* was held at the Hebrew University's Faculty Club "Beit Belgia" at the Givat Ram Science Campus in Jerusalem with a delegation of Israeli and European scholars in the frame work of the Hebrew University and COST Action G8 (European CO-operation in the domain of Science and Technology), an excellence network dealing with "non-destructive or minimally invasive analytical testing" of our archaeological, museum and architectural relics. This research is performed by all available and cutting-edge technologies existing to date.

Jan Gunneweg and Charles Greenblatt both of the Hebrew University in cooperation with Annemie Adriaens of Ghent University and head of COST Action G8, who from the beginning stood behind the start of our Working Group, have organized the inter-professional Qumran meeting. Further institutions in Israel that have been involved are the Israel Antiquity Authority, the Israel Museum and the Shrine of the Book that contains seven of the most complete Dead Sea scrolls on parchment and papyrus as well as the Aleppo Codex, a book representing the Hebrew Bible of 1000 years ago on paper.

Grants from COST Action G8 and the Hebrew University Research Center provided the budget for the Qumran meeting.

Thirty-five scholars from different fields lectured on various subjects, whereas others presented posters. The lectures and numerous discussions have resulted into a firmer cooperation between various multi-interdisciplinary domains in science as well into a future set-up of a "First-Aid" laboratory that will partly deal with the prevention of environmental and biological attacks on organic matter, and partly with non-destructive analysis of artifacts to extract historical information and their conservation for the coming decades or centuries.

We are in debt to all the colleagues who contributed samples without which research cannot take place. Furthermore, thanks to the contributors who made time to report on their current research. Finally, Gunneweg and Greenblatt thank the team of referees and specifically María Inés Zylber who have been involved in the successful compilation of this volume.

COST ACTION G8
NON-DESTRUCTIVE ANALYSIS AND TESTING OF MUSEUM OBJECTS

Annemie Adriaens

Department of Analytical Chemistry, Ghent University, Belgium
E-mail: annemie.adriaens@ugent.be

Abstract

COST Action G8 (2001-2006) aims at creating a Europe-wide network that would enable co-operation and interaction between two groups of professionals: people directly concerned with the maintenance of our cultural heritage - conservators, curators, art historians, archaeologists - and analytical scientists, including chemists, physicists, geologists, metallurgists, mineralogists and microbiologists. The main objective of the action is to improve the preservation and conservation of our cultural heritage by increasing available information on museum objects through non-destructive analysis and testing. The scientific activities of COST Action G8 include organising short-term scientific missions to train scientists from both groups in the other's field as well as to transfer practical experience among the European countries. Regular meetings in the form of workshops are organised in order to exchange the acquired knowledge within a broader group; six working groups are currently active, which allow close collaboration in a specific field.

Introduction

The conservation and preservation of our cultural heritage has become one of the main concerns within Europe today. In particular, the increasing need for non-destructive investigations is a major issue, as sampling is in most cases restricted in view of the value or the uniqueness of the object. Even in cases that allow sampling, non-destructive testing offers

the possibility of obtaining more information from one specific sample, as complementary techniques may be applied.

In the analytical sciences, many non-destructive techniques are available, such as ion beam analysis, autoradiography and optical spectroscopy, all of which can, in principle, be used in this field. Museums, however, do not always have access to these techniques, while many of the necessary research instruments and analytical facilities are located in specialised research institutes, as they require very specific expertise. Some techniques may still need to be introduced and established in the field of cultural heritage.

It is for these reasons that COST Action G8 has been established, which aims at creating an environment that enables co-operation and interaction between museums and natural scientists. COST is an intergovernmental framework for European co-operation in the field of scientific and technical research, allowing the co-ordination on a European level of nationally funded research projects (http://cost.cordis.lu/src/home.cfm).

Objective and benefits

The main objective of COST Action G8 is to improve the preservation and conservation of our cultural heritage by increasing available information on museum objects through non-destructive analysis and testing. This is accomplished by creating a Europe-wide environment, in which people directly concerned with the maintenance of our cultural heritage (ie art historians, archaeologists, conservators and curators) and analytical scientists (ie physicists, chemists, material scientists, geologists, etc.) can exchange information. A 50/50% balance between the activities of both groups is aimed at, which should result in greater interest. The expected benefits are twofold. First, the capability of answering questions related to museum objects, which cannot be readily solved now, will be enhanced. This includes the exchange of information on available non-destructive techniques and the requirements for performing investigations on valuable or unique objects. In addition, museums and similar institutes will have easy access to universities and research facilities that provide such techniques.

The first successful step in this direction has been provided by COST Action G1 (1995-2000). The focus of this action was confined to the use of Ion Beam Analysis (IBA) for art and archaeological objects. This technique was applied to various archaeological objects, such as paint layers, pottery, glass, enamels, obsidian, stone, tools, bronzes, coins and gold jewellery (Respaldiza 1997; Demortier 2000). The expansion to a multidisciplinary

community and the use of additional non-destructive techniques allows researchers to obtain further complementary information.

The scientific programme

COST Action G8 has three main scientific activities. The first one includes organising short-term scientific missions between participating institutions. The goal of these STSM (5 days – 3 months) involves the training of scientists from both professional groups in the other's field, as well as the transfer of practical experience among European countries. Priority here is especially given to young researchers.

Secondly, regular meetings in the form of workshops are organised, often in collaboration with museums and conservation institutes, to exchange obtained information in a broader group, to discuss new themes, and to build interest and create possibilities for new collaborations (Townsend *et al*. 2003). The goals of both activities are listed in detail in Table 1.

Table 1. Goals of short term scientific missions and workshops

Short term scientific missions	Workshops
- train scientists of both professional groups in the other's field as well as transfer practical experience between the European countries, - address specific problems concerning museum objects as well as collect and compare data, - compare the use of standing facilities and portable equipment, - exploit the advantages and limitations of the different techniques also in comparison to techniques commonly used today in the field of cultural heritage, - art historians, archaeologists and conservators obtain easier access to analytical research instruments.	- exchange (obtained) information in a broader group, - prove the non-destructive properties of the techniques, - build interest and give the possibility of new collaborations, - assist in choosing the method(s) best suited for a specific problem.

Apart from the yearly workshops and STSM between participating groups, separate working groups have been created. The working groups allow a close collaboration and an extended and efficient exchange of knowledge within a specific topic, and therefore a more efficient way of publishing the obtained results. The following themes are addressed:

- Technology and authenticity, involving the identification of the materials and their production techniques. Within this working group two distinct but related topics are studied: (1) the investigation and verification of ancient recipes starting from the Mesopotamian and Egyptian texts up to the 19th century books of technology including descriptions of how craftsmen prepared and made their products are made available and (2) the authentication of art and archaeological objects, ie the identification of fakes.
- Origin and provenance, including the characterisation and location of natural sources of the raw materials used to make (museum) objects. The main goal is to contribute to establishing patterns of raw material procurement, trade or exchange.
- Degradation processes, corrosion, weathering. This working group deals with the problem of alteration of museum objects and the way non-destructive techniques can be used to measure this damage or monitor it with time.
- Preservation and conservation. The working group is concerned with the treatment of works of art in order to slow down deterioration, the identification of the nature and extent of damage, the assessment of the causes of deterioration. Work in this field also implies the control of the environment in which the object is located, such as monitoring of the temperature, relative humidity and lighting, ensuring proper storage, support and security.
- Development of analysis procedures involving three main goals: (1) the use and improvement of truly non-invasive techniques (they do not require a sample to be removed from the object), (2) the maximization of information and minimization of consumed volume when a sample must be removed and (3) the development of portable / mobile equipment so that monitoring can be done on site.
- Biological and Material Culture of Qumran at the Dead Sea. This working group deals with three aspects of the study of material remains at Qumran, ie the biological and the material cultural ones and the conservation of this cultural heritage.

COST Action G8 started in February 2001 and will run for five years. At the time of writing, twenty-four European countries had joined. They are listed in Table 2.

Table 2. COST Action G8 member countries (October 2005)

Austria	Germany	Poland
Belgium	Greece	Portugal
Bulgaria	Hungary	Romania
Czech Republic	Israel	Slovakia
Cyprus	Italy	Slovenia
Denmark	Macedonia	Spain
Finland	Malta	Switzerland
France	Netherlands	United Kingdom

Further information

For further details and information, please contact the author or visit our web site at http://srs.dl.ac.uk/arch/cost-g8.

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FROM THE PHILOSOPHY TO REALITY IN THE QUMRAN PROJECT

Jan Gunneweg

Institute of Archaeology, The Hebrew University of Jerusalem, Israel
E-mail: jan.gunneweg@huji.ac.il

Many important historical events have occurred in ancient Israel. The country witnessed the exodus of mankind out of Africa during prehistoric times. For thousand of years, the country was the corridor between the super powers Egypt and Mesopotamia. Its population has provided the Western World with monotheism that has become the start of Judaism, Christianity as well as Islam, respectively. A huge amount of material finds of this civilization has been excavated and studied and the bio- as well as material culture has shed light on how the ancients lived, what they did to stay alive, and what were the reasons they became ill and died.

One of the important gifts that has come to us just by an accidental find are the Dead Sea Scrolls that are the backbone for checking the oral tradition between the spiritual writings of 2000 years ago and what is known today as the “Bible”. The Dead Sea Scrolls are the focus of our Qumran Project and scientific research has started to illuminate the background of these manuscripts.

During the past half-century, there have been 36 biannual international Archaeometry symposia. These meetings have been very productive in the various domains of science and many scientists have analyzed archaeological and art objects and have come to valuable conclusions.

On the other hand, the world of the Humanities and more specifically that which comprises archaeologists, art historians, and curators of museums and conservators of artifacts and political historians have to deal with the interpretation of what material remains in Art and Archaeology provide. If one were to estimate the presence of Humanists in Archaeometry meetings, one would arrive at a figure of the order of 5 percent. This is sad because Archaeological science is supposed to help the work of the humanists. Furthermore, it has been observed that the majority of humanists is not interested in the slightest in scientific

technologies and will, therefore, not be included in what follows. Most of them have only a vague knowledge of what science can offer for their specific needs. Some received their education in conservation and archaeology decades ago while science has developed tremendously, more than archaeology and art history have.

Some writers before me have recognized this phenomenon (Widemann 1982). Even in the most recent development of the Synchrotron radiation conference applied to Art and Archaeology at Grenoble, Mark Pollard asked the rhetorical question "if Synchrotron Radiation is so good, why we do not see archaeologists?" An answer to this is that I do not foresee on a global scale that the future will turn out much better than what has happened in cooperation between humanities and science so far. Perhaps there will be a small improvement but nothing spectacular.

I first and foremost want to suggest that the word "archaeology" does not cover the domain that is treated in this context. Perhaps it is better to use the word only in the case of field archaeologists who excavate a site. The word "Cultural Heritage" instead is broader and should be preferred because it encompasses everything that mankind has made and has preserved so far: Tools and utensils of every day life, objects of art, the written text and architecture.

As a solution to the problem of poor collaboration between scientists and humanists, it is suggested that scientists "convert" to humanistic domains. In other words a scientist must also become an expert in themes such as numismatics, ceramics, glass and metals or, at least, in that domain where he is expected to understand the problem he has to solve. In this context, there are already many scholars around the world who have done just this, among them my teacher and colleague Isadore Perlman whose expertise has been nuclear chemistry and who set up the Archaeometry Unit in the Hebrew University. Perlman studied archaeology, and he expected his collaborators in archaeology, in a like manner, to learn the principles underlying neutron activation. Not only did he ask that we study it, but also that we excel in it.

Why the Qumran Project?

The reason why it has been necessary to study anew Qumran and all its archaeology and the Dead Sea Scrolls has been the fact that thousands of papers and hundreds of books have described these finds according to a preconceived archaeology opinion on what purpose the Qumran site served. Initially, in the nineteen fifties, it was Roland Guerin de Vaux, Qumran's

excavator, who saw the site as a complex for a religious Jewish community very much like that of the convent of the Dominicans in which he lived himself in Jerusalem. Thereby, words as ‘refectory’, ‘scriptorium’, ‘community room’, ‘common meals’, ‘lavatory’ and the like became fossilized in time as the Qumran research developed. However, no scientific data, or hardly enough of them, have been advanced to back this up.

As time passed by, other fertile heads offered still other interpretations to explain the purpose of the Qumran building complex, because if one has not to prove anything, one’s guess is as good as anybody’s! So, the various theories of interpreting Qumran as a Roman villa or an agricultural place for growing dates and grapes or a garrison for soldiers, as well as a production site or a factory for balsam, salt, papyrus, pottery and the most recent opinion of fertilizer plant based on bones came into existence (Humbert and Gunneweg 2003).

The new Philosophy is based on the simple fact that if one wants the Humanities and Science to handshake, one must come up with an offer that neither of the two can refuse. In the movie industry, a good story reflects this. A story requires a good script that attracts good actors, which, in turn, attracts producers with the necessary means to make a movie. In our case, it has been the Qumran project that interested scholars from all over the globe and it has been a beehive for cooperation between many interdisciplinary techniques and approaches. This philosophy of physical and virtual “handshakes” has proved to be a success. It all boils down to presenting a good story and everybody who is interested will find a common area for collaboration.

Our Volume II of Qumran was first a collaborative project of 24 institutions from 17 countries and when the Qumran meeting took place in 2005 in Jerusalem we realized that among the lecturers and poster presenters there were 35 archaeologists, curators and conservationists, and 31 scholars in biology, physics and chemistry who participated actively. This is therefore the answer to the pessimists who have given up trying to establish a handshake between Humanities and Science not on a global, but on a specific local scale that in turn may grow out into a global one.

In the following paragraphs we will provide the global picture where we are standing on this moment. The famous Dead Sea Scrolls were found in nine caves. Two ostraca were found in two additional caves so that written material has come from eleven caves altogether. The general opinion today is that the scrolls came from the archive of Jerusalem's Temple in the first century A.C. However, none of the scholars who hold this opinion is able to bring forth a single proof that this is the right solution, quite the opposite. In turn, those scholars who hold the view that all scrolls were produced at Qumran cannot prove this either.

Our present Qumran project did not emerge in a vacuum. Scientific studies have been going on over the past 50 years since the Qumran excavations ended in 1956. These studies comprise the first data on the two different kinds of ink that were used, black carbon from lamp wicks for almost all scrolls and cinnabar (red pigment) on four Dead Sea scroll fragments (Nir-El and Broshi 1996a, b). The date of the script was established by paleography, whereas the date of the parchment itself by carbon 14 (C^{14}). The provenance of the pottery was analyzed by applying petrography that did not give a final answer. Often during the past fifty years the burials in Qumran's cemetery were counted and recounted, as if was going to obtain a clue for its very existential purpose, whereas an estimated 50 unearthed skeletons travelled from Jordan to France and Germany and are there until today. The glass collection of Qumran showed up in Louvain (Belgium). On the other hand, more than 500 bronze coins have disappeared from the surface of the Earth. Also half of the Qumran textiles were discharged in a carton box in a damp corner of a museum, whereas the second half studied earlier by G. Crowfoot has disappeared too. All this has taken place under the patronage of a myth that grew by the year that the Dead Sea Scrolls would uncover something that was not flattering for either the Christian or the Jewish faith. It was a kind of oral tradition to claim that the Israeli government was involved in hiding things, whereas at the same time the Vatican was accused of doing the same for its followers in agreement with Israel, all rather based on wishful thinking.

Initially, the Dead Sea Scrolls' exegesis was divided among seven Christian scholars whereas interested frustrated Jewish scholars had to live from the crumbs that fell from the 'elected' table. It was a gentleman's agreement that no Jew could touch the word given to the seven although the language in which the scrolls were written was in their language: Hebrew.

Finally, a Palestinian photographer who had emigrated to the United States triggered an enormous renaissance of studying the Dead Sea Scrolls by blowing the whistle in printing all the negatives of Dead Sea Scrolls photographs that he had taken in the nineteen fifties in Israel. Hereby he relieved the Israel Antiquity Authority under Amir Drori - with the poignant pressure of Hershel Shanks of Biblical Archaeological Review, better known as *BAR* - of its gentleman's agreement that opened the entire set of manuscripts and thousands of scroll fragments to a team of scholars at the Hebrew University instead of the VIP closed circle of Christian scholars who by now had diminished in number from 7 to 3. In 1997, the entire collection came into the hands of Emmanuel Tov who immediately started his monumental work on the translation and the exegesis of the texts with a group of scholars at the Hebrew

University and other institutions. Eight years later, in 2005, Tov finished his work with 39 volumes published by Clarendon Press, Oxford.

That same year, 1997, the author returned from sabbaticals at Harvard and Berkeley's LBL after a lot of soul searching. He met Jean-Baptiste Humbert at the Ecole Biblique in Jerusalem whose task it was to take care of the cultural heritage of Qumran of which de Vaux was its principal excavator between the years 1952-56. It was decided to run a pilot study on the provenance of Qumran pottery in collaboration with Marta Balla of the Technical University at Budapest who had expressed her willingness to cooperate by applying INAA to Qumran pottery to learn where the pottery was made hoping to deduct whom the Qumranites have been in contact with.

The second reason why we thought that such a research was needed stemmed forth from the simple question: Who wrote the Dead Sea Scrolls? Exegetical research with all its sub-research had neither been able to accurately date the scrolls nor to link the Qumran settlement with its cemeteries. The latter is postulated when one wants to take Qumran as a single homogeneous unit. In other words, the “Essenes” at Qumran were the ones who dealt with the manuscripts found in the caves and were buried in their own cemetery fifty meters away from their settlement.

The hypothesis came up that when one is unable to say where the scrolls originated on the basis of how the text is written and the parchment is made, there is another approach that departs from the premise that when the scroll jars were only used for shipping or hiding scrolls and these jars are only found at the Qumran complex including its caves and, furthermore, one will be able to trace the chemical composition to that of the place where the scroll jars were manufactured, and it results into local and imported jars according to their chemical fingerprint, then we have also a hint where the scrolls may have come from, or at least where they were used the last time before they were discharged and/or deposited in the caves on the cliffs of Qumran.

All this rationale took place at the Institute of Archaeology at the Mount Scopus Campus of the Hebrew University in Jerusalem. At the other side of town, at the Kuvin Center of the Department of Parasitology of the Hebrew University, a group of scientists had independently been busy under Charles Greenblatt to study the DNA of the parchments of the Dead Sea Scrolls in order to learn from what goat, ibex or sheep the skins were taken. Besides the intentional setup of a database of DNA results, the study tried particularly to address the Qumran parchment puzzle by analyzing the various pieces of parchment in order to help the restorers to piece the scrolls together. The team was also looking into the oldest authenticated

burial shroud encountered in Israel from the Second Temple period and into the paper that was used for the Aleppo Codex of thousand years ago.

This bio-culture research of organic materials at Qumran was foremost made possible because of the self-imposed isolation in which-culturally speaking- the Qumran population had placed itself, so that contamination with foreign cultural trends was reduced to a minimum, whereas on the other hand, nature has helped by preserving the Qumran culture due to the dry environment of the Dead Sea region in which the organic as well as inorganic remains were found intact.

Several ancient writers among which Pliny the Elder, Philo of Alexandria and Flavius Josephus have named a group of Jewish dissidents or sectarians who lived in Judea and along the Dead Sea. The name Essene was given to one of these groups. We will mention the name "Essene" in quotation marks since we are unable to prove whether they were the ones who once occupied Qumran or another group with a different name.

The analysis of the "Essene" bio- and material culture asked for a multi-interdisciplinary research that might bridge the physical and cultural environment and could be brought in line with the description of the Essenes by the ancient writers and tested by the description of sectarians in the Dead Sea Scrolls themselves.

In a subsequent encounter of scholars from Mount Scopus campus and the Medical School campus of the Hebrew University, under the auspices of Michel Stone of the Orion Dead Sea Scrolls Institute in Jerusalem, it was decided to collaborate in the future. The cooperation got the name of "The Jerusalem Task Force" but was initially, as already mentioned, a linkage of two scientific approaches: DNA to Qumran parchments and INAA to Qumran pottery. Scholars from both branches researched the roots of the scrolls and the local people in whose midst the manuscripts have been found.

Two years later, the final link for a large operation was laid by a casual encounter. In May 2000, the 34th Biannual Archaeometry Conference took place in Mexico City. There, Jan Gunneweg and Emmanuel Pantos met and discussed collaboration on an interesting problem. Gunneweg suggested that Qumran textiles would be quite attractive due to the purpose of identifying with certainty the type of each yarn of textile and the dyes that had been used to color them in order to learn more about the "Essenes". It turned out that Daresbury Laboratory could start this research immediately by identifying the textile fibres. In the next ten days, about twenty textile samples made their way from Jerusalem to Daresbury. There, Pantos' colleagues suggested taking the project to ESRF in Grenoble where Martin Müller of

the University of Kiel, an expert in cellulose fibres, would use synchrotron micro-XRD to characterize the fibre type.

Back in Jerusalem, Gunneweg decided to get the most out of these textiles and had them sent to Jan Wouters in Brussels who submitted them to SEM and HPLC and to Peter Vandenabeele in Gent who applied Raman spectroscopy to the pigments/dyes--all organic--whereas the AMS C^{14} setup in Groningen under Hans van der Plicht with Kaare Rasmussen was asked to date them, thereby giving a time marker to when the scrolls had been used for the last time before they were hidden in the caves, because the majority of the analyzed textiles are scroll wrappings. By a combination of the C^{14} date of the textiles and the thermoluminescence date of jars as well as their provenance that has been performed by Kaare L. Rasmussen in Copenhagen, one would be able to see the organic and inorganic research data in the same time frame that was postulated if one wants to see the Qumran site, the caves and the cemetery in the same chronological context.

In 2001, Gunneweg was asked to co-edit a book on Qumran that would contain all or the greatest part of the new scientific results. The book appeared in December 2003 and was the trigger to create a working group in the European Community COST Action G8 network in order to attract more researchers from all different fields to cooperate in science and technology (hence COST) applied to Qumran.

In February 2004 at Malta, representatives from 22 European countries and Israel held their Management Committee session during which it was decided that the Qumran project was to become a COST Working Group and simultaneously that a Qumran meeting was to take place in Jerusalem. The proceedings that follow are the fruit thereof[1].

A primary goal of the working group as well as the Qumran meeting was to draw together scholars in the domains of history, curators, conservation, art, forensic microscopy, physics

[1] At present, the Qumran Project consists of the establishment of reliable provenance of ceramic by neutron activation analysis, and secure dating by thermo-luminescence, magnetic susceptibility and Carbon[14].
Identification and stability of the textiles and fibers present by the Microfocus Beamline ID13, high magnification scanning electron microscopy (SEM).
XRF, XRD, petrography investigation and color image analysis of limestone species (vessels, cups, etc.) for assessment of alteration processes.
Research on organic dyes used for the coloring of the textiles.
DNA technologies, using specific nuclear and mitochondrial markers for analysis of parchment, leather, and agricultural products, etc.
Forensic microscopy.
Dating, authentication, conservation of historic building, stone and ceramic materials.
Understanding the role of various metals in DNA taphonomy, including "in situ" elemental chemistry of organic artifacts.
Identification of various plant-organic remains.

and chemistry to cooperate in the authentication of artifacts and their conservation for the generations to come.

The most important outcome of the section on pottery provenance, thermoluminescence and C^{14} dating, as well as DNA and parasitology studies, is that finally there will be a databank with results for each technique of materials collected at Qumran and beyond. This means that from now on, the discussion is open to everybody who is familiar with these analytical techniques as well as with their limits. Whether we have succeeded, will be seen, but it looks as if we have started to over bridge the distance between the study of the manuscripts and the archaeology of the site of Qumran with real people who lived there.

Hopefully, the present proceedings will ignite a spark in the minds of each of us to consider, comment and stimulate cooperation between curators, conservationists, archaeologists and natural science scholars in order to contribute to the general welfare of the cultural heritage at our disposal. It is precisely the cultural relics that have to be preserved for many years to come. Meanwhile the proceedings also publicize the results of our collaboration to the general public eager to learn more about its roots.

The present proceedings is divided into three sections: 1) Bio cultural investigations looking at the bio polymers that have been preserved in organic materials found at Qumran; 2) Material culture studies in the provenance of Qumran pottery and glass to learn who the “Essenes” have been in contact with and thermoluminescence to date that pottery, furthermore the identification of textile fibers and organic dyes used to color textiles that also may provide a C^{14} date for cloth found in the caves and the settlement of Qumran, whereas 3) Conservation studies on paper and DNA analyses of parchment and other organic remains from the Dead Sea region.

Finally, it has not been our purpose to finalize the many problems connected with the various biological and material matter found at Qumran and 'Ain Feshkha. We intended to provide an overview of the various laboratory techniques that were employed, and for that reason some papers have been included that do not touch on Qumran, but the purported techniques can be adopted in the future when a collaborative spirit is created between Science and Humanities as our study was the first fruit. The latter is a real desideratum.

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Section I

INTRODUCTION TO THE BIO CULTURAL RESEARCH OF ORGANIC MATERIALS AT QUMRAN AND THE DEAD SEA AREA

Charles Greenblatt and María Inés Zylber

Kuvin Centre and Department of Parasitology, The Hebrew University of Jerusalem, Israel
E-mail: greenbl@cc.huji.ac.il

The central premise of this group of short articles is that biology has only begun to talk to archaeology and it has very much to say. One of our authors, Mumcuoglu, will describe parasitism in ancient human populations with emphasis on the many aspects of delousing, the evidence of which has been found in many archaeological sites in the form of delousing combs. An example of such a comb can be seen in his article (Mumcuoglu 1988). We would simply like to point out that these beautiful items contain a number of stories. The comb was, for example, made of boxwood from Turkey. We can ask what made the artisan choose this wood and not another, how did the artisans fashion it, and how did it arrive in Qumran. Less obvious is why the wood, essentially the carbohydrate cellulose, should remain in a recognizable form after 2000 years. Trapped between the tines of the comb are human hairs. Another biopolymer of lasting appearance is present but this time it is a protein, keratin. These two biopolymers are the main component of many items of our material cultural heritage, including papyrus, paper, wood and wool. However, this is just scratching the surface. Attached to the hair is a louse. Now we have a third biopolymer in the form of its exoskeleton of chitin. This carbohydrate along with its derivative chitosan is the earth's most dominant biomass in the form of insects and molluscan shells. Other than being a part of the great organic moiety of our planet, the louse's story may be seen as quite a simple one of preferential bloodsucking in the region of the human head. Mumcuoglu will tell us that lice and people have been together for a long time and that in this association entire ceremonies of preening have arisen, going back to our primate roots. Yet our story doesn't stop there, since from that most intimate moment when this louse fed on some human it became filled with

blood, thus acquiring a remnant of its human host. In the Qumran comb louse there is only a shriveled up little flake of dried blood. Yet in it are hundreds of polymeric proteins or their breakdown products, but the biopolymer of most interest in this case is neither a protein like the collagen or keratin or the carbohydrates such as the cellulose or chitin, but one made up of nucleic acid bases – the DNA of the louse's victim. Here if the message is not too degraded we might learn whether the little child whose blood was suck was, in fact, to become by his inheritance a Jewish priest. One more biopolymer of great interest comes to mind, and this is collagen. If this little Jewish boy (many presumptions) grows up to be a scribe, he will write his holy scripts on parchment, and if we are to see his work – then the integrity of the text will depend on the ability of collagen to withstand the rigors of environmental forces and biological agents over millennia. Moreover, a hair of his can fall down and get trapped under a stitch when sewing together two pieces of the parchment, thus not only collagen but also keratin will be involved in this preservation story (see below).

In fact, much of the record of our cultural heritage is dependent on the four structural polymers – cellulose, collagen, keratin and chitin; and the information-bearing DNA. In Qumran the texts of the Dead Sea Scrolls written on parchment may be the first to draw our rapt attention. Yet the site is littered with thousands of organic artefacts, each of which, if we have the tools at our disposal, may reveal much about the people who lived there.

To put the bio-cultural aspects of Qumran into context, our colleague Shimon Gibson will first lay out the landscape archaeology of the site. This approach has often been missing in Qumran, with one archaeologist creating a world of the past based upon one particular area of the site while another creates another world, based upon an area a few hundred meters away. Had the soil been examined for the study of phytoliths and/or pollen, would these areas be better defined? Then, Mark Spigelman will describe the bodies found in the cemetery. Here we begin to see Qumran as the center of a major controversy. Who were the people who lived and were buried there? Why can't we deduce this simply from the bodies found over the last 50 years? Spigelman will tell us of the problems that obfuscate a simple answer. A few studies of our own laboratory have failed to find DNA of a sufficient quality to define the populations. Yet this work was done with already outmoded techniques, which within the shortest time will become able to cope with the problem.

If Gibson surveyed from the air and on the ground, and Spigelman reported on the bodies dug from the ground, the work of Azriel Gorski will take us to a higher level of magnification. Gorski is a forensic scientist whose specialty is trace evidence. He will describe how a forensic scientist deals with the organic remains of a 2nd Temple individual. In this case, his

bones were successfully examined for DNA and his burial shroud revealed a great deal of additional information about the man and his times. Then, in the context of Qumran he has examined the stitches that hold the scrolls together and from this he is able to tell us about scribal practices and how these are ingrained in culture. Occasionally there is another bit of evidence left behind – in this case a hair caught under a stitch. Hairs tell us much about the people on which they grew. Perhaps we will find lice and unkempt hair, or the hair may be clean and cut, especially if their DNA containing roots are still present. Gorski will also tell us of a shroud found in Jerusalem and how this time we were successful in obtaining DNA.

Below the level of microscopic observation is the molecular dimension. We have already hinted to the reader that our Hebrew University group's major interest is the degradation of bio-molecules. Indeed this field is beginning to yield new information thanks to molecular biology techniques. Our work, which Gila Kahila Bar-Gal will describe, is mostly focused on the DNA of animal and plant domesticates. Gila's first interest was in the domestication of the dog, but inquiries to Joe Zias (then the anthropology curator at the Rockefeller Museum) and Magen Broshi (Former Curator of the Shrine of the Book, Israel Museum) into the availability of canid populations led us to a more promising collection – the more than 10,000 unmatched fragments of the Dead Sea Scrolls. You will hear more about this work somewhat later, but it promises to reveal much about the practices of animal domestication. The basic methods have also been applied to plants and Benjamin Klein will give us an idea of progress in that field as well. Finally Zohar Karem will introduce us to other ancient bio-molecules. These are not the polymeric molecules, but the organic compounds that are absorbed on the everyday ceramics. Zohar will describe methods that distinguish red from white wines and tell us when the oils used were specific to olive.

These ancient bio-molecules are fragile organic substances, prone to natural aging under the best of conditions, but exposed to the apparently environmental conditions of temperature, humidity, and biological agents they have undergone even more change. However, the optimist in me says it could have been worse. The Dead Sea offers low humidity, and possibly sterilizing temperatures that have been a blessing in their preservation in a recognizable form. After excavation, human handling, storage, and transport have exposed them to humidity and biological agents. Just how we assess the damage and preserve and conserve these invaluable treasures will be one of the general challenges of the COST Action 8 and of this workshop in particular.

Therefore, after hearing something about the ability to decipher human activities by retrieving ancient bio-molecules, we will hear of our attempts to understand the process of

taphonomy, repel molds, and chemically intervene to stabilize the biopolymers. Matthew Collins has become a leader in attempts to understand the degradation of archaeological artifacts. His concept of “thermal age” makes it possible to predict the survival limits of collagen. A small bone protein, osteocalcin, is his focus of research in protein mass-spectroscopy. Itzhack Polacheck describes how fungal hyphae invade items of cultural history causing their degradation. Cellulose provides an energy source for many fungi so paper, wood and cotton are affected. Materials such as parchment and leather are also susceptible to damage by molds. Unique exo - and endo - hydrolyzing enzymes for each biopolymer are responsible for the attack. Finally, Avraham Domb, a polymer chemist, explores the structure of polymers and demonstrates where one can alter structure in order to obtain greater stability and longevity.

Hopefully in the coming years archaeology in a biological context will come of age, and this will in good part be due to the contribution of the tools COST Action G8 has provided.

MICROSATELLITE DNA SEQUENCES IN LOCAL VINES OF THE HOLY LAND

Cochavit Ben-Yair[1], Charles Greenblatt[1], Gila Kahila Bar-Gal[2] and Benjamin Klein[3]

[1]The Kuvin Centre for the study of Infectious and Tropical Diseases, Hebrew University - Hadassah Medical School, Jerusalem, Israel

[2]The Veterinary School, Faculty of Agriculture, Hebrew University, Israel

[3]Laboratory of Experimental Surgery, Hadassah University Hospital, Jerusalem, Israel

E-mail: benjamin.klein@gmail.com

Abstract: Ancient tradition indicates that viticulture and viniculture were widely practiced in lands mentioned in the Bible, and both text and archaeological findings give such evidence in Qumran. We aim to assign DNA identity-markers to a defined collection of indigenous grapevines considered to be "living relics". Results can be useful for a) as a database for ancient vine DNA, b) for comparison with other Mediterranean cultivars, and c) in cultivar conservation. Extraction of DNA from leaves of 20 local cultivars was amplified by PCR to determine simple sequence repeats (SSR) of 6 microsatellite systems conventionally used for vine identification (VVMD5, VVMD7, VVS2, Zag47, Zag62 and Zag79). These amplicons were examined: 1) by performing "gene-scans" to determine size and zygosity and. 2) by brute-force sequencing. The sequences were aligned for nucleotide comparison between cultivars. Trees based on sequence diversity between the cultivars were constructed. We also ranked the cultivars according to the use of alleles shared by the total allelic pool of the entire collection. The results show that these 20 cultivars are discernible by the use of these 6 microsatellite sequences. Some of them contain more than one nucleotide repeat sequence, and at least one is a type II repeat. VVMD5 amplicons contain (AT)n in addition to (TC)n repeats flanking the TC region. Sequences flanking the SSRs can be more diverse than the SSRs themselves. It is possible that some of the flanking sequences are part of transposable elements. Some preliminary results will be given on ancient grape seeds.

Keywords: grapes, wine, microsatellites, evolution, ancient seeds

There is ample testimony to the importance of viticulture in lands mentioned in the Bible. A vini / viticulture product "new wine" that was used in specific occasions is mentioned in the Qumran Scrolls. This indicates that the community either has grown vines in the area or somewhere nearby. We took the opportunity of the EU conference on Qumran organic finds to scout for possible technologies that might improve analysis of ancient grapevine DNA markers in archeological finds. We have extracted DNA from several grape seeds found in archeological excavations in arid zones similar to that in Qumran, e.g. Jericho and Timna (Early Bronze Age). Interestingly, ancient grape seeds are also available from Sataf, outside Jerusalem. The extent of DNA fragmentation in these seeds enabled the use of chloroplast DNA primers to confirm their belonging to the genus *Vitis,* and to identify in the Timna and Sataf seeds microsatellites corresponding to the VVS2 primer set (Fig. 1).

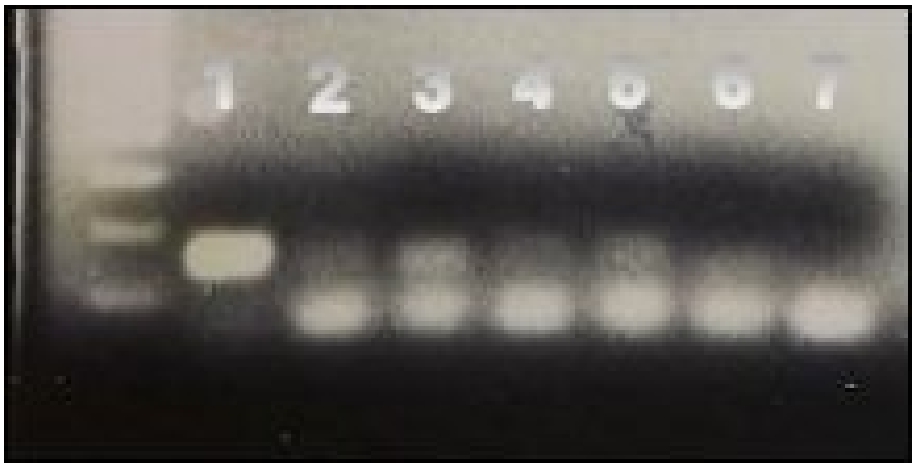

Figure 1. PCR for ancient samples from Sataf: (1) PCR positive control; (2) Sataf 1; (3) Sataf 2; (4) Sataf 3; (5) Sataf 4; (6) Extraction negative control; (7) PCR negative control

The VVS2 primer set represents one of the shortest microsatellites, 155 nucleotides and below (Fig. 2), indicating that the DNA fragments were not longer than 155 base pairs. Success in identification of ancient vines will require refinement of the present technology and yet use the same sets of primers because these are widely used as standards for vine identification. The interim aim of our work is to assign standard DNA identity-markers to a defined collection of grapevines considered as local cultivars indigenous to the region of Israel. Results can be useful for the following reasons: a) for comparative studies with ancient vine DNA from Qumran and elsewhere, when and if afforded by proper technology, b) for comparison with other Mediterranean local cultivars, c) as a database for students of vine evolution and domestication, and d) for cultivar conservation.

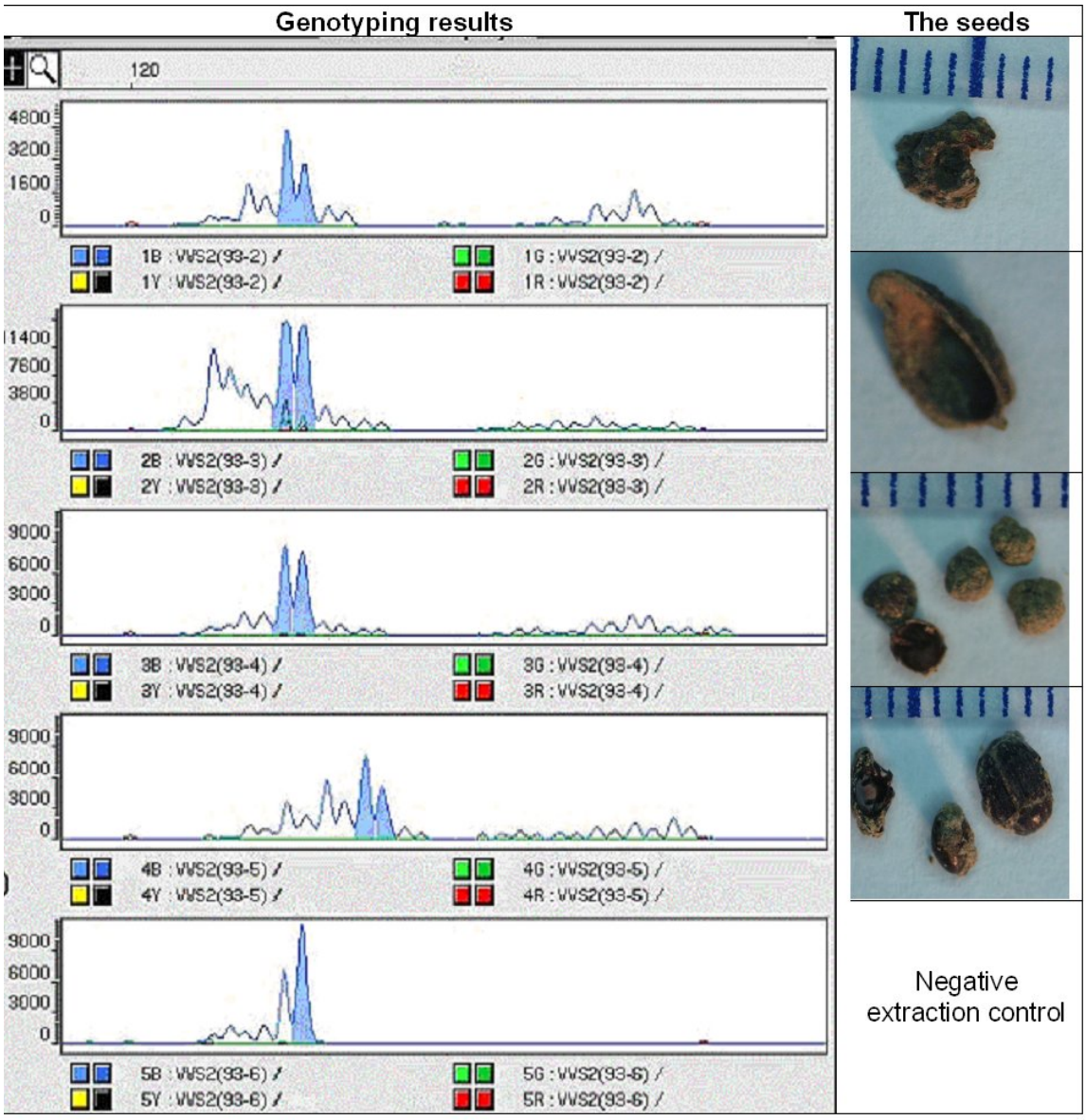

Figure 2. The ancient seeds with genotyping results for VVS2

Methods: DNA extraction was performed from leaves of 20 local cultivars, which are cared for by the Israel National Foundation and the Biblical Fruit Society. We used PCR methods to amplify simple sequence repeats (SSR) of microsatellites conventionally used for vine identification. These were VVMD5, VVMD7, VVS2, Zag47, Zag62 and Zag79. The resulting SSR amplicons were examined by two strategies: 1) by performing "gene-scans" to determine the amplicon size and zygosity status for each SSR in all the cultivars, and 2) brute-force sequencing of the amplicons disregarding their zygosity. The sequences were aligned for nucleotide comparison to distinguish between cultivars and document their identity. We constructed trees based on sequence diversity between the cultivars in reference to each

microsatellite alleles based on amplicon sizes, and also ranked the cultivars according to the use of alleles shared by the total allelic pool of the entire collection.

The **results** show that these 20 cultivars are discernible by the use of these 6 microsatellite diversity permutations. Some of them contain more than one nucleotide repeat sequence and at least one is a type II repeat. VVMD5 amplicons contain (AT)n repeats in addition to (TC)n repeats flanking the TC region. Sequences flanking the SSRs can be more diverse than the SSRs themselves. It is possible that some of the flanking sequences are part of transposable elements. The genomic SSR diversity is segregated from the haplotypic classification based on chloroplast DNA SSR diversity, suggesting that in these vines the evolutions of the genome and of the chloroplast represent independent processes.

The DNA from ancient seeds from Sataf (Calcolithic period) and Jericho (Early Bronze Age) was extracted and submitted to microsatellite analysis. The only primer set to give successful amplification was VVS2, the shortest among the ones used, yielding an amplicon 128-150 nucleotides long (Figs. 1 & 2). DNA within the nucleosome may be protected from degradation more readily than that between the nucleosomes; therefore we need to develop a method for the identification of the very same microsatellites but with shorter PCR primers.

ANALYTICAL METHODS TO DETECT ANCIENT PROTEINS

Mathew Collins, Enrico Cappellini, Michael Buckley, Kirsty Penkman, Rebecca Griffin, Hannah Koon

BioArch, University of York, York, U.K. E-mail: mc80@york.ac.uk

Abstract

'Palaeo-proteomics' is a promising new field of research, at the interface of archaeology, biology and geochemistry and underpinned by advances in soft-ionization mass-spectrometry. The BioArch initiative in York and the wider European GeneTime Early Training Site in Ancient Biomolecules (www.york.ac.uk/depts/arch/GT) share a common aim to exploit new advances in technology to improve the analysis of organic remains. We are beginning to discover that in certain environments the rate of protein degradation is so consistent that they can be used as molecular clocks to estimate the age biological materials and we are using this information to both estimate the age of fossils and the age at death of remains. In turn the consistency of this decay can be used to identify apparent limits to survival. In bones that are well preserved, these limits appear to be useful, but we are also trying to identify data that bucks this trend. Initial post-mortem processes have a great impact upon survival, whilst in some circumstances preservation is greater than ordinarily anticipated. It would appear that mineral binding is one such process, which enhances preservation. Using mass-spectrometry it is possible to examine the sites of cleavage of the peptide backbone and thus enlighten our understanding of patterns of decay. A further potential advantage of mass-spectroscopy is the ability to go 'molecular fishing' either with a specific target in mind - we use solid phase extraction to purify a specific protein to genus level to identify bone fragments - even when heated. Alternatively a 'shotgun' approach can be used to identify contributing proteins in an unknown mixture.

Introduction

If archaeometry, the application of scientific methods from the physical sciences and engineering to archaeology, is viewed as a mature discipline, its biologically oriented junior has grown up rapidly in the past two decades. Its science has formed the basis of films (*Jurassic Park I-III*), and television series (*Secrets of the Dead*, *Meet the Ancestors*). Its colourful history has been told in best selling science books (Seven *Daughters of Eve*, Bryan Sykes, Norton Books; *The Molecule Hunt*, Martin Jones, Penguin Books). Its findings have re-written the histories of humans, our diets and diseases, and has even help solve murders, ancient and modern. Much of the emphasis has rightly been placed up. Despite this, junior has proved controversial, with debate surrounding both data collection and analysis. Most of this controversy has surrounded the application of molecular biological methods. Lipids and proteins are less glamorous than older siblings that have provided less dramatic and, consequently, less controversial data.

Much of the controversy surrounds the interpretation of old and degraded material, and it is therefore sites such as Qumran that offer both the greatest prizes and largest pitfalls when analyzing organic materials. One approach to increase confidence in findings is to analyse a wide range of materials and biomolecular classes. Such an approach will offer evidence of the extent of decay as well as (occasionally) offering independent lines of evidence. Proteins are one obvious and widespread class of compounds. Unlike ancient DNA investigations, which increasingly identify the difficulties of contamination and degradation, ancient protein recovery and isotopic analysis (e.g. ^{14}C and ^{13}C analysis of collagen) is often considered mundane and routine. However, whilst collagen may be a ‘boring molecule’, neither the information it contains nor those of multiple other proteins likely to survive in the archaeological record have yet been exploited (Figure 1). In this short essay, we will consider the potential of proteins to contribute to the ‘non-destructive’ analysis of rare archaeological artefacts such as those found at Qumran.

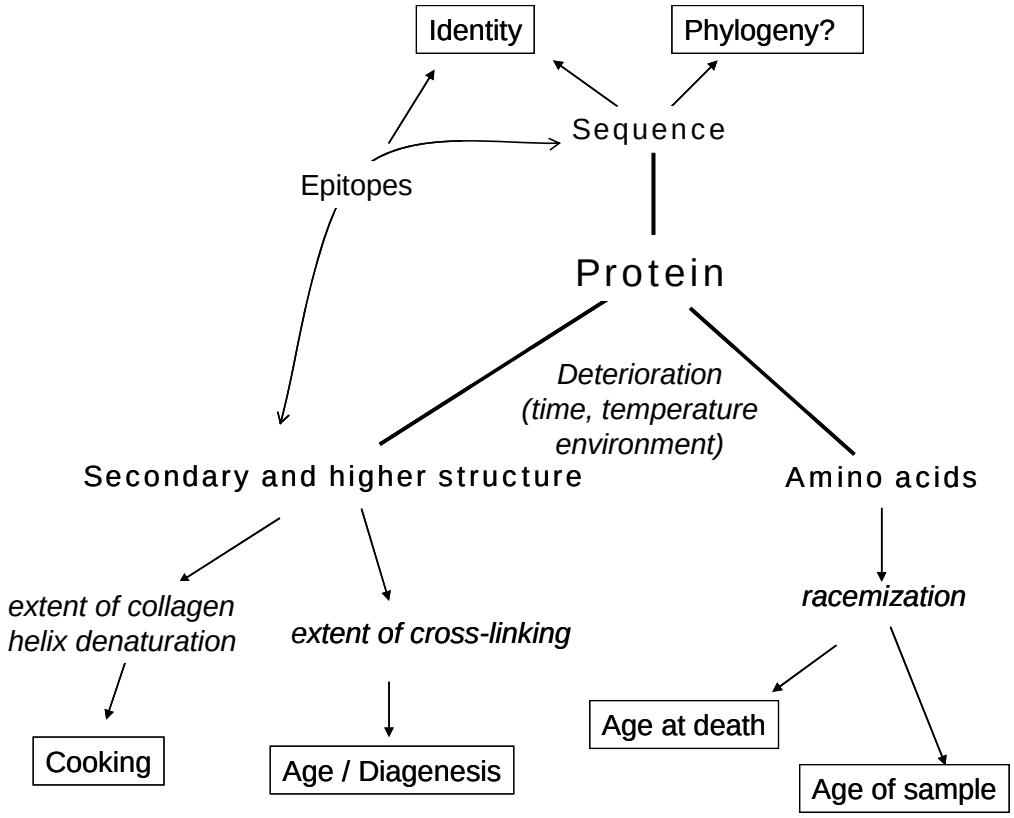

Figure 1. Proteins and their application in the analysis of ancient materials. The protein sequence (upper half of the figure) and their state of deterioration (lower half of the figure) can both provide information of use to archaeological investigations. However, in almost all cases it is necessary to carry out destructive sampling to complete the analyses.

Ancient Proteins, a brief primer

Amino acids the building blocks of proteins have been identified as widespread in ancient materials since the pioneering work of Abelson (1954). As Abelson discovered if the system is well defined, the **compositional pattern** of amino acids can **identify** the dominant protein, as well illustrated by the findings of ancient collagen based 'glue' at the from the Nahal Hemar cave by Arie Nissenbaum (1997). Not long after, Hare and Abelson (1968) appreciated that the rate of decay of proteins, specifically the inter-conversion of L to D amino acids (**racemization**) could be used as a **chronometer** to assess the relative ages of sediments from the same region. The larger the proportion of D amino acids entrapped in a sample, the more degraded and hence the older a sample was.

Information encoded by the genome is expressed as protein sequence and attempts were made to detect protein sequence and use this to both **identify** samples and to assess

phylogenetic relationships. Although some attempts were made to directly **sequence** proteins and protein fragments (Huq *et al*. 1990) or to examine distributions of peptides following **proteolysis** (Armstrong *et al*. 1983), both approaches were compromised because for optimal application they require extremely well preserved protein. **Immunology** which can detect small regions or structures (epitopes) proved to be the most simple and reliable method both to detect unknown protein **residues** (Cattaneo *et al*. 1990) residues and to infer phylogenetic distance (Lowenstein 1981).

Protein mass-spectrometry was first applied to fossil proteins by Ostrom *et al*. (2000) and holds great promise because small peptides can be identified by direct sequencing, thus in theory both **identity** and **sequence analysis** are possible, as is data on patterns of **deterioration**.

Here we will consider developments in these fields and their potential for future application at sites such as Qumran. Specifically we will examine strategies to assess the extent of deterioration (itself linked to age) and methods to identify specific proteins.

Racemization: age as the extent of deterioration

Protein decay should be predictable and therefore the extent of decay could be used as an age estimate tool as proposed by Hare and Abelson (1968). Unlike radiogenic methods, or methods which assess the dose of radiation objects have accumulated, protein decay occurs at a macromolecular scale. The process is therefore affected by the original structure and composition of the protein mixture, as well as a host of factors that will affect reaction rate (such as temperature, pH, the amount of water, etc).

In some cases the original structure of the protein has a dramatic effect upon the rate of racemization (Van Duin & Collins 1998), a most extreme example of which is the rapid racemization of aspartic acid in denatured collagen (gelatine), but extremely slow rates in intact skin and bone collagen (Collins *et al*. 1999). Weiner *et al*. (1980) elegantly exploited this phenomenon to assess and semi-quantify the extent of damage to the Dead Sea Scroll parchments from Qumran.

In order to render the clock useful it is therefore necessary to examine a defined system under defined conditions. (Goodfriend 1991) observed relatively consistent patterns of racemization of aspartic acid from land snails in the Negev. Currently we work with a single genus of gastropod, and mainly with just one species, a small freshwater snail *Bithynia*

tentaculata. The snail produces two fossils, as well as the typical coiled shell in which the animal lives composed of aragonite; it also produces a more stable calcite (opercula) that seals the shell when the animal withdraws. We have championed the use of intra-crystalline proteins (Russa *et al*. 1995) which are isolated following the approach of Berman *et al*. (1988). The closed system ensures that we can obtain a wide range of data from this substrate, including the changing composition of the amino acids and the extent of racemization in the whole protein pool and also in the fraction that has decayed to free amino acids.

Preliminary results suggest that this is a simple and effective age estimation system, which can be used alongside more conventional approaches. Although destructive, it is minimally so, using less than 3 mg of sample for a total analysis. In addition the extent of racemization can become a baseline estimate of the observed or predicted state of protein degradation.

The Palaeome: proteomic technologies applied to degraded proteins

If PCR represented a revolution in the study of ancient DNA (Jones 2002), then advances in soft-ionization mass spectrometry and mass analyser design hold similar promise for ancient proteins. These now offer the possibility of high throughput protein and peptide analyses, including recognition **sequence analysis** and detection of posttranslational modifications. In addition, informatics advances, means that **protein identification** is possible from masses and/or structurally diagnostic fragment ions generated from short cleavage fragments. These coupled technologies are particularly appropriate to the study of the small yields and fragmented remains that characterise ancient protein samples.

The field is still in its infancy and a number of major challenges remain outstanding. Ancient proteins are usually derived from poorly characterised, complex mixtures (e.g. Schulze *et al*. 2005). So far this problem has been largely avoided by selecting abundant recently synthesised proteins (Schulze *et al*. 2005) or persistence of specific sequences of robust protein from well preserved ancient samples (Nielsen-Marsh *et al*. 2002; Ostrom *et al*. 2000). One challenge will be to find ways to optimise extraction and sample handling procedures so that accurate and comprehensive studies can be performed reliably on small and partially degraded fragments. A second problem is that as proteins age in the environment or are cooked or otherwise processed, conventional informatics approaches, which assume intact proteins become increasingly less useful. Schulze *et al*. (2005) conducting a proteomic assessment of soil organic matter identified progressively fewer proteins in lower soil

horizons. A third problem for ancient samples is that in many cases there is very little that can be predicted about the sample and the organism may be extinct. Therefore comparison between the unknown and published genomic and proteomic data (the basis of most identification approaches) is of limited value.

Future directions

Proteins have justifiably been seen as much less useful that DNA in studies of ancient biomaterials. In most cases protein variety is limited. In both cases, (ignoring the contribution of collagen to ^{13}C, ^{15}N and ^{14}C analysis) the technologies are used primarily to (i) identify and (ii) to establish relatedness between samples. However, the amount of potentially extractable information is much greater for DNA than for protein and in the absence of robust and routine methods, proteins have largely been ignored.

The new technologies hold promise, but as yet only demonstration projects have been reported. Therefore proteins have been principally used to assess the state of deterioration (using amino acid racemization, Poinar *et al*. 1996) rather than to identify materials. However the integration of studies which assess the extent of degradation, the identity and (where relevant) the sequence analysis of ancient samples, must be close at hand. Proteins being more abundant than DNA can be analysed directly without amplification. In the right system, and using appropriate laboratory controls, discussion of which has so far been largely absent from the literature, contamination should prove a much less serious problem than for ancient DNA. The ability to identify organic materials will have widespread application, not only in the case of strange glues (Nissenbaum 1997) but food and floor residues. Similarly the fast throughput that characterises mass-spectrometric analysis offers novel approaches to identification of routine materials that are currently overlooked (e.g. bone fragments from floors) or for refining conventional analysis (e.g. the use of osteocalcin to resolve the question of sheep/goat in bone fragments).

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PRINCIPALS OF THE RECOVERY OF ANCIENT DNA - WHAT IT TELLS US OF PLANT AND ANIMAL DOMESTICATION AND THE ORIGIN OF THE SCROLL PARCHMENT

Gila Kahila Bar-Gal

The Veterinary School, Faculty of Agriculture, The Hebrew University of Jerusalem, Israel
E-mail: bargal@agri.huji.ac.il

Abstract

Evolutionary studies based on comparison of DNA sequences from living organisms is a rapidly developing field based on the advanced technologies in molecular biology. However, contemporary DNA sequences provide only indirect evidence of the historical processes that have formed them over long periods of time. Recovery of DNA from archaeological and paleontological remains enables one to study the genetic profiles of ancient samples in real time. Applying these advanced technologies to ancient samples provides a new perspective on the evolution of organisms and DNA. It is important to note that the recovery of DNA from ancient samples is far from routine, as the researcher has to contend with the fact that little and often no DNA survives in ancient tissues. Great precautions need to be taken to avoid contamination by robust modern DNA. In addition, several criteria of authenticity are essential for believing that DNA sequences are ancient. Domestication of animals and plants are important questions in the study of human evolution. Ancient DNA studies have made an essential contribution in the understanding of the domestication process, its origin and the co-evolution with humans. In our study we have demonstrated the potential of the molecular genetic approach in resolving questions in archaeology. I shall speak about these approaches as they relate to the Dead Sea Scrolls.

Introduction

Ancient DNA studies of the archaeological specimens contributed to the interpretation of the site answering specific questions that cannot be answered using a different methodology. Ancient DNA studies can also contribute to the development of hypotheses about past populations and understanding the process of domestication. In the last few years on top of the studies in archaeology, archaeozoology and anthropology to understand the transition to agriculture molecular genetic methods were addressed to study the same issue. Three main research concerning domestication were carried out: domestication of cattle (Bailey *et al*. 1996), horses (Lister *et al*. 1998) and wheat (Brown 1999). Most of the researches were to determine the origin, the number of times the animal was domesticated and the spread of the domestic forms. In our study we emphasized on the domestication of the goats with an approach to study the genetic change that occurred during the process.

Goats were one of the first animals to be domesticated. In Israel we find domesticated goats as early as the PPNB (8,000 BC). Our studies on goat domestication emphasized on the mitochondrial genes the cytochrome b and d-loop of *Capra* species dated to different period before, during and after domestication. Analysis of these ancient sequences qualified the rate of genetic change and the amount of genetic variability within and between selected species of wild and domesticated forms. Khirbet Qumran, dated to the late 1st BCE to early 1st CE, was one of the sites that was studied representing an after domestication sample. The location of Qumran and the finding of 408 Caprinae bones in the assemblage (Zeuner 1963) made it a suitable site for the study of goat domestication and the origin of the scroll parchment. The main assumption was that among the remains there are Nubian ibex remains together with domestic goats remains as the site is located in the home range of the Nubian ibex population. Because the bones of the early excavations were not available we sampled other organic material the scrolls. Scrolls were discovered in caves along the western shore of the Dead Sea but the most famous of these are the scrolls discovered in 11 caves near Wadi Qumran between 1947 and 1956.

Approximately 850 scrolls were found there, including books of the Hebrew Bible, sectarian writings of the local Qumran community, and about 200 previously unknown Jewish exegetical homiletic, liturgical and special works. Most of the scrolls were written on parchments made out of animal skins. Some of the Scrolls were nearly complete when found but the majorities were greatly fragmented. Some of these fragments could be pieced together by matching text patterns, scribal characteristics, ink, and characteristics such as physical

damage (Stegemann 1990, 1992). However, many others are still unmatched. Since their discovery the Dead Sea Scrolls (DSS) have been a subject of fierce controversy. The origin of the manuscripts, the identity of the Qumran community and the relationships between the archaeological site and the scrolls are the subject of dispute among scientists (Broshi 1999).

The main goal of this research was to provide additional samples of *Capra* from the late 1st BCE to early 1st CE period and to answer questions concerning the scrolls using aDNA methods:

1. Genetic identification of the animal species from which the parchments were made.
2. A study of the genetic profile of the DSS and the animal remains in the site. Comparison of these genetic profiles will determine the relationships between the two sources. A close relationship will suggest that the parchment were made out of those remains, meaning they were made from a herd at Qumran.
3. Identification of the fragments to the individual level. The identification of two fragments as derived from the same individual will enable to group fragment together to match new text and/or verify matches that have been done based on various other methods.

In this study we applied DNA analysis to the Qumran parchments and several *Capra* bones in order to examine the above questions.

Materials

This study is based on parchments from Qumran that were sampled under the supervision of the curators of the scrolls to prevent damage. The samples were cut with small delicate scissors or a blade at either the edges of the sheet, areas that are in area not crucial for matching in the future, or in blank areas. The sample size was small, approximately 0.5 cm^2, in order to minimize the damage.

Thirty-seven samples were taken from different scrolls and storage boxes for this study. The sampling was done in two stages: at first the Temple Scroll was sampled together with the samples from the storage boxes. The samples from the storage boxes were from two boxes: box one DSSF1, DSSF2, and fragments from cave 4: DSS 16, 17 and 18, the second box had samples from cave 3: DSS 3-14 and DSS 3-15. From the Temple scroll, the most complete scroll and the longest, eleven small pieces were taken from six pages and one stitch. On one page two samples were taken from different locations, one from the fragment attached

to the sheet and the other from the sheet itself. This sampling was in order to verify the morphological matching.

The second sampling was of four scrolls:

Serach: 5 samples: 4Q256 S(b) 905, 4Q256 S(b) 907, 4Q258 S(d) 140, 4Q258 S(d) 141, 4Q259 S(e) 810.

Isaiah: 5 samples: 4Q161 Is(a) 583, 4Q161 Is(a) 585, 4Q161 Is(a) 587, Is 2 (#188).

Hodayot: 8 samples: 1QH Col. 1 Plate 35 Sheet 1, 1QH Col. 5 Plate 39 Sheet 2, 1QH Col. 10 Plate 44 Sheet 3, 1QH Col. 13 Plate 47, 1QH Col. 15 Plate 50 Sheet 4, 1QH Col. 17 Plate 31, 1QH Fragment 26 Plate 57, 1QH Fragment 19 Plate 57.

Hoshea: one sample 4Q 167 Hos(b) 354.

In addition two goat/sheep bones were sampled from cave 24 basket 17 and 29. Cave 24, "Arobotyim" cave, is located close to the Qumran site and was the only bone sample as the bones from the site itself that were excavated in the 60's were not found. During writing this chapter another three goat bones were found in jars that were excavated recently in the site. These bones were also sampled.

DNA was extracted and analyzed twice and independently from the bones and the small pieces of parchment according to the methods described by Kahila Bar-Gal *et al.* 2002.

Results

Out of 37 parchments sampled, extraction of DNA was carried out on 26 samples and 5 goat bones. DNA was recovered from 20 scroll fragments from different sources and from one bone (Table 1). The results show 77% success in recovering DNA from parchments and only 20% from bones.

Although PCR of both cytochrome b and d-loop was addressed to all the samples only four samples have sequences of both regions (Table 1). For most of the samples one region was amplified from either cytochrome b or d-loop.

Storage boxes samples: The first two fragments sampled were the blank fragments (DSSF1, DSSF2) that came from the same storage box but differ in color and thickness. Despite the morphological differences, the DNA analysis, of the cytochrome b locus, indicated that they were identical sequences that differed in length 115 bp and 94 bp. The sequences were found to be closer to an ibex sequence (92.7% similarity). The comparison

with published Caprine sequences shows a higher similarity to C. hircus (90%) than to C. ibex (88%). Phylogenetic analyses using short sequences (96 bp) with three methods (distance, MP and ML) show that they branch together with the Temple scrolls (Figure 1). These close relationships are a bias of the shortening of the sequence. The deletion of base pairs caused elimination of the polymorphism between the two samples.

Table 1. Ancient DNA from Qumran site:

Sample	Cytochrome b	D-loop	Species identification
DSS Fragment 1	+		Ibex (*C. ibex nubiana*)
DSS Fragment 2	+		Ibex (*C. ibex nubiana*)
Temple Scroll 11QT1	+	+	Domestic goat (*C. hircus*)
Temple Scroll 11QT2		+	Domestic goat (*C. hircus*)
Temple Scroll 11QT3	+	+	Domestic goat (*C. hircus*)
Temple Scroll 11QT5	+	+	Domestic goat (*C. hircus*)
Temple Scroll 11QT5a	+	+	Domestic goat (*C. hircus*)
Temple Scroll 11QT7		+	Domestic goat (*C. hircus*)
Temple Scroll 11QT9		+	Domestic goat (*C. hircus*)
Temple Stitch		+	Domestic goat (*C. hircus*)
DSS 3-14 Cave 3		+	*C. aegagrus / C. hircus*
DSS 3-15 Cave 3		+	Domestic goat (*C. hircus*)
DSS 17 Cave 4		+	Ibex (*C. ibex nubiana*)
Isaiah 25 4Q161 583		+	*C. aegagrus / C. hircus*
Isaiah 26 4Q161 585		+	*C. aegagrus / C. hircus*
Isaiah 27 4Q161 587		+	Ibex (*C. ibex nubiana*)
Serach 4Q259 810		+	Domestic goat (*C. hircus*)
Animal bone Cave 24		+	Domestic goat (*C. hircus*)

From the same box another 2 samples (DSSF3-16 and 17) were studied. DNA was recovered from only one of them (DSSF3-17). The d-loop sequence (112 bp) obtained with primers 247-248 was closer to *C. ibex* subspecies (97%) than to *C. hircus / C. aegagrus* (94%). With Baladi the sequence had 96.2% similarity. Statistically these differences are not significant (0.15445+/-0.01092 Baladi and 0.16422+/-0.1174 Ibex).

Samples DSSF3-14 and 15 originated from cave 3 and stored in a different box were sampled and DNA was recovered from both samples. For sample DSSF3-14 only the d-loop was amplified using primers 247-248. The sequence, which is 113 bp long, was found to have only 86.8% similarity to Baladi sequence (Table 1) The comparison with published sequences indicates that the sequence is closer to *C. aegagrus* (93.25%) than to *C. ibex* (92%) or *C. hircus* (90%).

Two fragments, cytochrome b and d-loop, were recovered from fragment DSSF3-15. The cytochrome b, which was amplified using primers G_{11}-G_{12} (180 bp long), was found to be 100% identical to *C. hircus* (Baladi) and has a 95% similarity with *C. ibex* (Table 1). In the phylogenetic analysis, DSSF3-15 and DSSF3-17 (Figure 1, brace) branch together into one clade with most of the Temple scroll sequences. This group is very diverging and each sequence differs from the other. On the other hand, the d-loop sequence of DSSF3-14 (Figure 1, brace) branches to the other clade, closer to most of the published *C. hircus* and *C. aegagrus* sequences.

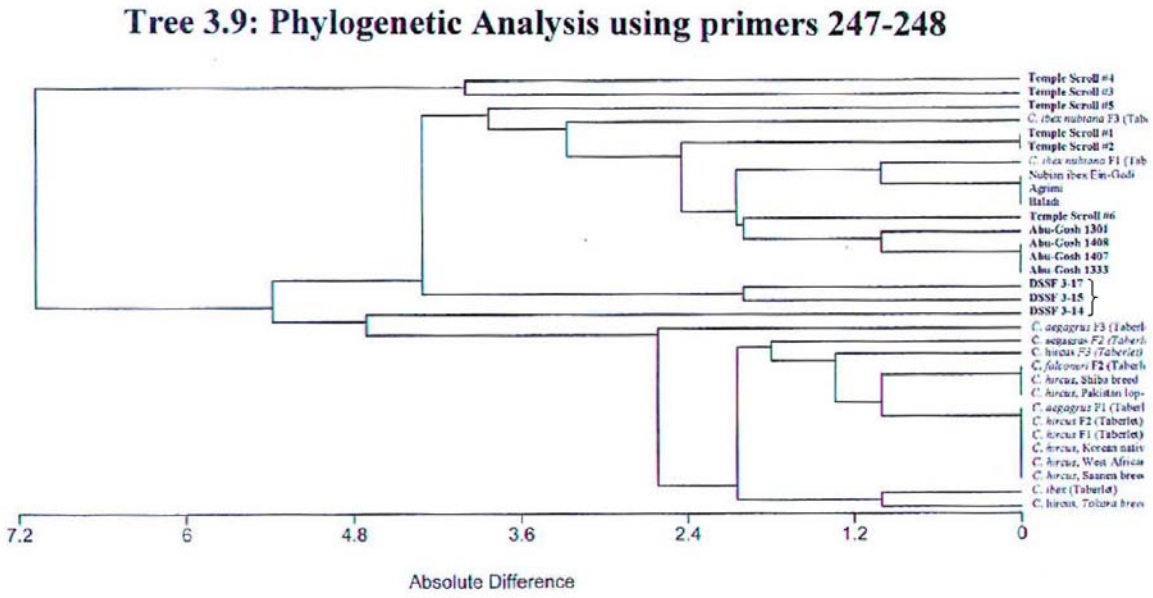

Figure 1. Phylogenetic analysis using primers 247 – 248

Temple Scroll: The cytochrome b sequences were obtained from ten samples, from different sheets, of the Temple Scroll and one sample of a stitch from the Temple scroll (sample12a). Eight sequences out of the ten were amplified using primer 116-117 (Table 1). All eight sequences were identical in length (115 bp long) and sequence. The sequences were

identical to the Baladi sequence and closer to the published domestic goats, *C. hircus* (100%) than to the Ibex and *C. nubiana* (96%) (Table 1). These relationships were found to be statistically significant, as it is identical (1.000) with Baladi. A comparison of the Temple Scrolls sequences with other ancient sequences showed close relationships to other goats from Abu-Gosh and Masada. In the phylogenetic analysis these relationships are presented (Figure 1). The Temple Scroll sample #11 is on the same branch with the Masada goat and on the same clade as most of the domestic goats.

The sequences obtained from the Temple Scroll using 247-248 primer differ from one another but are clustered together in the phylogenetic analysis (Figure 1). Phylogenetic analysis of the d-loop sequences (primer 247-248) indicates that the ancient DNA sequences from Qumran are closer to each other than to the modern sequences. Among the ancient sequences the Temple Scrolls branch together and differ from the others.

Other Scrolls: From the four scrolls that were sampled DNA was recovered from four samples out of nine that were extracted (45% success rate). The amplified DNA was of the d-loop using primers Gd_1-Gd_2. The DNA was of one sample from the Serach scroll (4Q259 S (e) 810) and three of the Isaiah scrolls (4Q161 Is(a) 583, 4Q161 Is(a) 585, 4Q161 Is(a) 587). The sequence of the Serach was identical to the Baladi sequence in all 191bp (Table 1). The Isaiah sequences were divided into two: sequences 4Q161 Is(a) 583 (190 bp) and 4Q161 Is(a) 585 (200 bp), which were closer to Baladi sequence (99%) and published *C. hircus* sequence (98%) than *C. nubiana* sequence (93 and 91%) (Table 1). Sequence 4Q161 Is(a) 587 (154 bp) was closer to Ibex sequence (95.5%) and published *C. nubiana* sequence (94%) than to *C. aegagrus* (91%) or *C. hircus* sequence (89%). The differences of this sample, 4Q161 Is(a) 587, with the other two is not just genetically they also differ morphologically in color and thickness.

Discussion

The study of the Dead Sea Scrolls by ancient DNA analysis demonstrates our ability to recover authentic sequences of ancient DNA from parchments. One of the main difficulties in ancient DNA analysis is the preservation of the DNA in the original tissue. The structure of the parchment and the dry climate of the Judean desert may have helped to protect the enclosed DNA.

Our molecular results indicate that most of the parchments examined here were made from domestic goat skin. Other parchments are made from Nubian ibex skin. The results are based on two different regions in the mitochondria, cytochrome b and d-loop, which strengthen the findings. These findings differ from those of (Ryder 1965). He identified most of the Qumran parchments as made out of hairy sheep, based on microscopic analysis of the size and density of hair follicles. The diagnosis of hairy sheep is surprising, as the hairy sheep is not known in the region. Using DNA analysis we have not yet identified any parchment as derived from sheep. The finding of high rates of goat skins can be supported by Zeuner's findings. Who published that some 408 out of 492 animal bones found in the first excavations in Qumran were identified morphologically as Caprinea.

As the Nubian ibex is one of the most common mammals in the Judean Desert and especially along the western shore of the Dead Sea, it is not surprising to identify it as been used for scrolls (such as in Isaiah) or for covering. These findings can be interpreted as indicating that the Qumran community may have hunted in the area.

A close study of the d-loop sequences obtained from the DSS yielded the population genetic characteristics. Comparison of the sequences showed that most of the sequences of the domestic goats are identical or very similar to each other. This indicates that it is possible that the studied scrolls were made from the same herd of goats. The origin of the herd is unknown yet. In order to answer this question the first approach should be to characterize the genetic profile of the goat like remains from Qumran. Unfortunately, those bones are not currently available so that we have not yet been able to characterize the goat population from Qumran. The cytochrome b sequence obtained from one bone was found to be closer to modern domestic goat sequence but its d-loop sequence was not recovered. Therefore, its relationship with the parchments cannot be determined.

As shown in this research color and thickness of the parchment are not criteria for matching fragments. For example DSSF1 and DSSF2 are from the same storage box but differ in color and thickness. Their cytochrome b sequence (115 bp) was found to be identical. The opposite example is the Isaiah samples. Sample 4Q161 587 looked different in color and thickness from the other two fragments. These morphological differences were found to be also genetically.

During this research one verification of matched fragments was studied. The match, in the Temple Scroll, was found to be correct as both fragments had an identical d-loop sequence.

These findings show the ability of the aDNA method to contribute in matching and grouping together scroll fragments. These results also stress the possibility to solve the problem of the 10,000 unmatched fragments using genetic analysis.

The genetic analysis of the sequences obtained from the samples contributes to the understanding of the animal species from which the parchments were made, while the identification of individual DNA polymorphisms determines the degree of relatedness of the animals used. The scrolls can be analyzed as a collection of animal skins from past ruminant populations. In addition to their importance in Dead Sea Scroll research, they will contribute to our knowledge of the genetic variation in past goat breeds as will be discussed in the next chapter.

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TRACES OF WINE IN ARCHAEOLOGICAL ARTIFACTS

Zohar Kerem and Baruch Rosen

Institute of Biochemistry, Food Science and Nutrition, Faculty of Agricultural, Food and Environmental Quality Sciences, The Hebrew University of Jerusalem, Israel
E-mail: kerem@agri.huji.ac.il

Archaeologists use ancient pottery to classify sites, establish dates of occupation, and describe and assign purpose and usage. Dating by appearance and by association with other finds at the site, remains a difficult and subjective process. Modern analytical tools already in use include radiocarbon dating, allowing the dating of plant or animal material. During excavations, many types of artefacts are uncovered, made of wood, bone, leather, metal, glass, ceramics and stone. Methods that can elucidate the mineral composition of shard and ancient pottery have been developed, including the stable isotopic ratios ($^{15}N/^{14}N$) elucidation of mineral composition through X-ray diffraction and neutron activation, that can tell us the geographical origin of clay, but also if a vessel contained a specific food or beverage (e.g. wine by tartarate residues). However, in contradiction to general belief, recent reports demonstrate that organic residues, such as resinous substances, can also be analyzed by an array of sensitive modern techniques, adding an ample amount of data to our knowledge of ancient technologies, preferences and even cultural evolution. Such a method is high-performance liquid chromatography (HPLC) using, for instance, mass spectrometry or diode array detection. The study of wine is important in understanding the technology, commerce and cultural habits of ancient cultures. The vessels containing it are of diagnostic value in an archaeological context and they have been studied using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), electron-microprobe and scanning electron microscopy. Distinct polyphenols (condensed and non condensed) and other small molecules can be extracted from artefacts that contained wine.

Introduction

During late antiquity, prior to the Muslim conquest of the Middle East, wine-producing districts in the southeast corner of the Byzantine province of Palestine formed the basis of a massive wine industry. Literary evidence and remains of ceramic amphorae inform us that wine (Figure 1) produced in areas presently included in the Gaza strip and in adjacent areas in Israel were consumed near and far, from close by Egypt to distant Britain.

Discernable characteristics of this ancient wine exporting system formed a route to modern wine international trade. For instance, it included a well-defined geographical origin, identifiable today by modern archaeologists. This important recognition served as a primal "Appellation d`Origine Controlee" and carried, as wine bottles do nowadays, a symbolic, non-literary, advertising message. The alleged exceptional quality of the wine was intensively publicized indirectly, through a careful manipulation of 'public opinion leaders' such as church personnel. The documented "world-wide" (i.e. Roman world) trade of wine may have lead to establishment of distinct quality indicators and measures of the product already in ancient times, It is suggested here that some of these quality markers can be detected today, using modern technologies.

Figure 1. *Vitis vinifera* and vessels used for storing wine

Materials and Methods

Samples: Ancient shards (sample codes SA-01-KK-21 and SA-01-KK-76) were kindly supplied by Prof. Y. Goren, from Tel Aviv University, and dated to mid-Imperial to Byzantine times (2^{nd}-7^{th} century AD). The samples were from a warehouse in use during the late Roman period (5^{th}-6th century AD). During the second half of the 6^{th} and the first half of the 7^{th} century AD, this warehouse was abandoned for storage and used as a dump for food and kitchen refuse, including broken pottery. The sampled shards belonged to this waste material. The whole room was buried by an earthquake around the middle of the 7^{th} century AD.

Samples of wine produced from vines grown in Sde Boker (Negev), were put at the end of malo-lactic fermentation into newly prepared ceramic vessels for an accelerated process (30˚C, 30 days), and then dried at room temp. The vessels were then broken and the shards treated as below.

Extraction: Inner and outer faces of ancient and newly prepared shards were scraped. The resultant powder (1g) was sonicated in 10 mL of 50% methanol in water, and the extract was passed through a 0.45 µM filter. The filtrates were concentrated under vacuum and were passed through a chromatograph. The HPLC system (Thermo Separation Products, Riviera Beach, FL, USA) consisted of an auto-sampler (AS3000), an injector (100 µL), a column oven (32°C), a pump (P3000), and a diode-array detector (UV6000). A reversed-phase C-18 column (250 × 4.6 mm, "Inertsil ODS-3V", GL Sciences Inc., Tokyo, Japan) was employed.

Results and Discussion

Shards, which were prepared by keeping modern wine in new ceramic vessels, produced residues and coloration that are apparently similar to the ancient shards (Figure 2). The similar appearance may suggest that the dark residues result from wine alone and not from the addition of other materials, such as resin, tar or waxes.

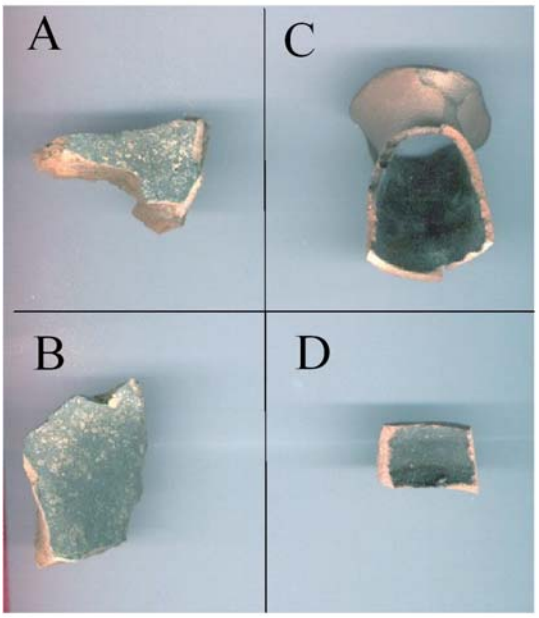

Figure 2. Ancient (A, B) and newly prepared (C, D) shards

A simple and rapid ultrasonic extraction of shards from ancient storage jars and from temperature-assisted aged modern wine, were analyzed by HPLC (Figure 3). Indeed, the dark appearing face of the ancient shards contained organic acids that are typical to wine. Specifically, tartaric acid is characteristic to grape containing products, and the ratios of malic to lactic acid found on the ancient shards resemble ratios of high quality modern white wine.

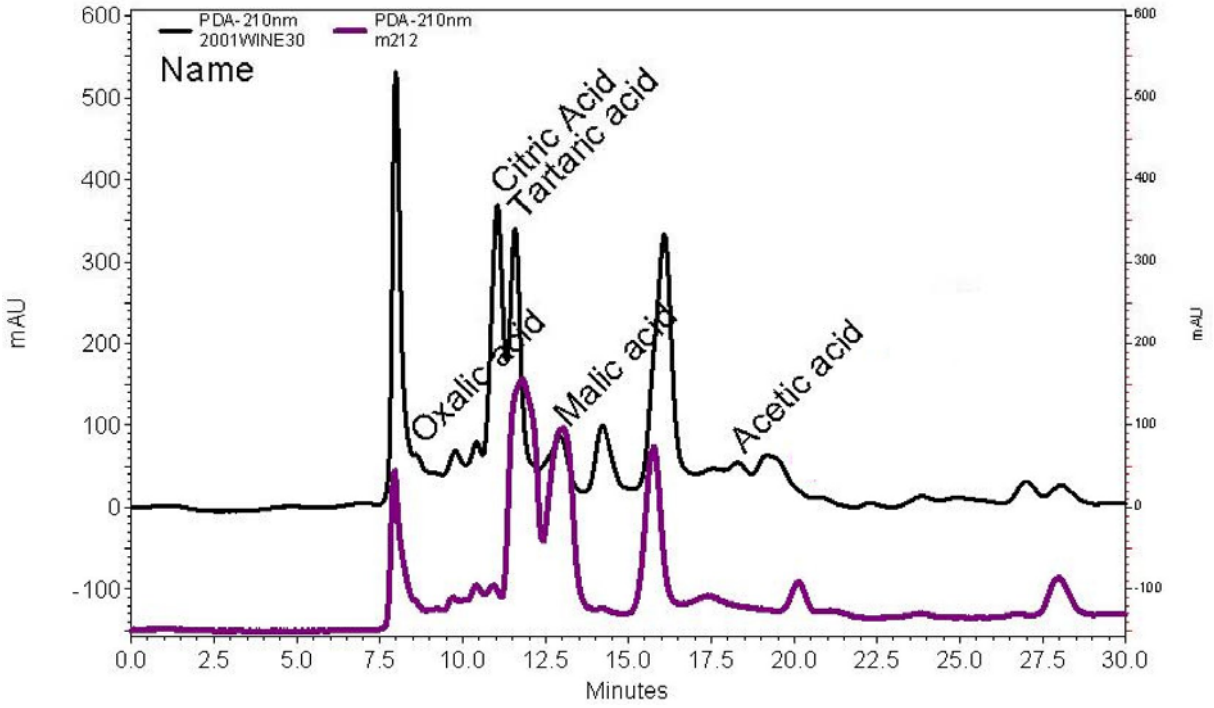

Figure 3. RP-LC chromatograms of organic acids extracted from shards (lower tracing/magenta) and from modern wine (upper tracing/black)

Archaeological pottery is an example of a highly complex mixture, as the retrieved substances are a result of the-often multiple-use of the amphora container for handling food or technological purposes followed by degradation and alteration processes during burial. Nevertheless, important dietary or functional information can be obtained by the analysis of included organic residues and in particular the lipid fraction or the organic acids fraction of the ceramics abundantly found on most archaeological sites. With the use of conservative extraction methodologies and mass spectrometry, a wide range of products were identified including several resins, epicuticular leaf waxes of cabbage and beeswax. These commodities were identified with the help of ‘‘biomarkers’’, i.e. lipid molecules that are characteristic for plant or animal species and which remain practically unaltered during burial. However, the analysis of fatty acid ratios of archaeological lipid extracts should be interpreted with caution as the original triacylglycerols are degraded due to oxidation processes, hydrolysis and microbial alterations. Nevertheless it was shown that carbon isotope ratios of individual fatty acids measured with on-line gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) are preserved during decay.

Our results demonstrate that a relatively inexpensive RP-LC method can be used to define not only the original use of an ancient vessel but also to prove the quality of the product that was kept in this vessel.

HUMAN PARASITES FROM QUMRAN AND THE SURROUNDING REGIONS IN ISRAEL

Kosta Y. Mumcuoglu

Department of Parasitology, Hebrew University-Hadassah Medical School, Jerusalem, Israel
E-mail: kostam@cc.huji.ac.il

Abstract

Lice are mentioned in the Bible as the 3rd plague visited on the Egyptians, while the Talmud distinguishes between lice of the head and those of the body. In Israel, 9,000 years-old head louse eggs were found from hair samples of an individual who lived in Nahal Hemar Cave near the Dead Sea. Head lice and their eggs were also found in combs recovered from archaeological excavations in the Judean and Negev deserts of Israel, including Masada and Qumran. The combs from Qumran contained a large number of lice and eggs, and were most probably not used by men. Examination and grooming to remove lice from the head of an infested individual was practically always a social interaction between mother and child. Essenians were therefore either living or had a close contact with women and children. Remains of a body louse were found in one of the rooms at Masada fortress, known as the "Casemate of the Scrolls". Eggs of the helminthic parasites *Ascaris sp. Taenia sp.* and *Trichuris sp.* were found in a locus in Qumran (No. 51), which is believed to be a latrine.

Keywords: Qumran, Masada, parasite, human louse, *Pediculus humanus*, helminths, latrine

Lice are mentioned in the Bible as the 3rd plague visited on the Egyptians when Pharaoh denied the request of Moses to let the Israelites go: “Then the Lord said to Moses, “Say to Aaron: Hold out your rod and strike the dust of the earth, and it shall turn to lice throughout the land of Egypt” (Exodus 8:15-17). From Sumerian, Akkadian, Egyptian and Biblical sources, it is evident that the ancient inhabitants of the Middle East were well acquainted with head lice, *Pediculus humanus capitis* (Figure 1) (Bodenheimer 1947/48, Driver 1971, Aufderheide & Rodriguez-Martin 1998), i.e., of the garments: the former have red blood; the latter white (Niddah 19b). Both are produced not by copulation, but by uncleanliness; and cleanliness is therefore the best means of getting rid of them (Shab. 107b; Ber. 51b; comp. Bezah 32b). It is sinful to kill a louse in the presence of other people on account of the disgust thus caused (Hag. 5a).

Nine-thousand year-old louse eggs were found in hair samples from an individual who lived in Nahal Hemar Cave near the Dead Sea in Israel (Mumcuoglu and Zias 1991), while in Egypt, head lice and their eggs were found on the hair of mummies (Ruffer 1921, Hoeppli 1956, Fletcher 1994).

Head lice and their eggs were also found in combs recovered from archaeological excavations in the Judean and Negev deserts of Israel, including from Masada and Qumran (Figure 2). Most of the combs were two-sided, while few were also single-sided. One side was used to open the knots, while the other one was used to remove lice and eggs. Most combs found in archaeological excavations were made out of wood, while some were made from bones and ivory, and are quite similar to modern day combs. Lice were found in 12 out of 24 combs examined from the Judean and Negev Deserts. In the comb from Wadi Farah, 4 lice and 88 eggs were found; two of them were operculated, showing that at this stage the eggs were viable with an embryo inside. In one comb from Qumran 12 lice and 27 eggs were found, ten of them operculated (Mumcuoglu and Zias 1988).

In a recent study, 3 head lice were found in 1 out 6 combs from an unidentified period from Nahal Zeelim. Lice and eggs were also found in 2 out of 5 combs from the Roman period excavated in Ein Rachel, while from 1 comb from an unidentified period from Ein Gedi no lice neither eggs could be isolated.

Figure 1. A first stage nymph of a head louse (*Pediculus humanus capitis*) (ca 1 mm).

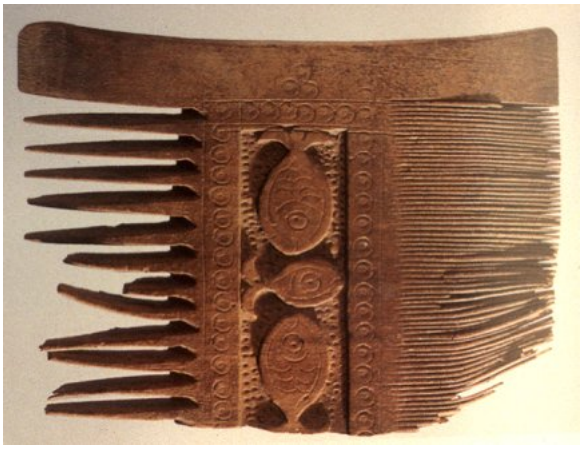

Figure 2. A two - sided delousing comb from unknown origin and period

While the debate continues as to whether Essenians from Qumran were living in only male groups or with their wives and children, I believe that the combs, which were found in Qumran and which contained a large number of lice and eggs, were most probably not used by men. Then, examination and grooming to remove lice from the head of an infested individual was practically always an activity achieved by the mother, a social interaction between mother and child. In an epidemiological study done recently in Israel, we found that in over 95% of the households, head louse diagnosis and treatment was responsibility of the mother (Mumcuoglu *et al.* 1990, 1991). Accordingly, Essenians were either living or had a close contact with women and children.

Royal combs from Pharonic times in Egypt were used for delousing (Kamal 1967). Head lice were recovered from the debris found among the fine teeth of a wooden comb excavated in Antionoe, Egypt, and dated between the fifth and sixth centuries A.D. (Palma 1991). The oldest combs, which are similar to today's delousing combs, are known from 1,500 B.C. (Zias and Mumcuoglu 1988).

Remains of a body louse (*Pediculus humanus humanus*) were found in one of the rooms at Masada fortress, known as the "Casemate of the Scrolls". Originally constructed during the last decade of King Herod's reign, the Casemate Room was converted into a dwelling unit during the first Jewish revolt against the Romans. Following the conquest of Masada, the room was used by the Roman soldiers as a dumping area. The context and the nature of the textiles associated with the louse clearly suggest a rebel origin (Mumcuoglu *et al*. 2003).

Body lice eggs were previously found in a pre-historic textile from Hallstätter Salzberg in Austria (Hundt 1960). This louse was also recovered from deposits of farmers in Viking Greenland and dated to AD 986-1350 (Sadler 1990).

Humbert & Chambon in 1994 decribed a locus in Qumran (No. 51), which they believed was a latrine. Microscopic examination of soil from this locus revealed the presence of eggs of three helminthes:

The roundworm, *Ascaris* sp., has two potential hosts: man and swine. Owing to dietary laws prohibiting the consumption of pork and the fact that pig remains have not been reported from the site, one can assume that these eggs belong to the human roundworm *Ascaris lumbricoides*. As only ruminants and ungulates were authorized for consumption, the eggs of the tapeworm, *Taenia*, found in this sample most probably belong to the beef tapeworm, *Taenia saginata*, and originated from the consumption of undercooked beef. The skeletal remains of cattle, which frequently appear in the excavated soils, support this assumption. The whipworm, *Trichuris sp.*, which is a common parasite of a variety of animals and man, is consequently also of human origin and therefore belongs to *Trichuris trichiura* (Harter *et al.* 2005).

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THE HUMAN REMAINS OF QUMRAN

Mark Spigelman

The Kuvin Centre for the study of Infectious and Tropical Diseases, Hebrew University - Hadassah Medical School, Jerusalem, Israel
E-mail: marks@md.huji.ac.il

Abstract

More ink has been spilt over the cemeteries of Qumran than all the blood in the forty bodies excavated there. The controversy, such as it is, is based on the studies of the forty bodies so far excavated and reported, which is unfortunate as they may not be representative of the over 1200 bodies to be found at Qumran. The work of the two anthropologists who have reported on these remains has been made difficult by several factors including: 1) the 40 plus years which have passed since the time of excavation until the time of study, 2) the poor preservation of much of the skeletal material available, 3) the possible failure of the excavators working in the early period to distinguish between the burial of the original inhabitants and later Bedouin burials, and 4) the sensationalism and lay press pressure for any facts relating to Qumran. The discussion will center on what is known, but will not give any answers, as I believe these are yet to be discerned.

Keywords: skeletons, males, graves, anthropology, east-west burials, north-south burials

Between 1953-56 Prof. Roland DeVaux, excavating the site of Qumran exhumed over 40 skeletons from the graveyard at Qumran. Shortly thereafter they disappeared, not to be seen until portions of the collection were revealed in 1998 in France, Israel, and Germany. Recent re-discovery of the remains has permitted experienced anthropologists to review the material (Broshi 2004).

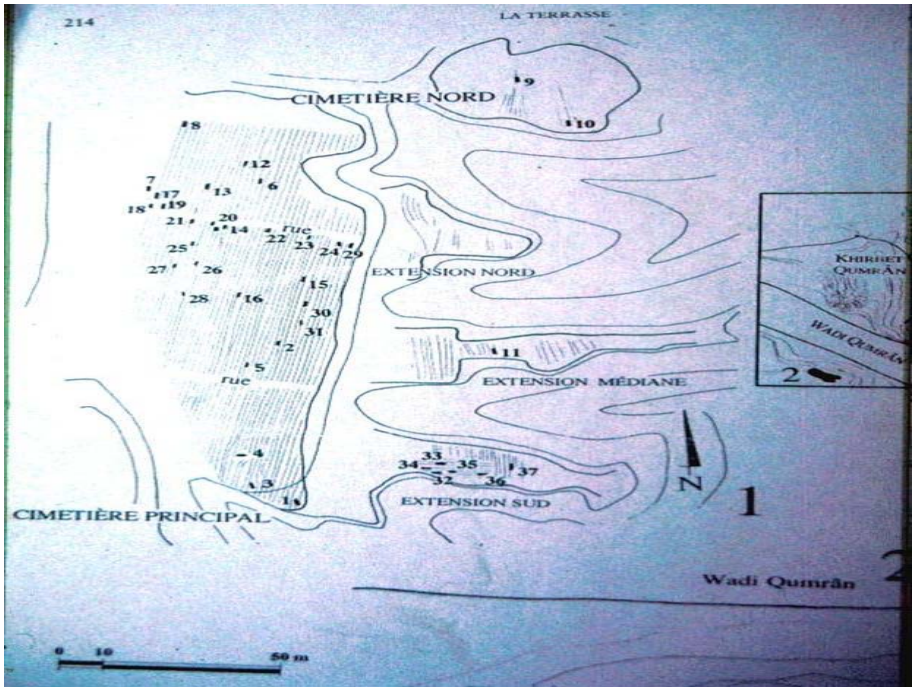

Figure 1. Map of the cemetery at Qumran

A number of scholars have studied and published their findings on these skeletons, including two highly regarded physical anthropologists Joe Zias (2000) and Sue Sheridan (2002, 2003), whose papers should be read in conjunction with this report as well as the papers from Olav Rohrer-Ertl *et al.* (2000). I point out that both Sue Sheridan and Joe Zias are experienced anthropologists who both have an extensive knowledge and association with the human remains from this area. Their views should take precedence over many of the opinions expressed by people who appear to have at best a passing knowledge of the area or even of the field of physical anthropology.

As Zias (2000) points out “Aside from de Vaux, Broshi, Sheridan and Puech, few if any recognized Qumran scholars have come from the world of archaeology which unfortunately has resulted in numerous errors and misunderstandings in attempting to interpret the site. In my opinion, it is precisely these three scholars whom have come the closest to correctly interpreting the site and the cemetery, whereas textual scholars and others understandably

have not been able to critically understand and evaluate the somewhat complicated archaeological and anthropological data at hand.

There have also been more theories as to the interpretation of this site than one can count. The original one claimed that this was an all male monastic site, and it has been repeatedly challenged by many learned and less learned ideas and theories. Scholars and others have tried to explain what and who used and did at this site, yet few if any of these alternate theories appear to have taken account of the material evidence from the human remains. It is hard to imagine that you can decide what people were doing at a site and yet ignore the people who are there in the 1200 burials. The few bodies recovered point in a certain direction, but these are too few to be conclusive, yet they cannot be ignored. Perhaps it is time to let the facts “speak”. This site is too important to allow theorist papers and reports which have not been properly based on fact to be sensationalised in the lay press without proper archaeological, scientific or anthropological backing.

Figure 2. Moslem beads

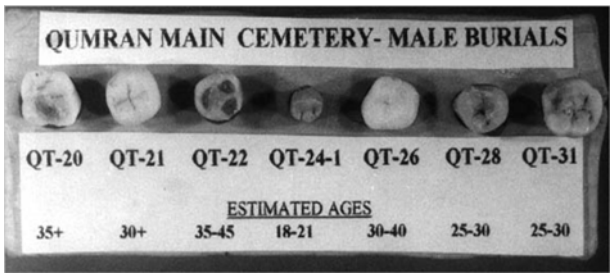

Figure 3. Teeth studied for DNA

The conclusions of Zias and Sheridan make some interesting points.

Sue Sheridan's conclusions:

1) Too small a sample size

2) Poor preservation of bony material

3) Absence of taphonomic record

4) Preponderance of men

5) No community profile possible

6) Misuse of available data? Possible mixing, varying curation conditions

7) Possible Intrusive elements prior to exhumation

In the French collection there is 1 woman (over 50), 1 teenage male (15-16), 1 elderly man by Qumran standards (over 60) and numerous younger males. The unusual remains are from Tombs A and B.

Zias talking about the women and children makes the following points:

1) The adult male burials in the main cemetery in rows a north-south axis with their head to south and their feet to north
2) Moslem burials are all east-west with the head to the west
3) 5 burials (Q32-36) of women and children, of R. de Vaux in extension *sud* were buried east-west, with the head to the west
4) Likewise, the same is true for the four anomalous tombs in the cemetery *sud* (particularly Tombs A and B)
5) Two burials were noted to have beads of Moslem origin.

It is to be noted that the Jewish practice was to bury their dead in a north-south direction and for Moslems to bury their dead in an east-west direction. When we visited the site this was quite clearly evident and one could see as well some differences between the two burials. Zias (2000) describes these.

There are a few rules in physical anthropology which bear mentioning in this context: (a) Until recent times any cemetery that did not contain over 30% of sub-adults does not reflect a normal community and (b) in ancient Israel there is no known practice of burying children (or women in a separate part of a cemetery).

My own conclusion from the evidence available would be as follows:

– There is much more information to be gleamed from the graveyard about the Qumran community. Current law in Israel does however prevent further excavation of the graves
– We need more bodies and a systematic excavation
– But currently most likely conclusion is that this was a group of men living in an all male environment
– There will be many more arguments; the next could well be an attack on this presentation

Broshi (2004) has detailed some of the scientific investigations that can be undertaken, and Sheridan's work in this field certainly shows what can be achieved (2003). We have undertaken a very small preliminary study on the DNA of some teeth from the German collection, which to date has yielded inconclusive results, but this does not mean that this line of work should be abandoned. Microbiology on ancient tissues is progressively opening up the field and we can do increasingly sophisticated research on the bio-molecules, which Chuck Greenblatt and Mathew Collins have referred to in this publication.

Figure 4. East-West burial

Figure 5. North-South burials

Finally, I do have a plea to the members of COST. This is a site of prime importance to the Judeo-Christian ethos. It must not be allowed to descend into a battleground for every theorist with a point to prove. Our visit to Qumran was personally disturbing as I noted that there were more tombs dug then can be accounted for by the bodies - whether this is looting, excavation as yet unpublished or even unauthorized I am not certain. Excavation of the site and its surrounds must be strictly controlled and efforts made to make sure full scientific studies are performed on any artifacts, remains etc. that are found. My plea is perhaps the lasting contribution of this meeting would be if we asked for this site to be world Heritage listed. There are problems with the need to consult various governments and authorities but this site is too important to allow it to be potentially pillaged.

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- To Dr. Jan Gunneweg for figure 5

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Section II

INTRODUCTION TO ‘MATERIAL CULTURAL RELICS AT QUMRAN’

Jan Gunneweg

Institute of Archaeology, The Hebrew University of Jerusalem, Israel
E-mail: jan.gunneweg@huji.ac.il

The present section deals with the material culture of Qumran. Under 'material culture' we understand everything that is man made whether it has been manufactured for daily household use or for a religious or ornamental purpose. The term ‘relic’ is used because it consist of what artifact survived of a specific individual, clan or tribe at any given time. The systematical study of the material cultural relics of the "Essenes" is of the utmost importance for a series of reasons:

- The various artifacts are analyzed for their chemical composition and for their strength to enable us to say something about the technique that the "Essenes" used locally at Qumran and why artifacts survived two millennia and more.
- The chemical composition provides also a way to distinguish between what is local to Qumran and what has been brought in from other sites, thereby accentuating the differences in the techniques between what the "Essenes" used compared to what others employed to manufacture artifacts.
- By studying the provenance and the dates of various artifacts we are able to reconstruct from the finds how the "Essenes" once lived on the shores of the Dead Sea.
- The material culture at Qumran is also necessary to be able to reread the manuscripts that have been found in the nearby caves in the light of the newly discovered evidence.
- A secondary benefice is that the chemical composition and the study of the manufacturing techniques can also shed light on the actual state of an artifact and its conservation in the short and in the long run.

In this section II, various scholars have studied various aspects of artifacts.

Salvador Butí *et al.* mention the first determination of wine residues ever found in amphora-35 found on the southern plateau at Qumran.

Lucía Canonica *et al.* have studied by XRF analysis a series of fifth century Roman window glasses and what they have learned for their conservation. The latter is also important for Qumran where glass recipients have been found.

Vladan Desnica and Manfred Schreiner show how a portable X-RAY Fluorescence Spectrometer van make life easier for the analysis of art objects that cannot be moved from the museum to the laboratory.

Marta Balla and Jan Gunneweg describe the provenance of Qumran Pottery by Instrumental Neutron Activation Analysis (INAA), especially the new data on the wine amphora-35 that has been excavated in 2004.

Martin Mueller *et al.* treat structural and elemental analyses of single textile fibres from Qumran using modern synchrotron radiation X-ray microdiffraction and microfluorescence techniques.

Kaare Lund Rasmussen shows a combination of Thermoluminescence and Magnetic Susceptibility that he used for the provenance of ceramics, among which those of Qumran. Samples have been analyzed from the same pottery that earlier had been analyzed by INAA.

Peter Vandenabeele *et al.* show how Raman spectroscopy can provide the identification of yarns as well as of dyes making use of textile samples collected from the Bar Kochba's "*Cave of the Letters"*.

Hans Van der Plicht *et al.* describe the long process of cleaning Qumran textiles and wood in order to prepare them for radiocarbon dating. Both clean and unclean textile C14 results will be shown to accentuate the importance of analyzing clean materials.

Valentin Vladimirov studied another aspect of the wash that was applied to the outside of Qumran storage jars by petrophysical analysis.

Leen Wouters approached the chemical composition of Roman glass found at Qumran and what can be learned from it when it is compared to other glass artifacts found in the Roman World.

It is hoped that with the first set of analyses applied to wood, ceramics, glass, textiles and wine residues by a variety of different scientific technologies in the domain of inter-disciplinary research, this COST Action G8 will be a boost to further research.

DETERMINATION OF WINE RESIDUES IN QUMRAN AMPHORA-35

Salvador Butí[1], Nati Salvadó[1], Núria Lope[1], Emilia Papiol[1], Elena Heras[2] and Jan Gunneweg[3]

[1] Departament d'Enginyeria Química, Universitat Politècnica de Catalunya EPSEVG, Barcelona, Spain

[2] Departament I + D, Miguel Torres S.A., Barcelona, Spain

[3] Institute of Archaeology, Hebrew University, Jerusalem, Israel

E-mail: salvador.buti@upc.edu

Abstract

Determination of tartaric acid in archaeological residues of vessels has been considered a chemical marker for the substances related to grape products. In this work the capillary electrophoresis (CE) and liquid chromatography (HPLC) techniques have been used in order to detect the presence of tartaric acid and others small organic acids in material residues found inside of a jar from Qumran site.

Introduction

The Site

Qumran is a site that is located on a plateau that borders the Dead Sea in Israel. The site has become famous after an estimated 950 scrolls (± 15.000 fragments) were found in eleven caves at Qumran itself and nearby. The manuscripts are written on parchment and papyrus. The scrolls are known as the Dead Sea Scrolls and contain texts written in Hebrew, Aramaic and Greek that confirm the authenticity of the ancient tradition of the Old Testament, as we know it today. About 200 scrolls deal with the Bible, whereas the rest are non-canonized texts as well as specific sectarian and liturgical writings dating from the 3rd century B.C. until the destruction of the site in 70 A.D. when the Romans took Jerusalem.

For Jews, the texts are of the utmost importance in showing that the oral tradition over two millennia has not changed anything substantial to the known text of the Old Testament. For a Christian, all the texts are of importance to show the context in which Christianity grew, especially in connection with Jesus, John the Baptist and Paul. For text critics, the original Hebrew text of the Bible is compared to that of the Greek Septuagint that seems to be nearer to the source that was also used in the Dead Sea scrolls.

Since three ancient writers, Philo of Alexandria, Pliny the Elder and Flavius Josephus have written about sectarians, sometimes called by the name "Essenes" who have been described as living in Judea in general and near the Dead Sea, the hypothesis was established that Qumran could well be the place where the "Essenes" dwelled.

For that reason, many people have been busy to connect the Qumran finds with the sectarian group of Jews who broke with the constitutional religion as preached in Jerusalem of those days and isolated themselves.

In 1998, Gunneweg and Balla started a pottery provenance project using INAA to trace the ceramic finds to the place where it was manufactured as pottery is the most important indication and the most copious one that has survived to trace the interrelations between families, clans, tribes and peoples. The fruits of this work were published in Gunneweg and Balla 2003.

The find

The 2nd of August 2004, Randall Price and Oren Gutman unearthed an ovoid jar with two loop handles that was sealed with an overturned bowl. When it was opened at the site in the presence of Jan Gunneweg, it was empty except for a four centimetre thick layer of debris, which we thought to be a residue mixed with remains of disintegrated ceramic. The jar got the name of Jar-35 (Figure 1). It was found on the southern plateau of Qumran, where no remains of architecture have ever been visible. The lack of architecture was explained by the fact that the plateau was used for agricultural activity. Price, however, excavated several cooking installations and Jar-35 was found in this context. We decided (1) to obtain a date for the jar by thermoluminescence in order to see whether it belongs to the same time period as that of the "Essenes", (2) to analyse it by INAA to learn where the jar originated, and (3) to analyse the residue for its content.

If wine was the substance, as we now know it was, then we have here the first physical evidence that wine was used at Qumran, proved by scientific techniques. According to stylistic studies of the pottery it has been decided that the ovoid jar-35 is of the same time

period as that of the Qumran Building Complex. The thermoluminescence date that would corroborate this, or refute it, has still to be checked once again. The INAA results are discussed in the paper of Gunneweg and Balla in this volume.

Wine, or "Tirosh" which is unfermented wine was prescribed to be drunk by the Priests and since the "Essenes" are of priestly offspring, it was also drank at Qumran if the Rule of the Community, which is the primary scroll according to which an "Essene" had to live and act, is indeed referring to the inhabitants of Qumran. Wine has been important for the "Essenes" even so that there was a yearly Wine Festival.

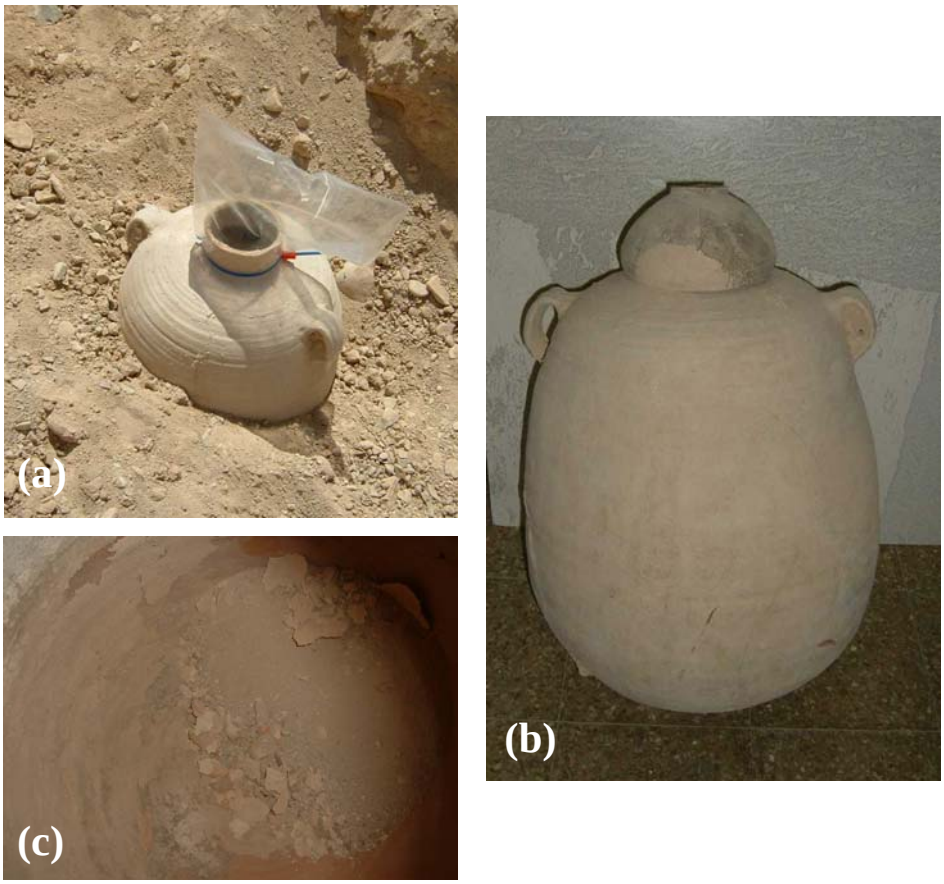

Figure 1. (a) Jar-35 as found on the southern plateau of Qumran; (b) Jar-35 with the lid that covered the jar; (c) Wine residue found within Jar-35.

Analysis of residues

The application of analytical techniques in the study of archaeological remains has become more and more an imperative tool to gain knowledge of objects and industrial/craft activities. The data that is obtained allows the use of the objects found to be determined and from this point a hypothesis about food habits and lifestyle in antiquity can be made. As a consequence of the fact that many materials have been preserved and transported in ceramic

vessels, we currently have the possibility to analyse both the residue adhered or deposited in these recipients or fragments of these. Without doubt, wine was widely consumed by many civilizations and contributed to commercial trade relations between people (McGovern 2003). Ceramic vessels were frequently used to transport and store this product.

Tartaric acid has been widely used as a chemical marker of substances related to grape in residue samples in amphorae (Michel *et al*. 1993, McGovern *et al.* 1996, Garnier *et al.* 2003, McGovern 2003, Guash *et al*. 2004). This is due to the fact that this substance is rarely found in nature except in substances related to grapes and due to its capacity to be preserved for long periods of time in ceramic. It is preserved thanks to its hydrogen bond with the silicates (Michel *et al.* 1993). However, because of the small amount of sample material normally available in these types of samples, in order to detect tartaric acid, highly sensitive techniques are necessary.

In the bibliography different analytical methods are discussed. For example: FTIR (Michel *et al.* 1993), gas chromatography coupled to mass spectrometry (Garnier *et al.* 2003) and liquid chromatography coupled to mass spectrometry (Guash *et al.* 2004).

In this work, capillary electrophoresis (Mallet *et al.* 1999, Saavedra and Barbas 2003, Esteves *et al.* 2004, Mardones *et al.* 2005) and liquid chromatography (Mardones *et al.* 2005) have been used to determine the presence of tartaric acid in residues in amphora-35 from the archaeological site of Qumran.

Due to the evolution of the products related to grapes over time, it is impossible to decide, with this analysis, if the recipient originally contained wine, juice, and vinegar or other products from grapes.

Experimental

Instrumentation

In order to perform the experiments CE equipment Beckman P/ACE system 5500 (Beckman Instruments, Fullerton, CA, USA) was used. The fused-silica capillary is 47 cm in length, 40 cm in length from the injection point to the detection window, and 75 μm in diameter (Polymicro Technologies). The temperature of the capillary was cooled to 25ºC (± 0.1) by the liquid coolant in the capillary cartridge. The CE is equipped with autosampler, automatic injector and Photodiode array detector. The electropherograms were recorded using a computer programme P/ACE Station, version 1.0 with interface Golden System.

A Waters "Alliance 2695" instrument with a PDA 996 detector for the HPLC analysis was used. The Software used was Empower Pro. The column Rezex RHM-Monosaccharide was used at a temperature of 40ºC.

Potentiometric measurements were performed using a CRISON micropH 2002 meter equipped with a CRISON 52-02 electrode (CRISON Instruments).

Chemicals

All solutions were prepared in Water Plus for HPLC (Carlo Erba). Ethanol, sodium hydroxide, hydrochloric acid and sulphuric acid ACS for analysis were supplied by Carlo Erba. L(+)tartaric acid and acetic acid (sodium salt) were supplied by Merck. Oxalic, L-lactic (sodium salts) and succinic acid supplied by Sigma. Tetradecyltrimethylammonium bromide (TTAB) and 2,6-pyridinedicarboxilic acid were both from Alfa-Aesor.

Electrophoretic separation conditions

Electrophoretic separation for the indirect detection method was used a power supply of -20 kV (current of -20 µA) at a temperature of 25ºC and detection at 230 nm.

The buffer was prepared with 5 mM 2,6-pyridinedicarboxilic acid solution, 0.5 mM tetradecyltrimethylammonium bromide (TTAB) and by adding NaOH to adjust the pH=5.6. El TTAB is a cationic surfactant that inverts the electro-osmotic flow in such a way that the surface of the capillary is positively charged. This substance is used in a concentration below its critical micelle concentration.

The capillary was conditioned by passing 1 M NaOH (aq) for 15 min, water for 20 min and the working buffer solution for 30 min. A voltage of -20 kV was applied for 20 min to the capillary filled with buffer solution. Every day, the capillary was conditioned by purging it with 0.1 M NaOH for 5 min, then with water for 15 min and, finally, by working buffer solution for 20 min. A voltage of -20 kV was applied for 10 min to the capillary filled with working buffer solution. In order to maintain the condition of the capillary and to minimise the hysteretic effect, the capillary was flushed between each run with water for 1 min and then with the running buffer for 3 min. Capillaries were stored filled with working buffer electrolyte.

All the solutions were filtered through a nylon membrane with a pore 0.45 µm. Before injecting the samples were sonicated for 2 min. The sample was injected hydrodynamically during 4 s.

The working solutions of the anion series were prepared of stock solutions of 100 mg L^{-1} of anions in water. Analyte peaks were assigned by comparing of their migration times with those of the reference compounds and a co-injection of each standard with the sample was made in all cases.

Chromatographic separation conditions

The column temperature was maintained at 40ºC. The mobile phase was isocratic 0.0025 M H_2SO_4 with 0.5 mL/min flow. Detection was at 280nm and the injection volume 25 µL. Analyte peaks were assigned comparing of their retention times with those of the reference compounds. Also, a co-injection of each standard with the sample was made in all cases.

Samples

The samples were prepared from 10 mg of solid residue from amphora (Jar-35) by treatment with ethanol; the ethanol was then evaporated and the residue dissolved in 1 mL of $5 \cdot 10^{-3}$ M HCl solution was then filtered with 0.45 µm. The samples thus prepared wer sonicated for 2 min before being analysed with CE and HPLC.

Results and discussion

Electropherograms were obtained from a standard solutions containing a mixture of the acids studied, tartaric acid, oxalic acid, lactic acid, acetic acid and succinic acid that are expected to be found in products related to grapes. The organic acids were well separated as can be seen in the Figure 2a, in the order of the migration times of each of the acids: oxalic, tartaric, succinic, acetic and lactic. The analytical determination of tartaric acid in this sample allows us to relate the residues to grapes and related substances. The determination of other organic acids allows this to be confirmed. The acetic, lactic and succinic acids are produced during the alcoholic fermentation. In our sample analysis we can determine tartaric acid, lactic acid and acetic acid using the capillary zone electrophoresis (CZE). In Figure 2b one of the electropherograms obtained can be seen. It is important to note the short separation time of the different ions. The presence of great quantities of chloride ions, produce small variations of the migration time of the ions.

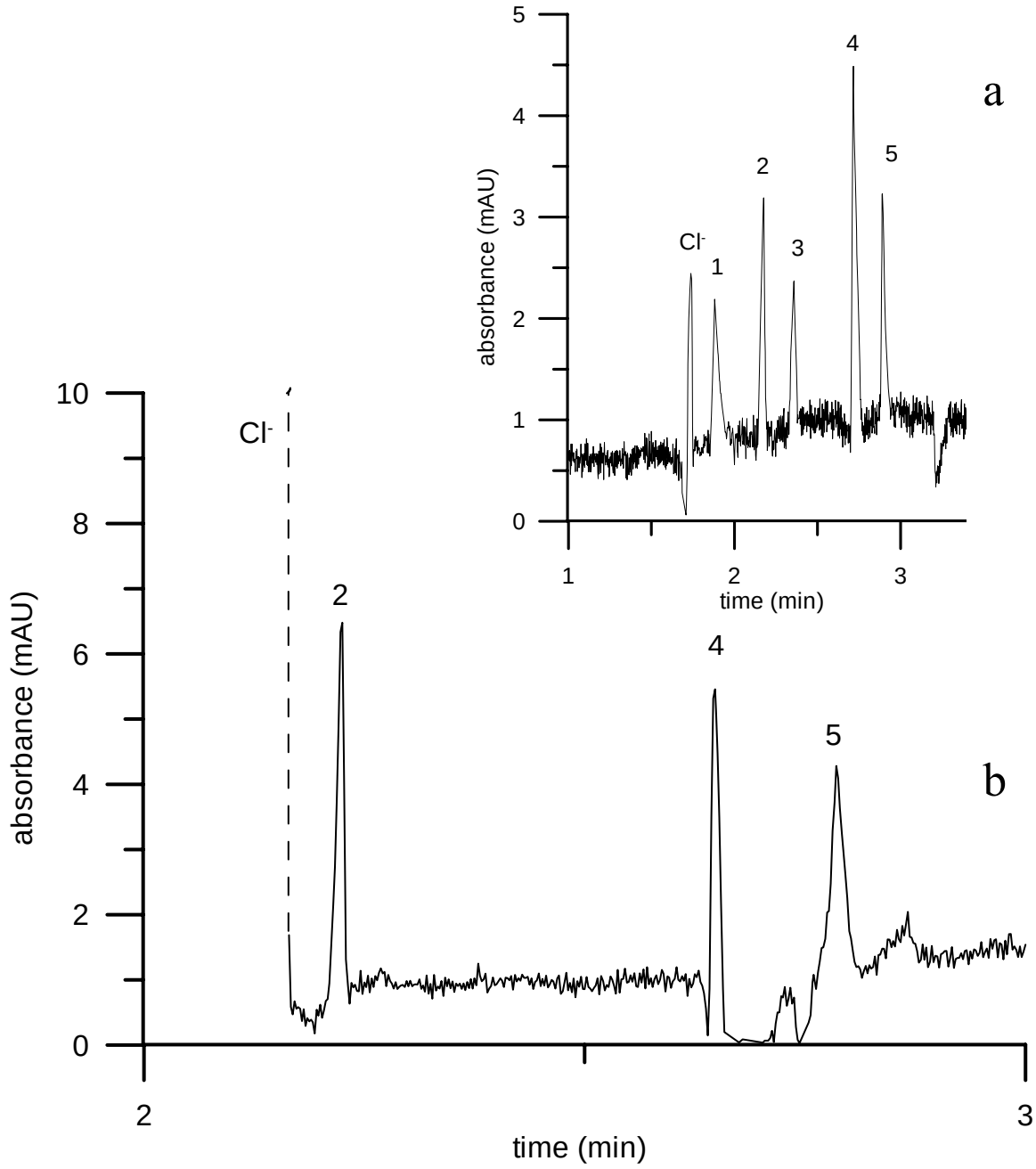

Figure 2. (a) Electropherogram of organic acids, at 8 ppm of concentration: (1) oxalic acid, (2) tartaric acid, (3) succinic acid, (4) acetic acid and (5) lactic acid; (b) Electropherogram obtained from residue sample of Jar-35.

The results were confirmed with the HPLC technique. A chromatogram is shown in Figure 3 where corresponding peaks of tartaric, lactic and acetic acids can be observed. In the same figure some chromatograms obtained from the sample can be observed in which different concentration of tartaric acid were added.

The use of wine or vinegar at Qumran has been established with certainty as also other sources mention wine in the 1st century AD.[1]

The archaeological caveat is that not every jar must be immediately cleaned of its interior. If that had happened here, barely any trace of wine would have been determined.

Jar-35 was found in the context of a site where cooking took place together with the find of animal bones that were buried under potshards. If we consider the buried bones are the remains of a communal meal then wine would make more sense than vinegar, also because the chemical substances that made this residue to a wine are present as has been indicated.[2]

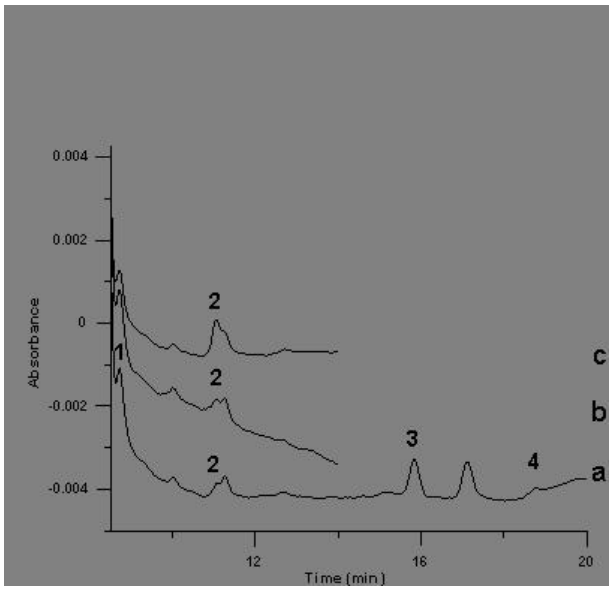

Figure 3. (a) Chromatogram obtained from the sample of Jar-35. Chromatograms in which different concentrations were added: (b) +1 ppm tartaric acid, (c) +5 ppm tartaric acid
(1) Oxalic acid, (2) tartaric acid, (3) lactic acid and (4) acetic acid.

[1] Wine consumption in the Gospels that depicts the time period in which the "Essenes" lived as well as Jesus is seen by Mat. 9:10-11; 11:19; Mk. 2:15-16 as an evil when they record that Jesus "drank together with publicans and sinners. Concerning the container of wine, during the Wedding at Cana, the guests drank wine stored from jars. Matthew (10:17), in turn, mentioned wine preserved in skins rather than ceramic containers.
The historical importance is one that has to do with the mentioning of wine in the Dead Sea scrolls, the New Testament and ancient writers. A few examples may suffice here. The Rule of the Community talks of the consumption of "*Tirosh*" that is unfermented wine as well as wine as it was known then and now. The *Rule of the Community* (1Q28a 2.11-21) says: "Because it is he [the priest] who shall bless the first fruits of bread and wine", which means that wine was consumed by the "Essenes". In 1QS, columns VI and VII, there are many references to the blessing of bread and new wine when the "Essenes" sat at the table according to rank. A novice as a candidate to enter the "Essene community" is not allowed drinking wine for two years (see 1QS 6.13-23 and 1QS 6.3-6). According to The *Temple Scroll*, columns 18-23, one even had a Festival of New Wine, feasted ninety-nine days after Passover (GM 158, 11Q19, 19. 12-14) and so there was also a New Oil festival (GM 159, 21.10-14). The Calendar scroll in 4QMMT A 1.1-5.11, mentioned that the Feast of Wine took place in the fifth month. The Qumran Isaiah scroll uses the word "*chomer*" (red wine), whereas Flavius Josephus mentions in his War, II, viii, 5: "It is customary to mix wine with water …" (Broshi, 1984, 33)

[2] Finally, three different Qumran scrolls depict a sacred meal of bread and wine. There are similarities between the literary style of certain Qumran scrolls and writings of the New Testament. For example, Paul mentions a ritual meal with bread and wine in 1 Cor. 11:26, the importance of the Eucharist celebration, which has always been pertinent to the Early Christian Church.

Conclusions

The primary importance of the present work is that laboratory techniques in tandem can provide useful information concerning the content of jars that once contained liquids connected with the grape.

The CE and HPLC are analytical techniques of separation that demonstrate their use in determining small organic acids in archaeological samples. The determination of tartaric acid in their residues found in the amphora of Qumran allows the use of this vessel to be related to substances derived from grape and wine. Also the presence of acetic and lactic acids is due to a fermentation process so that we rather talk of an alcoholic beverage than unfermented wine "*Tirosh*". No pips have been found in the residue. The latter suggests that Jar-35 contained rather wine, since unfermented wine would have held some grape skins and/or pips.

In all, this is the first time that we have found wine in a site that contains also scrolls that talk of wine and communal meals of bread and wine.

Acknowledgements

We would like to thank Randall Price and Oren Gutman to let us sample the jar with the residue.

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XRF ANALYSIS OF Vth CENTURY ROMAN WINDOW GLASSES

Lucia Canonica[1], Aurora Cagnana[2], Alessandra D'Alessandro[1], Alessandro Zucchiatti[1]

[1] Dipartimento di Fisica dell'Università e INFN, Genova, Italy
[2] Sovrintendenza per i Beni Archeologici della Liguria, Genova, Italy
E-mail: Alessandro.Zucchiatti@ge.infn.it

Abstract

The fully non-destructive XRF analysis of 25 Roman glass fragments (15 blue, 4 green, 2 yellow, 2 opaque, 1 reddish, 1 scrap) excavated in the Italian Site of San Martino di Ovaro, has been done using an Oxford ED-2000 apparatus. The fundamental parameter method, appropriately corrected to reproduce a set of standards, has been applied to analyse fluorescence spectra. The composition of glasses is typical of the Roman technology and the blue glasses are produced from cobalt pigments, probably from North Africa.

Keywords: XRF, Roman glass

Introduction

The archaeological site of San Martino di Ovaro (Udine) in northeastern Italy, excavated from 2000 to 2004, includes a paleo-Christian church (built around the middle of the Vth century) and a separated Baptistery. The archaeological site has monumental proportions (450 m^2) and reveals a specific connotation: that of a martyrial sanctuary, located in an uninhabited remote area, accessed periodically by people from the nearby Alpine valleys only for ritual purposes. The buildings have the typical features of the Aquileia architecture. The construction techniques are traditional late roman and rather simple with whitewashed stonewalls and earthenware floors but no mosaic. The most important and distinctive

architectural element is therefore the presence of flat window glasses in several parts of the Christian church (Figure 1). The fragments are green, blue, pale-yellow, and reddish. The original slabs can be partly recomposed and the location and quantities for each colour (Cagnana and Zucchiatti 2004) seem linked to the different liturgical use of the church areas: the Baptistery and the hall were equipped with clear glass to provide a brighter environment apt to liturgical ceremonies, while the narthex, reserved to meditation and pray, was provide with relatively large amounts of blue glass, to make the environment darker and more intimate. The site stratigraphy is well understood and therefore the glasses are confidently dated to the V century AD.

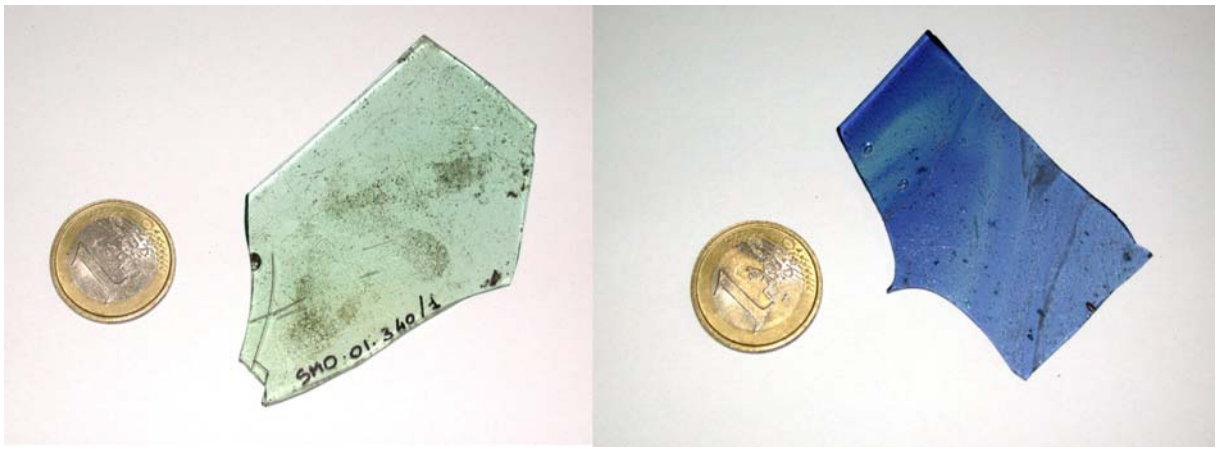

Figure 1. Two examples of coloured flat window glass fragments

XRF Analysis of Glasses

The fully non-destructive XRF analysis of 25 fragments (15 blue, 4 green, 2 yellow, 2 opaque, 1 reddish, 1 scrap) has been done using an Oxford ED-2000 apparatus. The vacuum chamber of the instrument is perfectly apt to host fragments a few centimetres wide like ours. We could therefore operate at HV= 25 kV, I= 0.4 mA using an Ag anode, in vacuum, with exposure time of 240 seconds. The beam spot was of the order of 2 mm and the samples have been exposed on their flat surface. The X-ray spectra have been deconvoluted by the AXIL-QXAS code and concentrations have been calculated from the fundamental parameters. Analyses of a set of standard glasses (alkaline or lead based) have been used to set the method (Caniconica 2004). We first calculated the average (from Na to Pb) fluorescence constant G = 8.97 E-07 and given the value as one of the fundamental parameters.

Contrary to the majority of elements the compositions extracted for standards revealed a systematic error on Na, Mg, Al, Pb, for which convenient correction factors and renormalisation were applied as in Table 1. The discrepancy should be due to the poor description of self-absorption in the sample and of dead layers in the whole system that affect primarily light elements.

Table 1. The correction factors as computed from the analysis of glass standards.

Compound	Correction	Compound	Correction
Na_2O	0,3	SO_3	1,1
MgO	0,54	K_2O	1,1
Al_2O_3	0,98	CaO	1,1
SiO_2	1,1	TiO_2	1,1
P_2O_5	1,1	MnO	1,1
Fe_2O_3	1,1	ZrO_2	1,1
CoO	1,1	SnO_2	1,1
NiO	1,1	Sb_2O_5	1,1
CuO	1,1	BaO	1,1
ZnO	1,1	PbO	1,3

The X-ray spectra allow a clear identification of constituent elements including Co in blue glasses. The results on the main glass constituents agree with recipes well established for the Roman epoch. The oxide concentrations of Na (3%-20%), Si (60%-78%) and Ca (5%-10%) (Figure 2) show, with only one exception, that the flux was Na almost certainly in the form of natron while calcite was used as the glass stabilizer (Mirti *et al.* 1993' Wouters *et al.* 2002).

Analysis of Blue Glasses

The green glasses, which constitute the majority of findings, are usually the result of spontaneous colouring by contaminants (Fe and Mn) in the sand (Figures 3 and 4). This is typical of the glass windows of Roman epoch which started to be used in Ercolano around 1-70 AD. The blue glasses, percentually more abundant in some areas of the site, are intentionally coloured. The colouring agent is quite always Co that is not present in glasses of other colours. In three cases Mn prevails in the formulation. The bulk of Co-blue glasses, those for which the Mn/Fe ratio is above 1.25 (Figure 4) are characterised (Figure 5) by a neat

cross-correlation of Mn, Fe, Co, Cu. The pigment seems introduced as a mineral aggregate including Co and the above elements. Analogies are found with data available (Mirti *et al.* 1993' Wouters *et al.* 2002) for roman glasses and oriental glazes: it could be a cobalt-manganese pigment from northern Africa where the cobalt content is reduced with respect to iron (Gratuze *et al.* 1996). Nevertheless the data are too few to firmly establish the source.

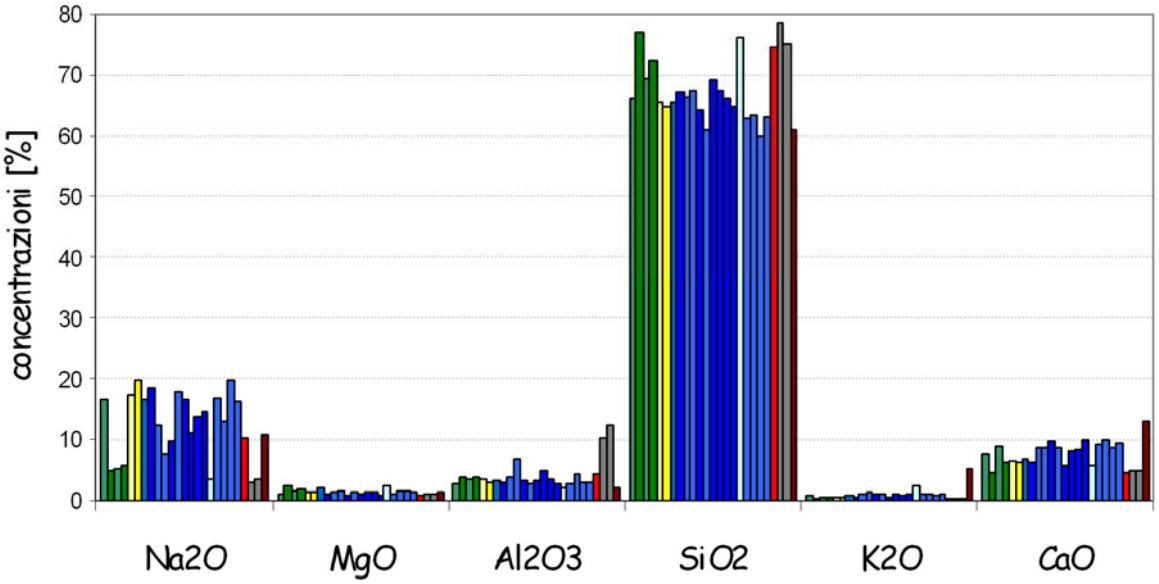

Figure 2. The oxide concentration of glass main elements

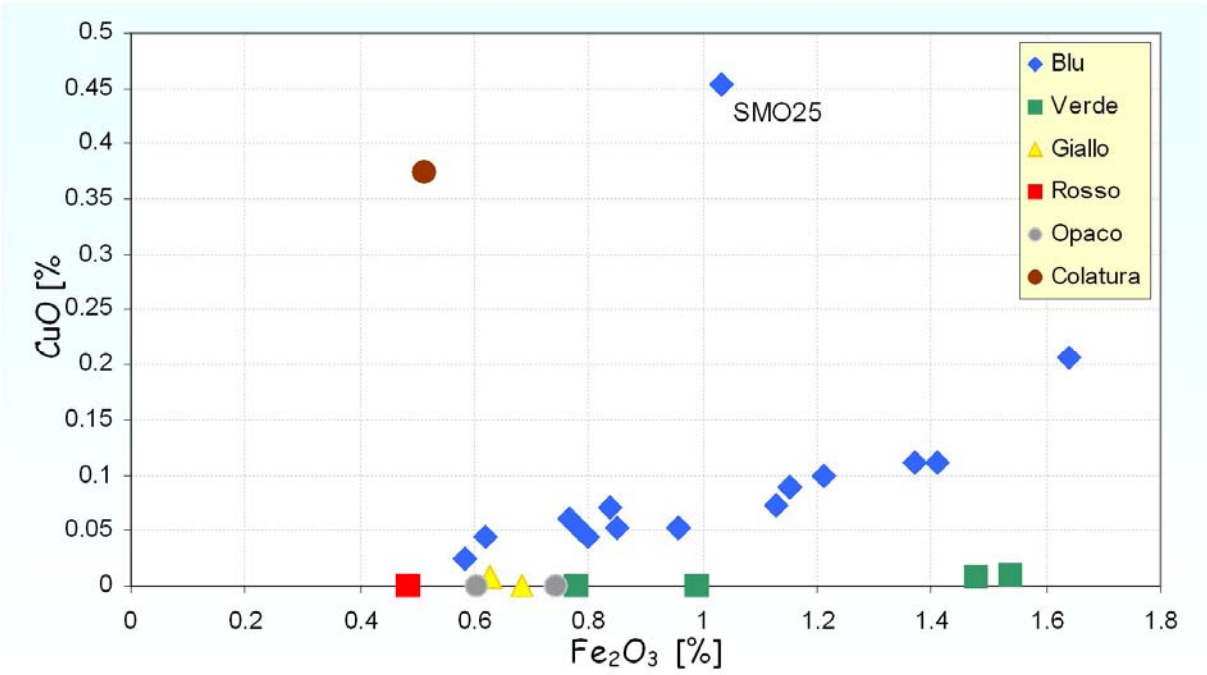

Figure 3. The CuO concentration vs. the Fe_2O_3 concentration for all colours

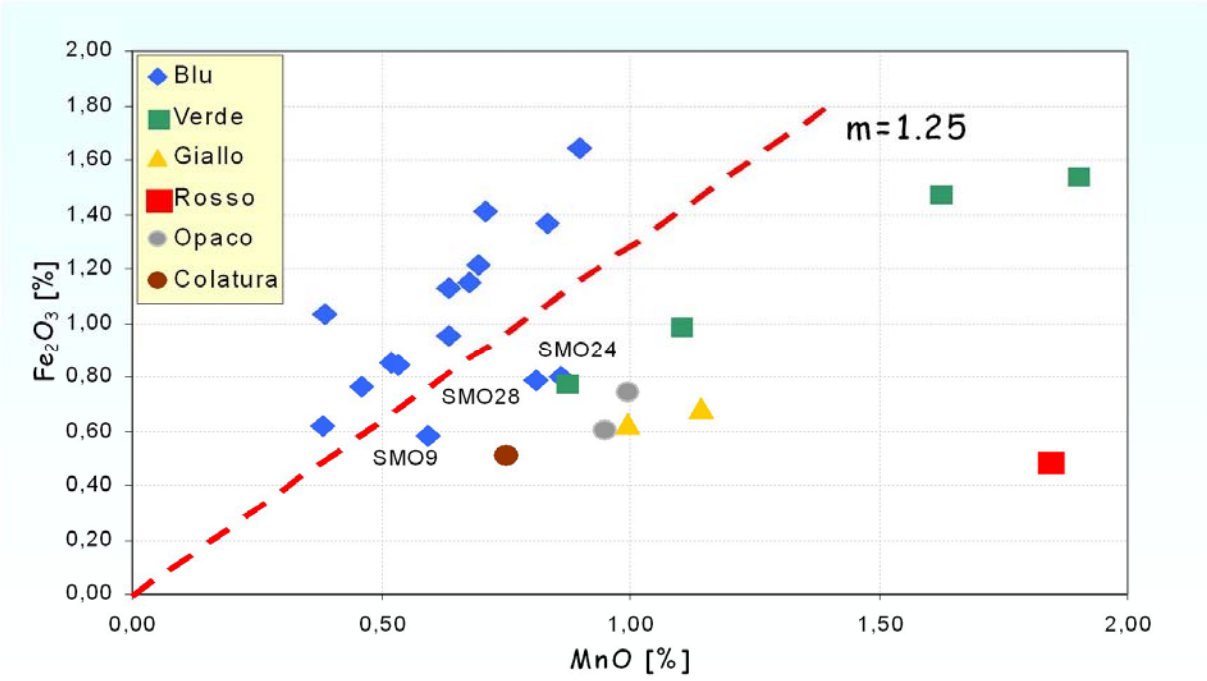

Figure 4. The Fe_2O_3 concentration vs. the MnO concentration for all colours

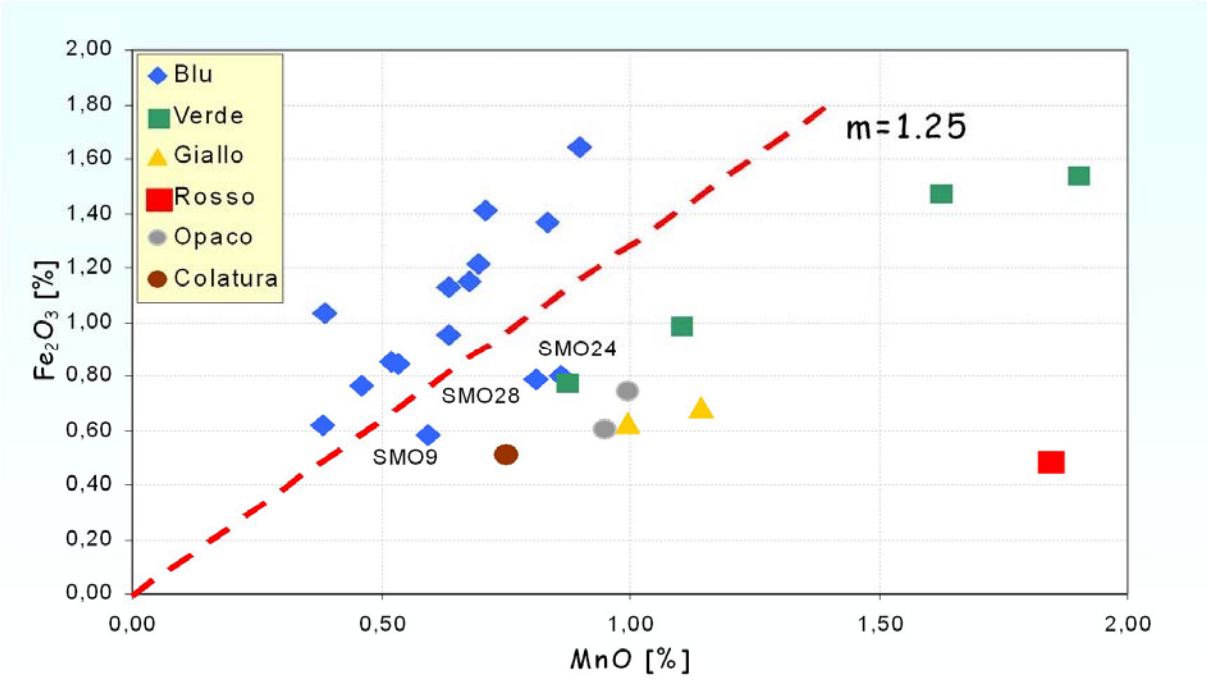

Figure 5. The correlation of Fe_2O_3, MnO, CuO, CoO for all cobalt based blue glasses

Conclusions

The study has shown that the glasses are made with a typical roman technology. In all colours we have found strong correlations amongst minor elements. The study is clearly to be extended to many more window fragments (more than 250 were excavated) and to the other glasses of San Martino (ritual chalices). Data from nearby contemporary archaeological sites should be hopefully compared to the San Martino ones with the aim of reconstructing the fabrication recipes and identifying the mineral content of the pigments.

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A PORTABLE X-RAY FLUORESCENCE SPECTROMETER FOR THE ANALYSIS OF ART OBJECTS

Vladan Desnica and Manfred Schreiner*

Institute of Science and Technology in Art, Academy of Fine Arts, Vienna, Austria
E-mail addresses: vladandesnica@yahoo.com; m.schreiner@akbild.ac.at

Abstract

A field-portable X-ray fluorescence (XRF) analyzer was developed and assembled at the Academy of Fine Arts in Vienna in order to enable in-situ examinations in the field of archaeometry. The system is based on energy dispersive XRF using a 50 W X-ray tube of Oxford, type XTF5011, a silicon drift detector (SDD) of Röntec, type XFlash 1000, and two lasers as pointing devices. A software package based on National Instruments LabVIEW was developed for simultaneous digital control of all system components, for readout of the acquired data as well as for convenient presentation and analysis of the spectra. Subsequently, the measured or stored data could be analysed using a conventional software package like the WinAxil© Software from Canberra Eurisys/Belgium. In the paper the system's analytical capabilities are compared with the results obtained by a laboratory XRF and a comparative evaluation of the systems is established. In combination with the overall miniaturization of all devices it was possible to assemble a really portable computer controlled measurement system which can be used for in-situ examinations and studies of art objects in museums and galleries, ceiling frescos in churches and cathedrals, or archaeological findings at the excavation sites.

Key words: X-ray spectrometer, portable, non-destructive art analysis, mural painting, pigment

* Corresponding author

Introduction

The widespread use and number of different instruments that have been developed and employed for the application of X-ray fluorescence analysis (XRF) illustrates well the established value, great advantage, and expanded usability of this analytical method in the field of art and archaeology (Cesareo 2003, Sugihara *et al.* 2001, Ferrero *et al.* 1999, 2001). The development of XRF instrumentation suitable for portable employment expands the range of use of this technique to an even wider area, by allowing in situ measurements on objects disregarding of their shape, size or place where they are stored and/or displayed (Cesareo 2003, Szökefalvi-Nagy *et al.* 2004, Moioli and Seccaroni 2000, Karydas *et al*. 2004, Cesareo *et al.* 1999). The most general use of this technique is turned towards the characterization of materials, i.e. the determination of the chemical composition. As an extensively non-destructive method it is vastly used for investigations on artistic, historical and/or archaeological samples/objects.

This paper describes the development, constructional details and a case study for the analytical application of a portable small beam XRF instrument for in situ measurements in the field of archaeometry. It explains and demonstrates especially the principles of a self-developed software based on National Instruments LabVIEW, applied for controlling and monitoring of the instrumentation, as well as for presentation and analysis of the obtained data.

Device and components

A schematic drawing of the whole XRF system is presented in Figure 1. As an excitation source a mini-focus side-window X-ray tube with Rh anode (model XTF5011, Oxford, CA, USA) with 50 W maximum power (max. anode voltage 50 kV, max. anode current 1 mA) and a nominal focal spot size of 87 μm was chosen. The tube is the strongest one that can still be air-cooled (and therefore easily transported), providing a good base for fast and accurate measurements. In many cases, hand-held XRF spectrometers have used radioisotope excitation. However, since several years, the development in the field of X-ray tube technology enabled the application of high-tech devices as an alternative source for excitation. The tubes have gotten smaller, lighter, and can be simply air-cooled. Though in principle

radioisotopic sources can be and still are used as well, aspects related to radiation hazard and system performance lead to prefer X-ray tubes (Thomsen and Schatzlein 2002).

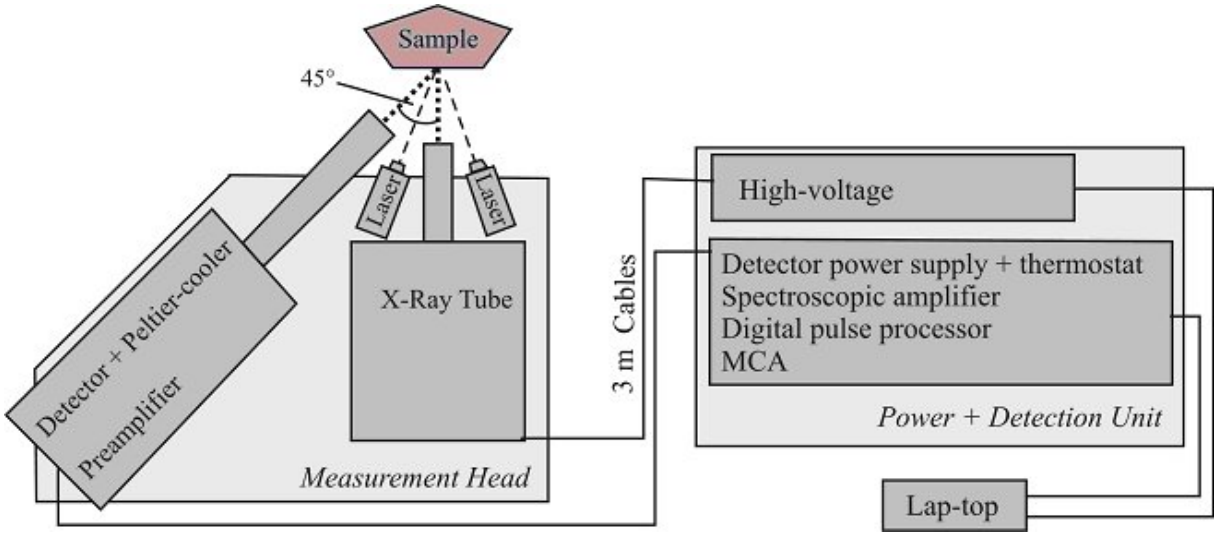

Figure 1. Scheme of the entire XRF system. In reality the plane defined by the two Laser beams is perpendicular to that of the x-ray beam and the detector axis.

For collimating the X-rays a 1 mm pin-hole brass collimator was constructed. Figure 2 depicts a schematic drawing of the X-ray tube (The Oxford Website 2004) with the collimator mounted on a convex brass support. The radius centre of the convex support is in the focal point of the anode, to enable easy adjustment and finding the optimum collimator alignment, thus ensuring high X-ray intensities.

A system of 2 pin-holes with different diameters (4 and 1 mm) was constructed inside the collimator tube in order to avoid interactions of the primary beam with the inner side of the collimator, and hence secondary radiation from the brass material itself. In addition, the inside of the collimator tube was coated with a 1 mm thick aluminium foil, which contains beside Al mostly light elements [e.g. Mg, Si as minor components (traces)], whose characteristic radiation does not affect the measurements. Between the aluminium foil and the brass tube an additional 1 mm thick lead cylinder is mounted for safety reasons.

For the detection of the fluorescence radiation a Peltier-cooled silicon drift detector (SDD) with a 5 mm^2 active area is employed (model Xflash 1000, Roentec, Germany). Using a Fe-55 radioisotope an energy resolution of 155 eV FWHM @ MnKα (at 1 μs shaping time) was measured. The signal-processing unit is a Max Flash Spectrometer (Roentec, Germany),

which encloses detector power supply and thermostat, spectroscopic amplifier, digital signal processor and multi channel analyzer (4096 32-bit deep channels).

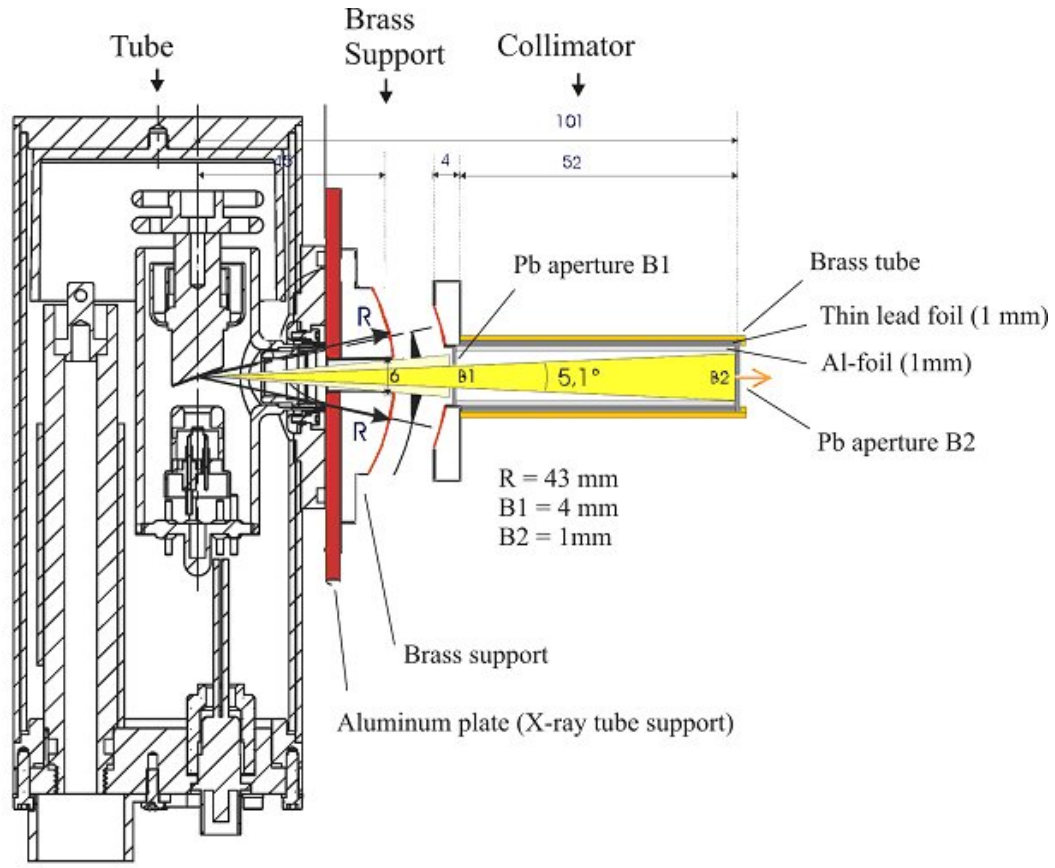

Figure 2. Cross section of the X-ray tube and the collimator showing the different parts in the cylinder.

X-ray tube and detector are mounted on an Al plate of 21 x 30 x 0.5 cm^3 in a 45° geometry (Figure 1). For easy and reproducible alignment of the sample (object) in front of the X-ray source and the detector, a two-laser beam system is used. The lasers are aligned in such a way that the point of their beam intersection coincides with the cross-point of the X-ray tube and detector axes (Figure 1).

The complete measuring head weighs only ca. 4.4 kg and is fixed on an extension arm, which can be stabilized on a tripod using a counter weight. A set of different extensions and joints enables to position the measuring head in virtually every direction, according to the different shapes and sizes of objects, which are in the field of archaeometry often very fragile, bulky and can not be moved or turned around easily. The high voltage generator, power supplies, cables, and spectrometer electronics are placed in a separate case, with dimensions 30 x 30 x 60 cm^3, so it can be taken virtually anywhere.

Software

Although other software systems were taken into consideration, we developed our own software for the following reasons. The first is that we wanted to have the convenience of a simultaneous control of all independent components of the analyzing system, meaning, all digital commands for the instrument controls should be accessible using a single software package. Furthermore, we needed the software flexibility when choosing the hardware components and possibility for further system improvements and retrofitting over the course of time. These steps, of course, assume constant adaptations and modifications of the software, which is usually not possible with commercial software packages. Therefore, we needed a solution that was less tiresome than programming in Visual Basic or C++, relatively platform independent, and adaptable to changes in experimental demands or hardware. The second reason for making our own software was, as so often with the research institutes engaged in studies of cultural heritage and art objects, that of financial nature.

With these considerations in mind, we based the measurement controlling, data acquisition monitoring, and spectrum analysis and display options on the National Instruments graphically oriented programming language G, more commonly known as LabVIEW (Lab Virtual Instrument Engineering Workbench) (The National Instruments Website, 2005). LabVIEW is a well-established language that is supported in UNIX, Windows and Macintosh operating systems and is readily ported between platforms. As a high level graphics-oriented language, LabVIEW has built-in graphics displays and other graphical objects, such as switches, numerical displays and text panels. Additionally, LabVIEW includes a library of mathematical subroutines and other utilities, including a growing library of drivers for many kinds of hardware. Other advantages are its inherent modularity, in that each subroutine is written and tested as a stand-alone program, and that it supports multiple tasking. It delivers a powerful graphical development environment for signal acquisition, measurement analysis, and data presentation giving the flexibility of a programming language without the complexity of traditional development tools. Each (sub) routine (so called VI) is composed of two levels – the front panel, which is the graphical user interface (GUI) containing controls for input operations and indicators for output operations, and the block diagram in which the actual programming code is structured by interconnection icons representing operations, values and actions.

The software manages on one side a custom produced I/O analog card for communication with majority of the hardware components and on the other side the RCL 2.2 standard

interface from Roentec/Berlin for controlling the signal-processing unit. Over the first serial port the software sets the on chip DACs of the I/O card to control the operating voltage and current of the X-ray tube, controls the interlock circuit and turns on and off the laser positioning system. Over the second serial port it manages the parameter adjustments of the detector, controls the DAQ process and reads the acquired data from the MCA, which is displayed by the LabVIEW GUI (Figure 3). The numerical data sets displayed above the main display allows verification of the instrumental and measuring conditions as well as monitoring of information relevant for data acquisition during measurement. The buttons to the left of the main display (Figure 3) allow carrying out of the specific control, test and analysis subroutines. The details of the whole software package are described by Desnica and Schreiner (submitted for publication).

The spectrum, i.e. the measured intensities per channel, could be stored in a file in ASCII format. Thus, the spectra can be subsequently evaluated quantitatively using a spectrum-processing package like WinAXIL (from Canberra Eurisys, Belgium), which also includes a module for quantization by means of the fundamental parameter method (He and Van Espen, 1991).

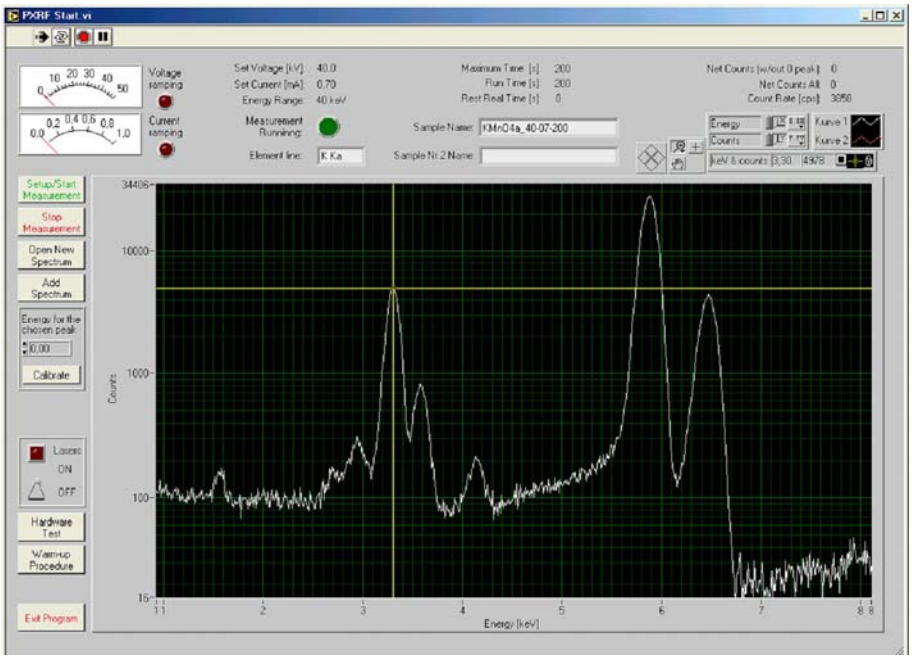

Figure 3. User interface to the LabVIEW application for controlling the XRF components and for data acquisition.

Experimental and case study

Classical cryogenic detectors, like Si/Li and HPGe, offer satisfactory energy resolutions – typically of the order of 140 eV FWHM at the Mn Kα line (5.895 keV) and 1000 cps. The main disadvantage is a complicated cooling system, which requires liquid nitrogen, and is therefore certainly not suitable for portable field applications. The SDDs for X-ray spectroscopy are unmatched in the combination of their properties and performance. They work well at room or moderately low temperatures, do not require liquid nitrogen cooling, and are at least a factor of 10 faster than conventional detection systems based on positive intrinsic negative (PIN) diodes or Si/Li detectors (Lechner *et al.* 2001). They have a rather large sensitive area with a small value of the output capacitance, which allow for a high resolution high count rate spectroscopy.

The pulse processor included in our spectrometer is a XSPV 60 (Roentec/Berlin) with a maximal impulse density of 150 kcps. The energy resolution at 1 kcps is 155 eV FWHM at 5.895 keV; the signal shaping time is 1 µs. The optimum filtering time for a silicon drift detector is indeed to some extent longer (~ 2 µs) and in that setup an even better resolution can be achieved. In contrast, the best resolution obtained with PIN-diodes and conventional Si/Li detectors are reached with filtering constants ranging from 10 to 24 µs (Leutenegger *et al.* 2000).

The performance of our self-built portable XRF spectrometer could be tested during several measurements in the laboratory environment on reference materials, and by carrying out comparative measurements with the lab XRF Spectrace 5000 of Noran Instruments/USA employing a cryogenic detector. In particular, Figure 4 shows two fluorescence spectra of a Fe-alloy (Fe = 83.18 wt%) of known chemical composition, obtained with a laboratory XRF (Si/Li detector) and with the portable XRF, both measured under similar measurement conditions. Elements in low concentration, like Mn (0.18 wt%), can be clearly identified in both spectra. An interesting occurrence concerning the Fe sum peaks can be observed at the energies of 12.8 keV (double the energy of FeK_α X-ray line) and 13.45 keV (energy from FeK_α + FeK_β line). In the inserted spectrum (on a linear scale) the difference between the spectra obtained with two different detectors can be clearly seen. The sum peaks of Fe are rather strong in the spectrum obtained by the lab XRF with a Si/Li detector, whereas in the self-built portable XRF spectrum using a SDD they are hardly visible. Because of the extremely small overall capacitance of this type of detector, very short shaping times can be

achieved. Consequently, extremely high-count rates (up to 10^6 cps) are possible (The KETEK Website 2004), where nearly no problems with sum (pile-up) peaks occur.

In the meantime, our measuring system had proved its practicability and usefulness in various case studies. The following example demonstrates the advantage of the low weight and real transportability. In the year 2003, during restoration and conservation of a side roof of the St. Nicholas Church in a small village of Winkl in Lower Austria (near Vienna), a mural painting, presumably dating from the year 1220, was discovered. The painting shows among others the representation of a scene from the Old Testament, namely Adam and Eva in front of the apple tree. In order to employ proper techniques and materials during their work, the conservators should have the exact knowledge of the pigments and paint materials used in the paint layers and the ground. Due to the unique character of the object it was not possible to take samples for analysis in a lab. The investigations had to be carried out in situ, directly in the attic of the church. However, the only access to the mural painting was through a small hole in the wall (Figure 5). Therefore, the scientific equipment for investigations and determination of the pigments needed to be small, compact, and mobile.

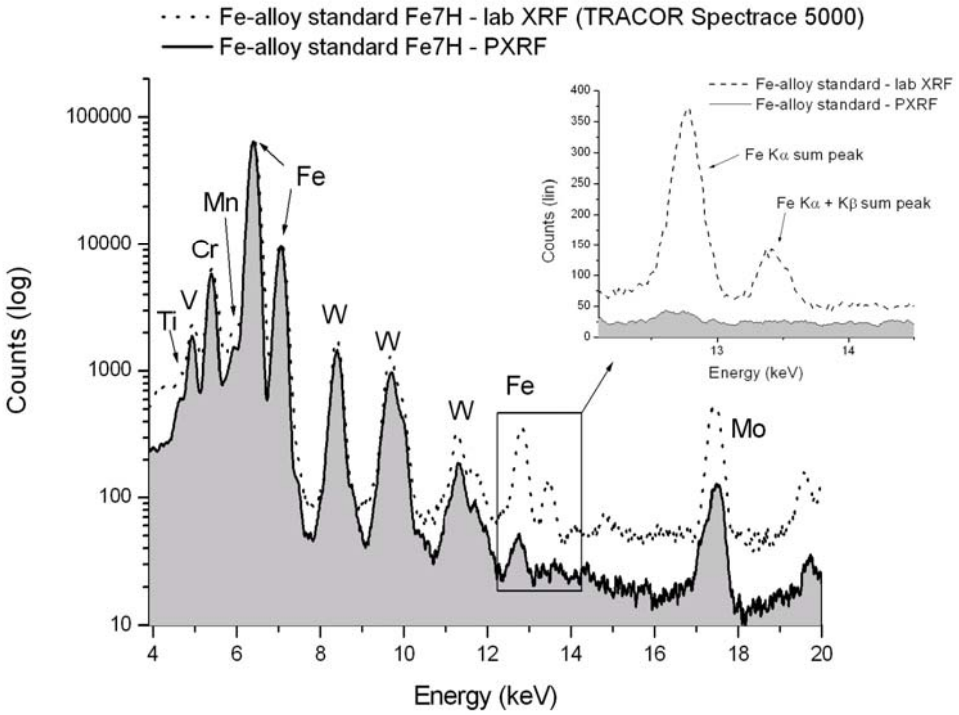

Figure 4. Spectra of a Fe-alloy with known elemental composition. Strong Fe sum peaks appear in the spectrum obtained with the lab XRF Spectrace 5000 of Noran Instruments/USA. This instrument is equipped with a Si/Li detector. The effect of the Fe sum peaks in the spectrum of the self-built portable XRF is significantly lower. (Note the different scales in both spectra.)

Using the XRF method, the pigments in a painting are determined only indirectly, by identifying the chemical elements in the colorant. These are characteristic for particular pigments and in most of the cases the characterization is rather unambiguous. There are either specific elements which can be found only in particular pigments, or a comparison of relevant element intensities between painted and unpainted areas has to be carried out. For example, in an area painted red higher Fe intensities compared to the background (which can also exhibit substantial Fe intensities) indicate that probably red ochre (iron containing silicate) has been used as pigment.

Figure 5. The Church of St. Nicholas in Winkl (near Vienna), where a mural painting from the 13th century was found. Until its discovery in the year 2003 the wall with the painting was hidden by the side-roof of the church (left), and is now accessible only through a small hole in the wall, as seen in the background of the right image (arrow).

The spectra (Figure 6) of the measurements performed on the background of the mural painting yielded Ca and Fe as main constituents with K, Ti, and Mn as accompanying elements. Traces of Cu, Zn, and Sr were determined as well. These results enable the calculation of a Fe/Ca ratio that characterized the paint material of the background. Comparing this value with the Fe/Ca ratios of other investigated areas yields valuable information regarding the colouring substance. If the Fe content (relative to Ca) of the colouring material is 2-3 or even more times of the Fe content, which was determined in the background, it can be presumed that an iron-containing compound (e.g. red ochre) is present as a pigment. However, when doing such comparisons, one should consider that elements with a high atomic number like Hg and Pb in the paint layer arrangement (red cinnabar –

HgS, red lead (minium) – Pb_3O_4, or lead white – $2PbCO_3 \cdot Pb(OH)_2$, often used as admixture) might attenuate both the incident radiation to, and fluorescent radiation from Fe and Ca in the grounding. This yields much lower initial Fe and Ca background intensity values and alters the background layer information. In that case, an iron increase stemming from red ochre will yield a much higher percent difference and have a much stronger impact on the change of the overall Fe/Ca ratio. Therefore, not only the Fe/Ca ratio should be considered when investigating the colorants, but the varying of the overall Fe and Ca radiation intensities in dependence of other elements like Pb should be taken into account as well (Figure 6).

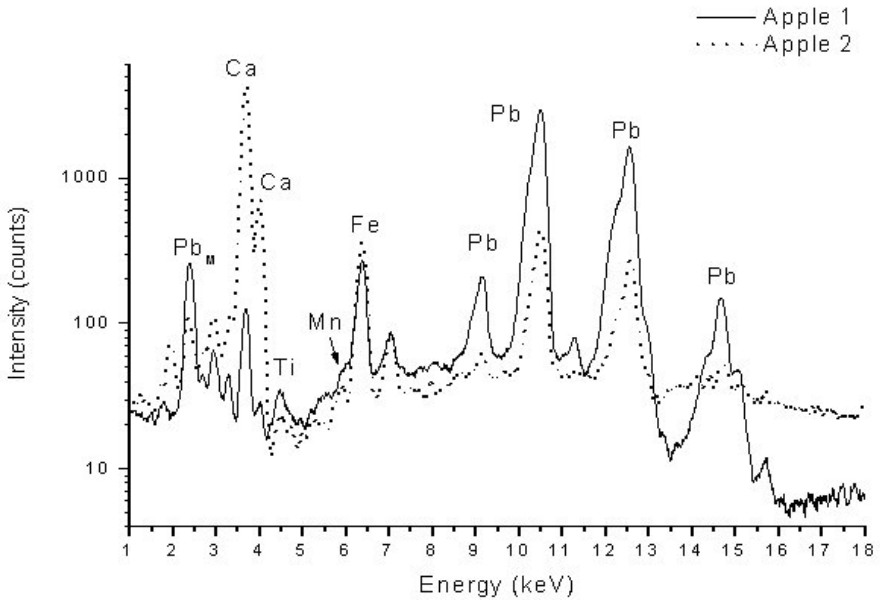

Figure 6. Spectra obtained at two measuring points corresponding to Apple 1 and Apple 2 of the mural painting. Lower Ca and Fe concentrations at the Apple 1 (partly stemming from the background, partly from the pigment) may be explained by the higher Pb content in the pigment used for Apple 1, which alters the information from the layers beneath.

Conclusions

A portable XRF instrument for non-destructive elemental in-situ analysis (in air) of artistic, historic and archaeological objects was designed and constructed. Relatively strong and fast components were used, yielding results comparable with the results obtained by commercial lab instruments. An air cooled 50 W X-ray tube and a Peltier-cooled silicon drift detector provided a strong excitation source and a very efficient detection system resulting in fast measurements with very good precision – two highly important features in the field of

archaeometric examinations. National Instruments LabVIEW based software was developed and employed, which allows simultaneous controlling and monitoring of all hardware components and enables efficient and convenient spectral presentation and analysis. The compactness and versatility of the measuring head provides a perfect tool for elemental investigation of art objects in museums and galleries, of mural paintings in churches and cathedrals or of archaeological findings at excavation sites. Its possibilities and advantages are demonstrated during pigment investigations of a Romanesque mural painting in a St. Nicholas Church, in a small village of Winkl in Lower Austria (near Vienna).

As a next step, further improvement of the system will be a CCD camera that records the analyzed area, for convenient and accurate selection and documentation of the investigated points. A subroutine for display and storage of such pictures can be easily incorporated in the existing LabVIEW software package.

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THE PROVENANCE OF QUMRAN POTTERY BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Jan Gunneweg[1] and Marta Balla[2]

[1] The Institute of Archaeology, The Hebrew University of Jerusalem, Israel
[2] Institute of Nuclear Techniques Technical University of Budapest, Hungary
E-mail: Jan.Gunneweg@huji.ac.il; balla@reak.bme.hu

Abstract

As part of the multidisciplinary project, the primary objective was to trace Qumran ceramics by their chemistry to site-specific manufacture centers, to define possible trade patterns and interregional contacts. Neutron Activation Analysis is considered the most suitable technique to receive qualitative and quantitative abundances of about 25-30 elements in ceramics. Clearly formulated archaeological questions were drawn from the exegesis of the scrolls, historical research and archaeological evidence. Systematic sampling and subsequent analyses have resulted into a data bank of ceramic materials from Qumran and the Dead Sea area from the time period of 200 BC-70 AD. Multivariate statistics have been applied, whereby compositional groups were created and placed into spatial perspective. The main goals of the project have been reached: the connection between the Qumran pottery in the settlement and those in the caves, as well as a diverse interrelation with people and sites of the Dead Sea area.

Keywords: Qumran, INAA, Pottery provenance, Jericho, Dead Sea

Introduction

As part of the multidisciplinary project, aimed at the study of Qumran and its people by scientific means, provenance studies of potteries have been performed by the technique of Instrumental Neutron Activation Analysis (INAA). The main goals of this project were to trace Qumran pottery by its chemistry to their place(s) of manufacture, to establish the relation between the pottery found in the Qumran settlement and the surrounding caves, to define possible trade patterns and interregional contacts (Gunneweg and Balla 2003a).

Peculiarities of Qumran's ceramic corpus studied according to style led to a general opinion that all the pottery was made at the site, propping the idea of a closed ascetic community as Qumran's inhabitants. A stylistic approach however has its shortcomings; style is a cultural trait, without geographical specificity. Nevertheless, pottery has a specific characteristic giving a definite answer concerning its provenience: its chemical composition. By determining the chemical fingerprint of pottery vessels or shards they can be traced back to their place(s) of manufacture, thus enabling us to establish trade links or provide proofs for human relations.

A number of chemical methods, instruments and analytical protocols may fulfill provenance objectives. Reliable scientific information must be based on results produced by an analytical technique, which has an appropriate accuracy, precision, sensitivity, resolution power and fitness of purpose to be applied to the archaeological problem. Performance capabilities of the INAA method ensure such a privileged position among analytical techniques, it satisfies all the requirements.

Experimental

The basic idea of INAA is that by irradiating a sample by neutrons, high-probability nuclear reactions are induced, producing from stable isotopes of different elements concerned radioactive nuclides, whose characteristic radiations can be used both to identify and accurately quantify the elements of the sample. Determinations are based on the detection of the highly penetrating gamma-photons of discrete energies. The measurable parameters are the energy of the emitted gamma-quanta and the half-life of the nuclide. For quantitative analysis the intensity is used. By optimized irradiation and counting procedures 30-35 elements can be determined with sensitivities at ppm level and below. Standardization is

potentially easy and accurate, there are no laborious or time-consuming processes, and so series of samples can be analyzed, providing statistically meaningful data sets. INAA lends itself to a successful provenance study.

Samples

A representative portion of the original de Vaux's assemblage of pottery of all sorts of household ware, and site-specific pottery from the caves has been selected for the analyses. 34 samples were taken from materials thought to serve as Qumran reference materials, as well as 166 other samples taken from pottery that consisted of a variety of styles, including the unique scroll-jars. Ceramic material from further archaeological sites, such as Jericho, Jerusalem, Hebron, Callirhoe, En Gedi, Masada and 'Ain Feshkha were also sampled and involved into the research. A special set of 41 samples from potteries with traces of writing on them (ostraca) has been taken to find proofs for the connection of caves and the settlement through writing activity (Gunneweg and Balla 2003b). The total number of analyzed samples reached 236.

Analyses

Analyses were performed by a validated method of INAA for archaeological ceramics, in the accredited (ISO IEC 17025) Radiochemistry Laboratory of the Institute of Nuclear Techniques, TU Budapest. Batches of samples were irradiated in the pool-type reactor of the Institute with a thermal neutron flux of 2.4×10^{12} n cm^{-2} s^{-1} for 8 hours. Gamma-spectrometric measurements have been performed by a Canberra HPGe Well-type detector (resolution 1,95 keV, rel. efficiency 20,5%) that is connected to a Canberra S100 Multichannel Analyzer. Standardization was made by the single comparator method (De Corte 1987), using gold as the comparator element. Zirconium foils monitored the thermal/epithermal flux-ratio.

Data treatment

While elemental concentrations, with their determinable degree of analytical precision have an inherent objectivity; the incorporation of chemical data into a cultural or economic model is of highly inferential nature. The bridge between analyses and interpretation is provided by various statistical methods. There are different attempts to apply numerical procedures to achieve partitioning of the data sets. Simple methods, such as bivariate scatter-plots and various pattern-recognition techniques are widely used, but the well-quantified data-matrices are generally treated by multivariate statistics.

To help place the derived analytical data into archaeological context different procedures of multivariate statistics have been applied. By an iterative classification treatment (Balázs 2003) the partitioning of the data set has been achieved, five distinct compositional groups were created and placed into spatial perspective (Figure 1).

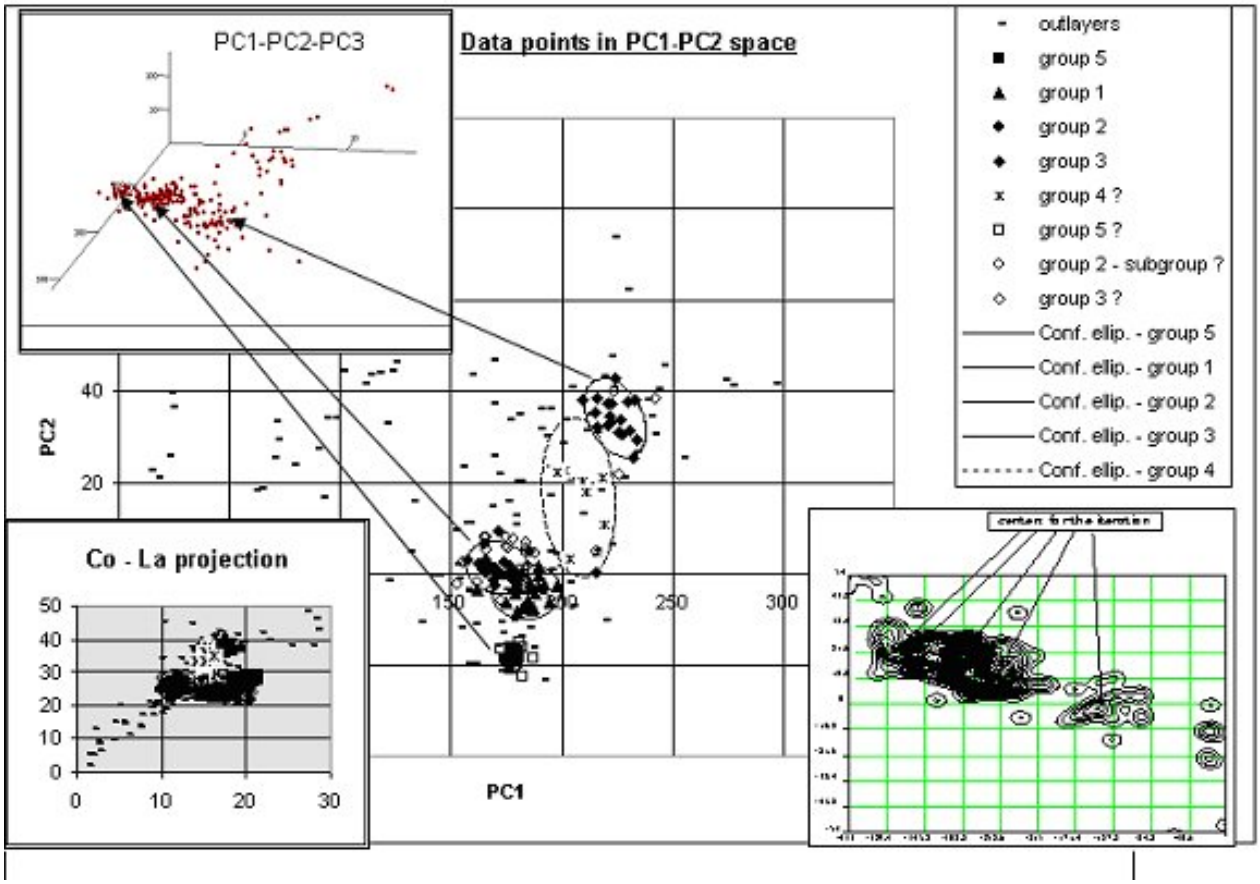

Figure 1. Chemical groups of Qumran pottery samples:

Group1: Local Qumran

Group2: Hebron type Motsa Clay

Group3: Jericho

Group4: Jericho

Group5: Edom/Nabatea

Figure 1 exhibits different approaches for the representation of the subdivision of Qumran pottery samples. The basis is a two-dimensional plot, where data points are projected into the plane of the first two principal components, containing the maximum variance of the related data. The upper left segment shows the projection of sample points to the PC space, determined by the first three components. The bottom left figure is a bivariate plot of raw

data, while in the bottom right Parzen-Rosenblatt density functions with local maxima as iteration centers are presented.

The power of the technique has been proved, but to exploit its great potential to address cultural and social issues, involving ceramics, it must be applied within a clearly formulated archaeological context. Results of scientific provenance studies are irrelevant by themselves. Where a vessel comes from is of limited value, unless it can be interfaced with an existing social and cultural structure and basic forms of human behavior.

The Qumran pottery project meets these requirements. On the basis of the immense knowledge built up by the means of exegesis, historical research and archaeological evidence, definite questions have been formulated and answered by scientific means.

Results and discussion

As a result of the analysis of all these samples a data bank of ceramic materials has been developed, comprising the chemical profile of different pottery types of Qumran and the Dead Sea region, in the time period of 200BC-70AD.

The following mayor archaeological conclusions have been drawn:

- Qumran's local chemical fingerprint has been defined
- Analysis of clay and ceramic samples from other sites of the Dead Sea region provided reference data to help workshop assignment
- Results of analyses refuted the previous theory, that the entire pottery assemblage was manufactured locally at the site. It was possible to determine five chemically different groups of pottery and to localize their probable provenance. It was determined, that only 33 percent of the analyzed pottery were locally produced at Qumran. A relatively large part of pottery has connection with Jericho, another bigger group of vessels have a chemical fingerprint of the Hebron (Beit 'Ummar) type Motsa Clay, while there is quite some pottery ware alighting a possible Edom/Nabatea connection.
- The claim that pottery serves as a connecting link between the settlement and the caves has been corroborated; there is no difference in the chemical composition between the pottery from the settlement and that of the caves.
- The question of the settlement's isolation has got a different new light through the ceramic material: A diverse interrelation proved to be traceable, not only with sites and people near Qumran, but also with people on the Eastern shore of the Dead Sea.

– Provenance studies of ostraca furnished further evidence for the connection between Qumran living quarters and its caves, through scribal links: certain scribal remains appeared on pottery that was made locally in Qumran and also found in the caves. Furthermore, written evidences corroborate a Jericho, as well as the Edom/Nabatea connection.

In the past few months some new samples have been analyzed and the elemental data have been processed by the same abovementioned treatment. The INAA data are plotted in the graph of Figure 6 at the end of this paper.

South Plateau Qumran

The August 2004 excavations at Qumran's southern plateau by Randall Price and Oren Gutman yielded a jar that has been found sealed by a lid. The jar has been given the excavation number: Jar-35. The jar and the lid have been submitted to INAA and have been numbered QUM 359 and 362 respectively (Figure 2). Also a sample of the neck of a large cooking pot was analyzed (sample QUM 363, Figure 3).

Jar-35 was important because it contained a thin transparent residue that certainly came from the content of the jar and that has been preserved because of the lid that covered the jar. The deposit was analyzed at the University of Barcelona (samples QUM 352 and 353). Nativitat Trinitat et al. treat the jar's content in this Volume. According to INAA, Jar-35 is the only jar found at Qumran whose chemical composition matched that of the Motsa Clay at Jerusalem itself. Whether the jar arrived at Qumran with its liquid content cannot be solved by INAA. Additional information regarding Jar-35 is the form of the bowl that has been used as the lid of the jar. Many types of these bowls have been found in Qumran as well as in Jericho and it is the first time that one can see the two placed together by the ancients.

The results for the cooking pot (Figure 3) are similar to the previous four analyzed cooking vessels at Qumran for which no provenance was found.

Kiln Dump Qumran

Sample QUM 324-327 (Figure 4) consists of four fragments of jars found in the kiln area debris to the East of L.64. The shards can be considered as kiln waste that has been discharged as such. One of the jar shards has the chemical composition of the Qumran pottery as it has been established in a previous study (Gunneweg and Balla, 2003a), whereas the other

Figure 2. Jar-35

Figure 3. Cooking pot

shards also have a similar composition and belong to Qumran pottery too. The same shards are also petrophysically studied by Valentin Vladimirov in this volume.

King Herod's Winter Palace at Jericho

Rachel Bar-Nathan provided two samples of jars that she has found in Herod's winter palace at Jericho to which the laboratory code of JER 101 (Figure 5) and 102 was given. In almost every paper concerning Qumran pottery that mentions similar jars as the scroll jars in Qumran, there are only two quotes, one at Jericho by Bar-Nathan (Bar-Nathan 2002) and another one at Qwailbah in Jordan by Ma'ayeh (Ma'ayeh 1960). The jar from Jericho has been mentioned as the only jar in Israel that was similar to the scroll jars of Qumran, whereas the Qwailbah jar has so far not been depicted anywhere.

The Jericho jar consists of only a partly preserved rim and neck together with a vertical loop handle (Figure 4). Already the loop handle is a feature that indeed point to dissimilarity with real scroll jars at Qumran, as real scroll jars are without handles. The INAA result of this Jericho jar points to Jericho itself as the place of origin, and has thus also chemically no connection with Qumran. As this jar is entirely different from its counterpart in Qumran, there is no further confusion about the possibility that other sites have scroll jars that originated in Qumran. In a previous study it was proven that the bulging jar QUM 198 from Cave 1, now on exhibit at the Shrine of the Book and labeled as a "scroll jar" features small horizontal handles and its provenance has previously been traced to Jericho and is thus not indigenous to Qumran.

Figure 4. Four slipped jar shards from the kiln dump to the East of the potter's workshop

Figure 5. The wrongly dubbed Jericho "Scroll" Jar with handle

A second jar (JER 102), ovoid in shape and without handles was also submitted to INAA, and the statistical analysis showed that this ovoid jar came from Qumran where is probably was manufactured. This means that there was a connection between the two sites in both directions, although we were able to show only a single sample to back this up. The reason for the latter is that we have not analysed Jericho pottery in a similar way as we did at Qumran.

In order to show where the new results are located vis-à-vis the previous database of Qumran pottery, we have included the individual plots in Figure 6. Figure 6 is a bivariate scatter-plot of the previous Qumran data set, including the numbers of the „new" samples. The graph shows that the two Jericho samples are of a different provenance: one is local to Jericho whereas the other can be related to the local Qumran group.

Jar-35 and its lid proved to be manufactured of the Hebron type Motsa clay. The deposit from inside and the soil adhering to the bowl of Jar-35 is a substance with a completely different chemical composition. The cooking-pot turned out to be a chemical outlier, without identifiable provenience.

The four samples from the kiln area L. 64 in the Qumran settlement were locally made, as it was expected (see also the petrophysical account of these shards by V. Vladimirov in this section).

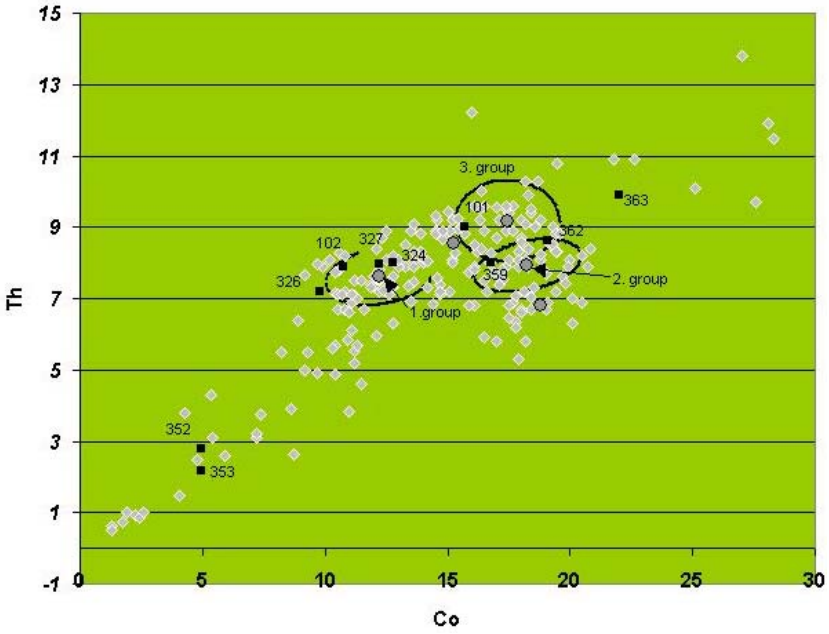

Figure 6. Co-Th plot of the new INAA data against the already existing pottery groups on our data base.

Conclusions

The main goals of the project have been reached: Qumran pottery was traced by its chemistry to their places of manufacture. The connection between the Qumranites, or "Essenes" and the ceramic remains in the caves has been positively proved, and a diverse interrelation with people and sites around the Dead Sea was traced too.

Furthermore, the enigmatic "scroll jar" found at Jericho is first of all no scroll jar as we know from Qumran and also chemically is a local product of the Jericho kiln.

A careful inquiry in the settlement's set-up, the study of the distribution of pottery types and possible functions of the different rooms in the light of the analytical results might help understand who the people were who once lived in Qumran and of what nature were their contacts.

The southern plateau provided an ovoid jar that could be traced to Jerusalem's Motsa Clay Formation and the jar is of a greater importance because of the wine/vinegar it contained (see S. Buti and N. Salvado's contribution in this volume). Finally, because of Jar-35's content, there is a high probability that ovoid jars were used to contain liquids.

Moreover, Jar-35 has also been subjected to Thermoluminescence at Odense (K. Rasmussen) to determine its date. However, the results are not yet ready to be published in this volume.

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STRUCTURAL AND ELEMENTAL ANALYSIS OF SINGLE TEXTILE FIBRES FROM QUMRAN USING MODERN SYNCHROTRON RADIATION X-RAY MICRODIFFRACTION AND MICROFLUORESCENCE TECHNIQUES

Martin Müller[1], Bridget Murphy[1], Manfred Burghammer[2], Christian Riekel[2], Jan Gunneweg[3] and Emmanuel Pantos[4]

[1] Institut für Experimentelle und Angewandte Physik der Christian-Albrechts-Universität zu Kiel, Germany

[2] European Synchrotron Radiation Facility, Grenoble Cedex, France

[3] Institute of Archaeology, The Hebrew University of Jerusalem, Israel

[4] Daresbury Laboratory, Keckwick Lane, Warrington, UK

E-mail addresses: mmueller@physik.uni-kiel.de, murphy@physik.uni-kiel.de, burghammer@esrf.fr, riekel@esrf.fr, jan.gunneweg@huji.ac.il, e.pantos@dl.ac.uk

Abstract

Single 2000-year-old archaeological fibres from textile fragments excavated in the caves of Qumran in the Dead Sea region were investigated by a combined approach using microscopy (optical and SEM), X-ray microbeam diffraction to determine the structure and X-ray microbeam fluorescence in order to identify trace elements. In comparison with modern reference samples, most of the fibres were identified as plant fibres (flax), some as wool. The molecular and supermolecular structure of both keratin (wool) and cellulose were found remarkably intact. Only few fibres show signs of external (fibre surface) and internal (supermolecular structure) degradation. The power of theses techniques for small and non-ideally preserved samples is clearly shown.

Keywords: X-ray diffraction, synchrotron radiation, microbeam, microfluorescence, archaeometry, Qumran, textile fibres

Introduction

The aim of an extended study on textiles found in Qumran is to find out the type of fibres and relate this information to the archaeological questions surrounding the mysterious Essenes, members of an eclectic religious sect, who are reported to have lived there 2100 years ago. This identification of fibre type is important since some authors suggest that the textile fragments are not from the time before 68 AD when the site of Qumran was destroyed. The information on the textiles will also allow conclusions on the trade of the Essenes in the historical context of the Dead Sea region.

The classical approach to analyse textiles is via optical and electron microscopy. Optical microscopy readily reveals the handedness of spun yarns. The shape of fibres allows for the discrimination between animal and plant fibres. The next step is a shape investigation in more detail using scanning electron microscopy (SEM) images. Identification can be difficult if the fibre surface is degraded and the typical shape of a fibre not retained.

The microscopic techniques mentioned above were applied to textile samples from the Qumran sites (Rogers 2003, Müller *et al.* 2003), identifying wool and plant fibres like flax and cotton. However, some open questions remained, particularly concerning the plant fibres. The intact textile samples were initially investigated using synchrotron radiation X-ray diffraction with a beam of 0.2 mm in diameter (Müller *et al.* 2003, 2004). The non-destructive experiments yielded diffraction diagrams, in which sharp and intense powder diffraction rings were observed. These dominating features stem from the fine mineral particles of the soil adhering to the fibres. The fibre diffraction diagrams of the small cellulose crystallites (typically 4-7 nm in diameter), so-called microfibrils, are difficult to resolve because of their diffuse character (small crystallites) and the non-ideal fibre orientation in the spun yarns and woven tissues. Quantitative analysis of the highly complicated resulting diffraction patterns is impossible.

The recently established technique of X-ray microbeam diffraction (Riekel 2000) overcomes these difficulties by combining a high spatial resolution of a few μm with a micrometer size probe. A focused synchrotron radiation X-ray beam with a high flux density can be used to collect diffraction diagrams of single fibres of a weakly scattering material like cellulose or wool within a few seconds (Müller *et al.* 1998, 2000, Kreplak *et al.* 2001).

In the present paper, the combined analysis of microscopic and microdiffraction data used in the first part of the study (Müller *et al.* 2003, 2004) is exemplarily demonstrated on a second set of textiles from the Qumran caves. The results of these investigations are presented

in detail and discussed together with the previously published data (Müller *et al.* 2003, 2004) to give an overview on both the potential of the techniques used and on the features of the different Qumran textiles. This article thus summarizes the status of the project to identify the Qumran textiles.

Experimental Details

For the present study, three textile fragments made from plant fibres were investigated in order to complement our already published work on textiles from Qumran (Müller *et al.* 2003, 2004). Samples unidentified by other methods were chosen in order to highlight the strengths of X-ray microbeam diffraction. The samples were found in different caves of the Qumran site. The numbering corresponds to those in Rogers (2003) and Müller *et al.* (2003), where the classical analysis (in the sense of the introduction) and results of the first microdiffraction experiment are reported in detail. Photographs of some of the samples are shown in Figure 1. QUM 510 (Figure 1a) is a heavily soiled fragment of a linen textile, the yarn is spun left-handed; two threads are dyed blue (visible as dark in the black and white photograph). This sample was investigated earlier (Müller *et al.* 2003) and is shown here again as it gives a good impression of the high quality of the woven material found in Qumran. The remaining three samples were not in perfect condition. QUM 531 (Figure 1b) is spun right-handed from undyed fibres; QUM 534 (not shown) looks very similar but is spun left-handed. The fragment QUM 535 (Figure 1c) consists left-hand spun plant fibres of unidentified type (QUM 535c and e) and pieces of plant tissue (QUM 535d). Some thick, straight and unspun dark fibres resemble hair (human or animal; QUM 535a); thinner ones could be wool (QUM 535b).

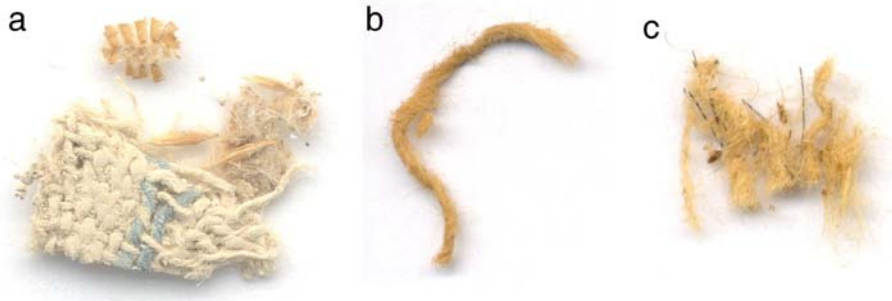

Figure 1. Photographs of textile fragments found in the caves of Qumran (a: QUM 510, b: QUM 531, c: QUM 535)

Single fibres of a few millimetres in length were carefully extracted from the samples. Adhering fibres were cleaned from the piece of plant tissue (QUM 535d). Compared to modern textile fibres, the archaeological fibres were extremely brittle, indicating a certain degradation of the material. The individual fibres with diameters between 10 and 20 µm and the small piece of tissue were glued to a sample holder (plastic frame), which was mounted on a goniometer head and optically aligned with the help of a video microscope.

Diffraction patterns were collected at the Microfocus Beamline ID13 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Details of the scanning diffraction set-up at ID13 may be found in a recent review by Riekel (2000). X-rays of 0.0976 nm wavelength were used in the experiment. The synchrotron radiation was focused to a spot size of 2 µm using a combination of pre-focussing Kirkpatrick-Baez mirrors and a tapered glass capillary. The incident beam intensity was monitored with an ionisation chamber in front of the sample. A Pt/Ir aperture placed 1.5 mm before the sample removed most of the X-ray background from the beam path further upstream. The sample holder was scanned through the microbeam with accuracy better than 1 µm. In an automated scan all single fibre samples of one frame were subsequently scanned in three horizontal lines, separated vertically by 10 µm, in 16 steps of 5 µm. Acquisition time was about 10 s per step, depending on the actual time to acquire 2,500,000 monitor counts. Two-dimensional diffraction patterns were recorded on a MAR CCD detector with 64.45 µm × 64.45 µm pixel size. The sample-detector distance was calibrated with a corundum standard and was approximately 102 mm.

Microbeam X-ray fluorescence spectra (Berglund *et al.* 1999) were simultaneously acquired using a very compact, high counting rate detector (Röntec XFlash) in about 5 mm distance from the beam position (Figure 2).

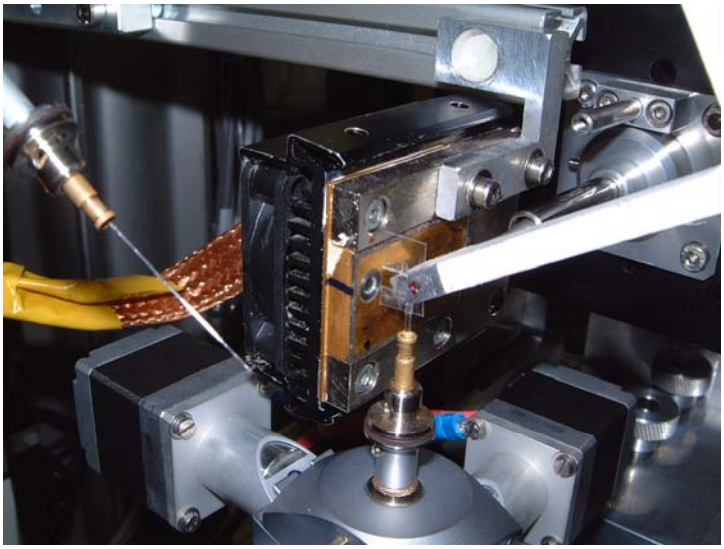

Figure 2. Combined microdiffraction and microfluorescence set-up at the Microfocus Beamline ID13, European Synchrotron Radiation Facility (ESRF; Grenoble, France)

X-ray fluorescence radiation emitted under about 90° and in the direction of the open side of the sample holder frame could directly pass to the detector window. As the scans described above were always wider than the fibre diameter, background spectra were obtained as well. They were mainly contaminated by platinum and iridium fluorescence lines (originating from the last aperture in the beam, around 9.5 keV) and the one of argon (from the air path, around 3 keV). The usable spectral range was between 1.5 and 11 keV.

The ESRF image processing software FIT2D (Hammersley *et al.* 1994) was used for analysis of the two-dimensional diffraction patterns (e. g., averaging, azimuthal integration; see below).

SEM images of the samples (coated with gold) were obtained with a LEO 1530 microscope (20 kV) in the ESRF Microimaging and Micromanipulation Laboratory.

Results and discussion

Microscopy (optical and SEM)

The textile samples from the caves of Qumran show almost no signs of degradation in the optical microscope. Practically all individual fibres in a single thread remained intact after nearly 2000 years in the sediment of the caves. As already mentioned in the previous section, the mechanical properties of the fibres, in particular the pronounced brittleness, indicate some internal degradation of the fibre material though.

Figure 3 shows exemplary SEM images of some parts of the complex sample QUM 535. In Figure 3a single fibres (QUM 535c) with a diameter of about 8 µm are shown. They display the typical twisted appearance of cotton fibres. However, the fibre surface is not as smooth as normally expected for cotton, an indication for surface degradation of the cellulosic material. Figure 3b makes it obvious that QUM 535b is indeed a fragment of some plant tissue. In the centre of the image, polygonally shaped cross sections of plant cells are clearly visible. Their diameter is around 20 µm and the cell walls are thin. The thick dark fibres in the sample QUM 535a have a diameter of 100 µm and look frayed (Figure 3c). There is no smooth fibre surface visible which would allow the identification of hair by the scale-like periodic structures of the cuticula; the cuticula is maybe completely disintegrated. Single fibrils at the end of the fibre have a diameter of 5-7 µm.

Degradation of textile fibres usually means an altered morphology and a different surface appearance. The identification of the samples presented in Figure 3 was only possible with X-ray microdiffraction (see later).

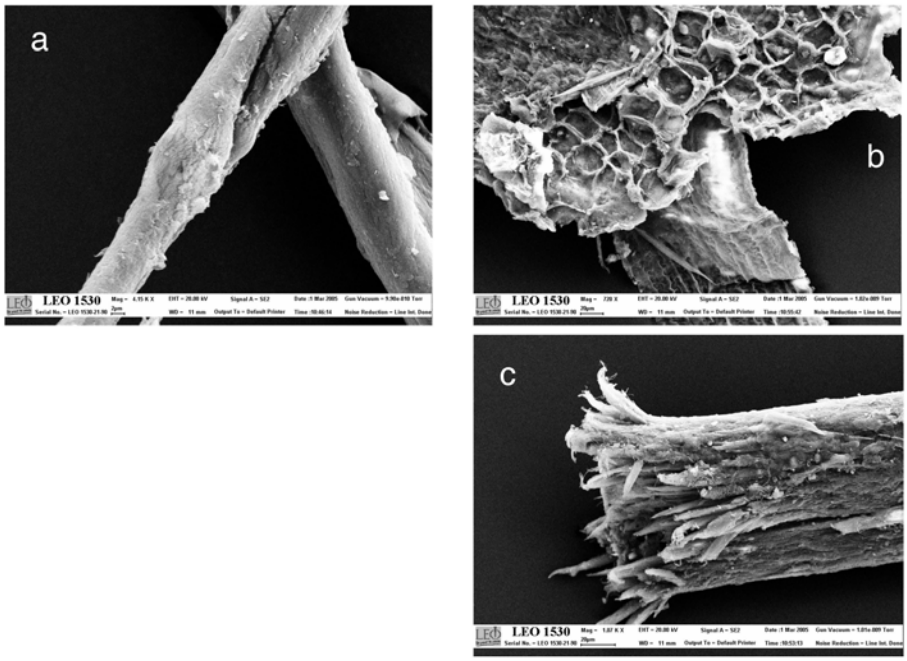

Figure 3. SEM images of samples QUM 535c (a), 535d (b) and 535a (c). The scale bars are 2 µm (a) and 20 µm (b, c)

Compared to SEM investigations on Qumran fibres reported earlier, the present samples seem to suffer more from degradation effects. In contrast to textiles found in the Cave of Letters in the Dead Sea region, the samples are almost devoid of soil particles on the surface. The Cave of Letters fibre surfaces were often covered with microscopic and sub-microscopic soil particles as expected for textile fragments found in the cave sediments and even aggregates of non-fibrous, probably inorganic material intimately connected with the fibre surface (Müller *et al.* 2006). Thus, the Qumran caves seem to generally have a favourable microclimate for preserving textiles, with QUM 535 with visible degradation being rather an exception.

X-ray microbeam diffraction

The diffraction diagrams obtained from single fibres made the distinction between fibres of plant and animal origin possible. Only two general types of diffraction patterns were found. Examples of both types are shown in Figures 4 (QUM 534, 535e and 531 in Figures 4a, b and c, respectively) and 5 (QUM 535a and b in Figure 5a and b, respectively).

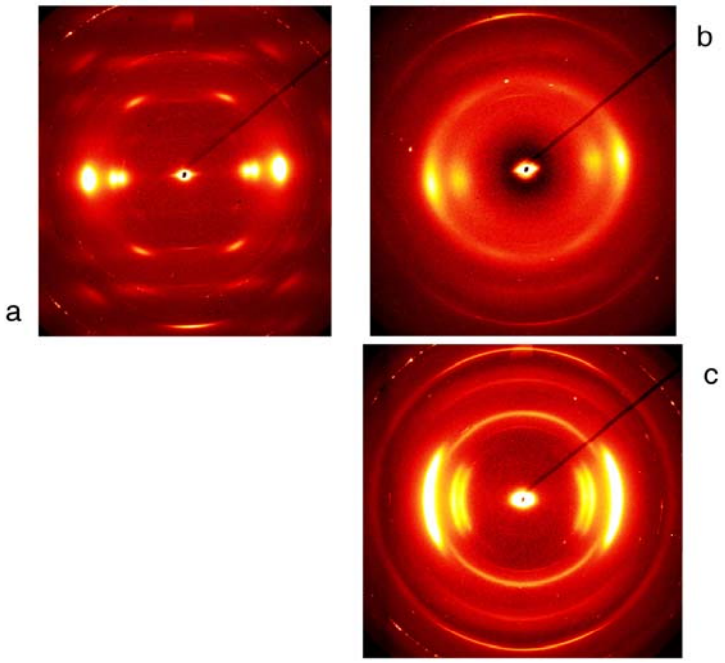

Figure 4. X-ray microdiffraction diagrams of archaeological cellulose fibres
(a: QUM 534, b: QUM 535e, c: QUM 531)

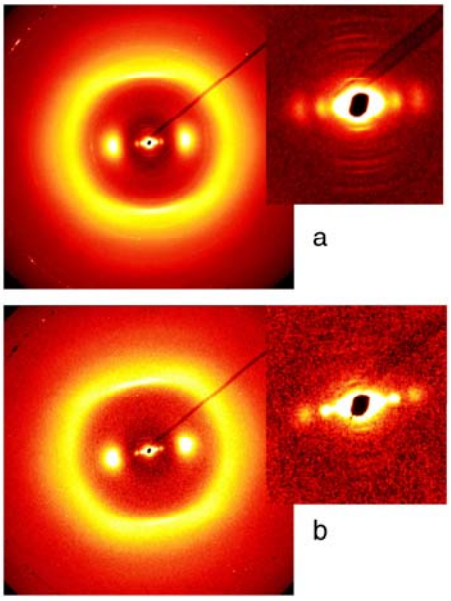

Figure 5. X-ray microdiffraction diagrams of archaeological wool or hair fibres (a: QUM 535a, b: QUM 535b). The insets show a close-up of the small-angle region

The broad peaks in the diffraction diagrams are from the fibre material. The inherent fibre texture, with all molecules essentially aligned parallel to the longitudinal fibre axis, leads to a so-called *fibre diagram*. With fibres oriented vertically as in the experiments presented here, the equator of the fibre diagram is oriented horizontally, the meridian vertically.

The diffraction pattern of QUM 534 (Figure 4a) is a perfect match of a fibre pattern of well-oriented cellulose (Müller *et al.* 2000). The clearly visible Bragg peaks up to higher orders reflect the crystalline order of the cellulose molecules in the fibre. In contrast, Fig. 5a from sample QUM 535a, which posed identification problems with microscopic techniques (see above), exhibits all expected features of X-ray diffraction from wool or hair (Briki *et al.* 2002). Wool fibres are well ordered on longer length scales and thus display sharper diffraction spots mainly in the small-angle region (see inset of Figure 5a). By means of microdiffraction, the threads of QUM 534, 535e and 531 (Figure 4) are identified as cellulose fibres of plant origin, QUM 535a and 535b (Figure 5) are wool or hair.

In the following, we will discuss in detail the features of cellulose fibres and wool fibres separately.

Cellulose fibres: cellulose is a semi-crystalline material with small cellulose crystallites (typically 4-7 nm in diameter), so-called *microfibrils,* embedded in an amorphous matrix. Fig.

4a (single fibre of sample QUM 534) is a very typical fibre diffraction diagram of cellulose fibres with high orientational order (Müller *et al.* 2000). The three strongest cellulose reflections $1\bar{1}0$, 110 and 200 (from the beam centre; 200 is strongest) are found on the equator of the diagram (Woodcock and Sarko, 1980).

The orientational properties of the cellulose microfibrils can in principle be seen directly from the raw data where the azimuthal arcing (broadening) of the Bragg reflections is a direct measure for the internal orientation of the cellulose. Bast textile fibres like flax, hemp, jute or ramie are characterised by a very high orientation of the cellulose microfibrils along the direction of the fibre axis. For a quantitative analysis, an area of the QUM 534 pattern around the 200 reflection was integrated radially to yield an azimuthal scan, shown in Figure 6b (black).

The shape of the scan is almost identical to that of modern textiles fibres (flax and ramie in red and green) with the peak width slightly larger. We can attribute the small difference to normal variations inside a cellulose fibre on microscopic length scales (Müller *et al.* 1998). The 200 reflection half widths (HWHM) of all three cellulose samples are given in Table 1 in comparison to the values for modern samples. QUM 535e cannot readily be identified, however, QUM 534 is very probably a bast fibre and QUM 531 could be cotton as suggested by the very broad arcing of the 200 reflection.

To corroborate these findings, the radial equatorial intensity profiles were also compared. The fibre diagrams were azimuthally averaged in an angular region of about 20 degrees around the equator. The radial width of the relatively broad equatorial reflections contains information about the cross section dimension of the cellulose microfibrils, which is specific for a given plant species (O'Sullivan, 1997). The thus obtained one-dimensional diffraction curves (Figure 6a, c and d) contain just the three reflections mentioned above in the range of the wave vector transfer $Q = (4\pi/\lambda) \sin\Theta$ (scattering angle 2Θ) from 5 to 21 nm^{-1}.

One reason for the differences between the diffraction curves of modern flax and ramie and of QUM 534 could be a different content of amorphous material. This should give rise to a very broad background peak centred at about 14.9 nm^{-1} (Isogai and Atalla, 1991). A small variation of the background intensity would change details of the intensity profile. A change of the amount of amorphous material, in particular a loss of it due to aging of the archaeological fibre, could also explain the brittleness of the ancient fibres as the amorphous material forms the soft matrix of the composite material cellulose. The cellulose microfibrils

are much harder than the entire fibre (Ishakawa *et al.*, 1997) and do not have the flexibility of the fibre.

Table 1: Crystallographic parameters (crystal sizes, calculated from the 200 reflection; lattice constant *a*; azimuthal HWHM of 200 reflection), probable identification and degradation state of the samples investigated in the second part of the studies on textiles from Qumran. For the differently treated modern flax and ramie fibres average values and errors (in parentheses) are given. Primary wall data are from Him *et al.* (2002), data for modern cotton from Müller *et al.* (2003).

Sample	Crystal size (Å)	*a* (Å)	HWHM 200 (°)	Identification
Modern flax	42(1)	7.96(3)	5.3(8)	-
Modern ramie	48(2)	7.935(5)	4.6(9)	-
Modern cotton	61	7.88	no fibre texture	-
Primary wall	18	8.40	powder texture	-
QUM 531	41	7.88	27	cotton (highly degraded)
QUM 534	36	7.97	5.2	flax (slightly degraded)
QUM 535e	26	8.13	13.2	cellulose fibre highly degraded)
QUM 535a	-	-	-	hair or wool (surface degraded)
QUM 535b	-	-	-	Wool (slightly degraded)
QUM 535c	-	-	-	Cotton (surface degraded)
QUM 535d	-	-	-	plant tissue

Despite the good orientation of the cellulose microfibrils in fibre QUM 535e, integrated one-dimensional data, however, prove a very low crystallinity. The comparison to the QUM 534 diffraction diagram (Figure 6c) reveals major differences: The 200 peak is found at lower *Q*, 110 and $1\bar{1}0$ merge to a single broad peak. Cellulose of this kind is often classified as cellulose IV (Gardiner and Sarko 1985), in contrast to the more ordered form of native cellulose, I. The larger lattice constant *a* (Table 1) as well as the very broad reflections indicate a poor lateral organisation of the cellulose molecules in the microfibrils of QUM 535e. It is still better than that of cellulose IV, which usually occurs in primary plant cell walls (Him *et al.*, 2002), not in the dominant secondary walls of fibres relevant for textiles. Cellulose in primary walls, however, is not aligned with the cell axis but rather isotropically oriented. It might thus be that the fibres of QUM 535e are highly degraded.

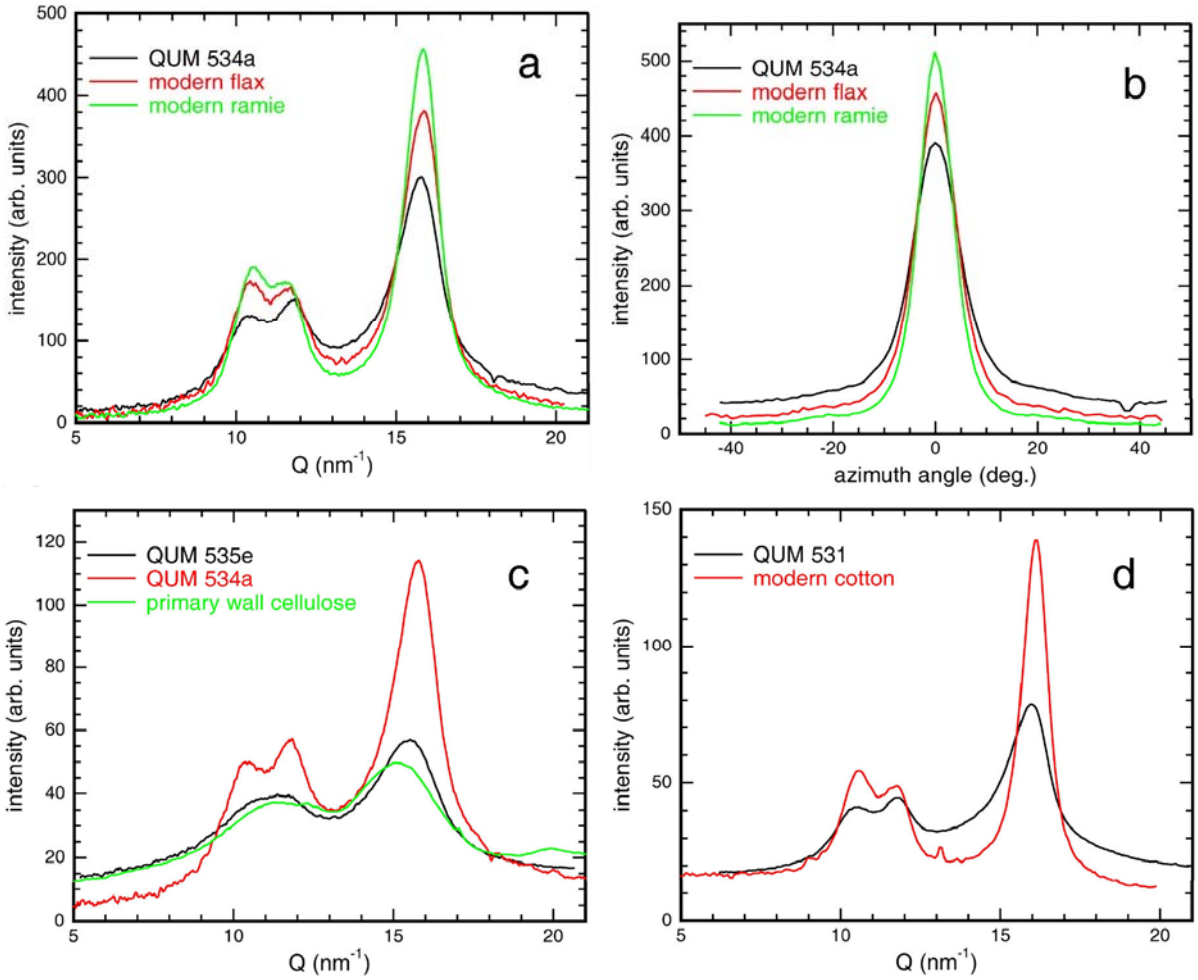

Figure 6. Radial (a, c, d) and azimuthal (b) intensity distributions of the two-dimensional diffraction diagrams of cellulose fibres (Figure 4)

The equatorial profile of QUM 531 is compared to that of modern cotton in Figure 6d. There is no good match, in particular the reflections of the archaeological sample are much broader that those of modern cotton. For a quantitative comparison, the peaks widths (given in 2Θ) were converted into apparent crystal sizes using the Scherrer equation (Azaroff, 1968) and listed in Table 1. The most reliable value is obtained from the width of the single 200 reflection, which does not overlap with other peaks. It can be regarded as the diagonal of the cellulose microfibril cross section. The microfibrils in QUM 534 are indeed much smaller (41 Å) than the 61 Å measured for modern cotton. This difference is too large to be explained by natural variations. The reason is probably degradation. The crystal size of QUM 531 (36 Å) is only slightly smaller than that of flax. The small microfibril dimensions in QUM 535e (26 Å) corroborate the findings about degradation (above).

The textiles made from cellulose fibres investigated in this study are less well preserved than those investigated earlier (Müller *et al.* 2003, 2004) and those from the Cave of Letters

(Müller *et al.* 2006). In conclusion, QUM 534 is flax (linen), QUM 531 cotton and QUM 535e a degraded fibre of the bast family.

Wool fibres: wool mainly consists of the fibrous protein α-keratin whose architecture is based on α-helices oriented parallel to the fibre axis. The two-dimensional diffraction patterns of the single fibres of sample QUM 535a and 353b (Figure 5) are typical for keratin. The sharp lines of the meridian indicate the 0.515 nm helix pitch projection, the diffuse equatorial peaks the 0.98 nm distance between helix axes (Briki *et al.* 2002). Furthermore, the supermolecular structure is also intact as shown in the insets (zoom into the small-angle region of the diffraction diagram): the well-defined equatorial reflections correspond to a characteristic 8.8 nm distance of the packing of keratin protofibrils into filaments (Briki *et al.* 1998), several orders of sharp meridional reflections indicate a periodic morphology along the fibre axis.

Concerning the long-range structure in meridional direction, QUM 535a exhibits more orders of the sharp reflections compared to the intensity of the equatorial order peaks (insets in Figure 5). Even though the frayed appearance of the thick fibre QUM 535a (Figure 3c) suggested a high degree of degradation, the molecular and supermolecular structure is surprisingly well intact.

In summary, the morphological features of wool were preserved during the two millennia that the Qumran textiles have been lying in the sediments of the cave. Similarly well-preserved structures of keratin have also been found in hair of ancient Egyptian mummies of about the same age (Bertrand *et al.* 2003).

X-ray microbeam fluorescence

Examples of the obtained fluorescence spectra are shown in Figure 7a. The spectra of one scan across the single fibre were averaged. The pronounced double peaks of calcium (K_α energy 3.690 keV) and iron (K_α energy 6.397 keV) are present in all spectra and were used for internal energy calibration. Significant concentrations of these two elements could even be detected in the modern fibre samples. Around 3 keV and 9.5 keV there are artefacts visible due to background subtraction (see Experimental Details section). The energies of fluorescence lines of all elements found are given by dotted lines in the plot. The complete results are given in Table 2. Very strong fluorescence is marked by ++ (e. g. the Ca and Fe lines in the spectra of Figure 7a) and a strong contribution by + (e. g. Zn in the spectrum of QUM 535d in Figure 7a). If only traces are found, like for example Cu in QUM 535c, see

Figure 7a), this is indicated by an open circle. No symbol means absence of fluorescence lines of the respective element.

Table 2: Overview on results of microscopy, microdiffraction and microfluorescence on archaeological fibres (sample names QUM + name in table). The symbols in the elemental distribution columns mean very strong (++) or strong (+) fluorescence lines or traces (o). No symbol indicates that this element could not be detected. Modern reference samples only show significant concentrations of Ca and Fe.

Name	Type	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
535c	Cotton						++					++	++	o	+	
535d	plant tissue	o	o	+	o	+	++	+	o	o	o	++	++	+	+	
535e	degraded cellulose		o	+	o	+	++					++	++	+	o	

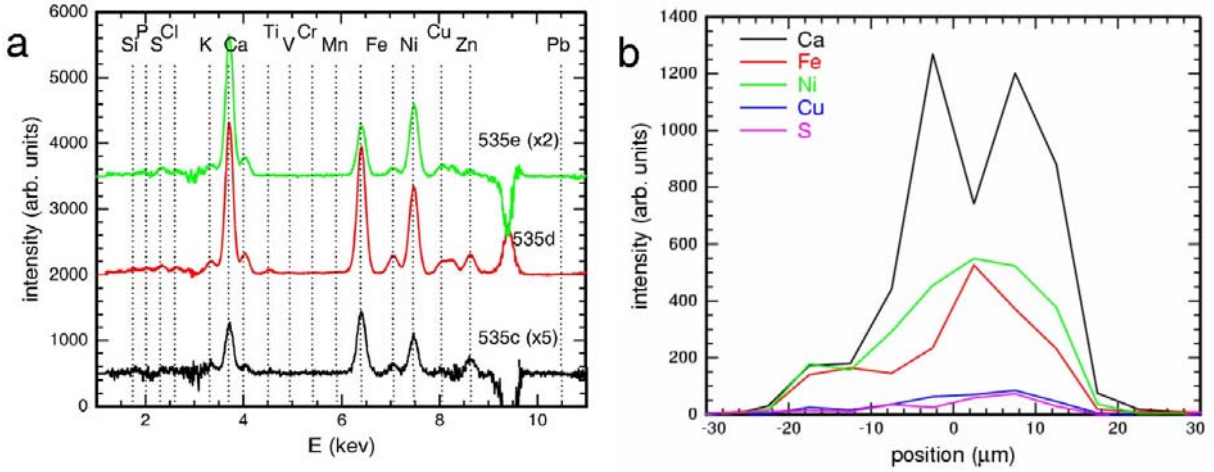

Figure 7. (a) X-ray fluorescence data obtained with a 2 µm wide microbeam, averaged over the fibre diameter of single cellulose fibres (QUM 535e, 535d and 535c). Negative peaks and/or noise around 3 keV and 9.5 keV are artefacts from background subtraction. (b) Results of microfluorescence scans across a single fibres of QUM 535e. Data correspond to intensities of fluorescence line of the respective elements

The elemental distribution is similar among the samples discussed here, thus constituting a fingerprint of the soil in the Qumran caves. The strong presence of Ni is in contrast to findings from the Cave of Letters in a similar geological formation (Müller *et al.* 2006).

There are only very few special cases that require a more detailed investigation. Additional information about the location of a specific element in a fibre or at its surface is

found in the position resolved spectra, yielding local elemental distribution maps. Figure 7b shows such a map of the fibre QUM 535e for some selected elements. For a homogeneous distribution of an element the fluorescence intensity should be proportional to the volume of the material illuminated by the X-ray beam. For most of the elements (Ni, Cu, S) this seems to be the case. The sharp pronounced peaks of the Ca and Fe distributions rather hint to mineral grains adhering to the fibre surface.

Conclusions

The fibre source of some particularly difficult samples has been identified by the non-destructive technique of X-ray microbeam diffraction. Of the cellulosic fibres, QUM 534 is flax (linen) and QUM 531 and QUM 535c are cotton. QUM 535e is a degraded fibre of the bast family. QUM 535a was identified as hair and QUM 535b as wool. Similar trace elements were found in all samples.

There are a number of advantages of the method used here over microscopic techniques (optical and SEM) and standard X-ray diffraction: (i) only single fibres (a few μm in diameter) of the material are required; (ii) the characteristic orientation distribution of cellulose in different plant fibres can be directly measured; (iii) the high spatial resolution enables one to collect diffraction data that are almost not at all influenced by small adhering soil particles; (iv) the method provides a probe to determine the degree of degradation of a fibre material.

The crystalline parts (microfibrils) of the cellulose and the keratin in archaeological plant fibres from the caves of Qumran stayed remarkably intact during their storage period in the caves: The diffraction diagrams from most of the single fibres are as clear as those of the respective modern plant fibres. Only very few samples, in particular those presented in this article, showed severe signs of degradation, both at the surface and on the molecular and supermolecular level.

Almost all fibres investigated in the two experiments could be identified (Table 1, (Müller *et al.* 2003, 2004)). Most fibres found in the two parts of the study were of plant origin. The cotton textiles were C14-dated to be much younger than the 2000-year-old linen textile fragments; the use of cotton in biblical times would have been very unexpected (Sheffer 1989).

The combination of microdiffraction with microfluorescence will be of advantage for the planned study of the dyed wool textiles found in Qumran. First promising results could already be gained in a study of textiles from the Cave of Letters with those techniques (Müller *et al.* 2006).

Acknowledgements

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PROVENANCING CERAMICS

Kaare L. Rasmussen

Department of Chemistry, University of Southern Denmark, Odense M, Denmark
E-mail: klr@chem.sdu.dk

Abstract

During the international work, which resulted in the publication of volume II of the Archaeology of Qumran, a large body of ceramics was investigated by different techniques. The present author was given access to a selection of samples of scroll jars, as well as local and imported ceramics. Through measuring the magnetic susceptibility and the thermo luminescence sensitivity on these samples it was attempted to see whether the scroll jars were manufactured from local Qumran clay or were imported from elsewhere. This newly established method of clay provenance determination has been demonstrated to be able to distinguish clay sources at several other locations in the Mediterranean area, besides numerable locations in Northern Europe. The results of the measurements showed that scroll jars (samples K1-K5) did form a distinct group. This group coincided with what was judged by other techniques as well as archaeological evidence to be of local Qumran origin, samples K7-K11. K11 can with exceptional certainty be labeled 'local', as it was a piece of the firing kiln at Qumran. The only certain import piece was sample K6, which also proved to be very distinct from the rest of the samples. However, two samples from the local group were positioned slightly away from the rest (K10 and K12). K10 was judged also by the NAA results of Bella and Gunneweg to be a possible import sherd, and K12 was TL-dated to be no more than a hundred years old. These results seem to indicate that provenance determination by measuring magnetic susceptibility and TL sensitivity is a viable method to apply to Qumran ceramics. The results support the hypothesis that the scroll jars were made locally in Qumran.

Introduction

Ceramics is perhaps the most abundant group of finds at archaeological excavations, especially so in the Mediterranean area. Since the dawn of archaeology ceramics has been used for dating purposes – a method that relies on the assumption that size, shape, decoration, colour, and fabric of the ceramic objects change in a unique way, much in analogy with the automobile design through the last 50 years. Besides being used for dating, ceramics is also in some cases used to track ancient trade routes, a venture that relies on the ability of the archaeologist to determine the provenance of the ceramics. To facilitate the determination of the provenance classic geological and chemical methods have been applied for several decades now. These methods consist of mineral identification under the microscope done on prepared thin sections, microprobe analysis of selected mineral grains, and 'whole rock' analysis by various chemical techniques such as Atomic Absorption Spectroscopy or Neutron Activation Analysis. Thin section observations requires large samples, is very tedious and rather expensive. The most rewarding method is probably the 'whole rock' chemical analysis followed by a statistical analysis of the date produced. It is in this light that the present method should be seen. It is a new technique that is applied to 'whole rock' samples, and which offers an alternative way of provenancing ceramics, burnt redbrick and clay sediments.

The measuring technique

The provenancing method is a relatively new method (Rasmussen 2001). In short this method consists of measuring two parameters on small samples of ceramic material. The first parameter is the magnetic susceptibility. This parameter is measured by subjecting the sample to a low intensity alternating magnetic field at ca. 900 Hz introduced by at set of Helmholz-coils surrounding the sample. In this way the magnetic domains of the ferro-, ferri- and diamagnetic minerals are forced back and forth through a slight hysteresis loop. The magnetic susceptibility is defined as the ratio between the external magnetic field (H) and the induced magnetization in the sample (J). The induced magnetization can be deduced from the drop in the external field, which is measured by a second set of pick up coils surrounding the sample. This measuring technique leaves the samples completely unharmed – it is not exposed to light, heat, or any mechanical stress, and due to the low relatively intensity of the external magnetic field any permanent magnetization is left unaltered in the sample.

The second parameter is the thermoluminescence sensitivity, which is measured on a regular TL-equipment, which is normally used for dating the firing event of ceramics in archaeometric laboratories. Here a sub-sample has to be crushed and sifted and 8 mg heated to 400^{o}C in order to reset the thermoluminescence palaeosignal. After cooling the 8 mg sample is irradiated for 1 minute under a strong beta-emitting radioactive source. In this way a well-defined portion of the electron traps are filled with electrons. Following the irradiation the sample is read for its TL-signal by first annealing it at 200^{o}C for 30 seconds and then slowly heated to 400^{o}C while the light intensity is measured. The light curve is integrated from 202 to 235^{o}C and the number corrected for various parameters such as machine drift and sample size. The final result reflects the number of electron traps per milligram of ceramic material.

The two parameters, the magnetic susceptibility and the TL-sensitivity, are plotted against each other in a log-log diagram, and it is our experience that differences in clay provenance almost invariably show up as different locations of the points in this plot.

The size and nature of the samples

The amount of sample consumed by an archaeometrical investigation is often of great concern to the conservators and the people responsible for the museum collections. Similar interest is devoted to any other alteration or imprint done to the archaeological object, and to be frank there is no such thing as a non-destructive analysis. The question is rather how the object is interacted with and how much of it is destroyed.

In this method of provenancing ceramics the direct consumption is variable. However, in a normal situation, where preservation is of minor significance, we consume 8 mg of sample in the grain size interval between 100 and 300 µm. This analysis is normally repeated 3 times, so the normal consumption is 32 mg of sifted ceramic powder. In order to get 32 mg in the grain size interval of 100-300 µm we use ca. 100 mg of sample, which has to be cut out of the shard in the museum collection. The magnetic susceptibility can be measured either directly on the original shard itself (provided it is smaller than ca. 3 x 8 cm) or on the part cut out for TL-sensitivity prior to crushing.

In situations where preservation is of utmost importance smaller amounts can be used. The smallest sample consumption we have utilized so far is a total of 5.9 mg taken from a Greek phiale in the J.F. Willumsen Museum collection in Denmark. These 5.9 mg was sufficient for both a provenance determination and a TL-dating (alas, the phiale proved to be a

fake!) (Schmidt and Rasmussen 2002). It is conceivable that even smaller sample sizes can be used. With the equipment at SDU, we can probably go down to ca. 1 mg, but other TL-laboratories using a single grain technique could limit themselves to even smaller samples sizes. There is, however, a problem with the very small sample sizes, namely the fact that the data of decreasingly smaller samples becomes increasingly less representative of the shard from which it is taken.

Under normal condition we find that an ideal sampling is 4 x 8 mg for ca. 20 different shards from one context or provenance. The 20 samples will normally scatter in the diagram to such an extent that the borders to other clay provenances in the area can be distinguished. It should, however, be stressed that it is our experience that the method should be limited as much as possible in space and time. Only simple questions should be posted and attempted to be solved by this method. The reason is that taking in too large geographical areas of interest invariably leads to overlapping clay provenances in the area.

There are few other considerations for the sample selection. It seems that neither the firing temperature nor the addition of stabilizing substances such as burnt cow bones, burnt flint, or burnt granite play a significant role in the placement of a sample in the log-log plot.

Examples of provenance determinations

The method has been tested on well over 50 locations in Scandinavia and the Mediterranean (Feveile *et al.* 1998, Rasmussen 1999, 2001, 2003, Kristensen and Rasmussen 2001, 2004, Bonde *et al.* 2001, Rasmussen and Lund 2004, Petersen *et al.* 2005, Rasmussen and Hjermind 2006). Figure 1 shows a provenance determination from the Medieval Nyborg Castle in Denmark. The samples are taken from two parts of the east façade of the main building. The difference in clay provenance is clearly seen.

The method has also been tested on a limited set of samples from Khirbet Qumran. The sample set consisted of 12 samples, 5 of which were from Dead Sea Scroll jars, one was a known import piece, and 6 were local Qumran pottery. The data is shown in Figure 2. Our tentative conclusion is that the jars are made from the same clay as the local pottery. The only caveat is that the number of samples is on the limit of being too small to allow a certain provenance determination. This goes in particular for the import ceramics, which is represented by a single sample only.

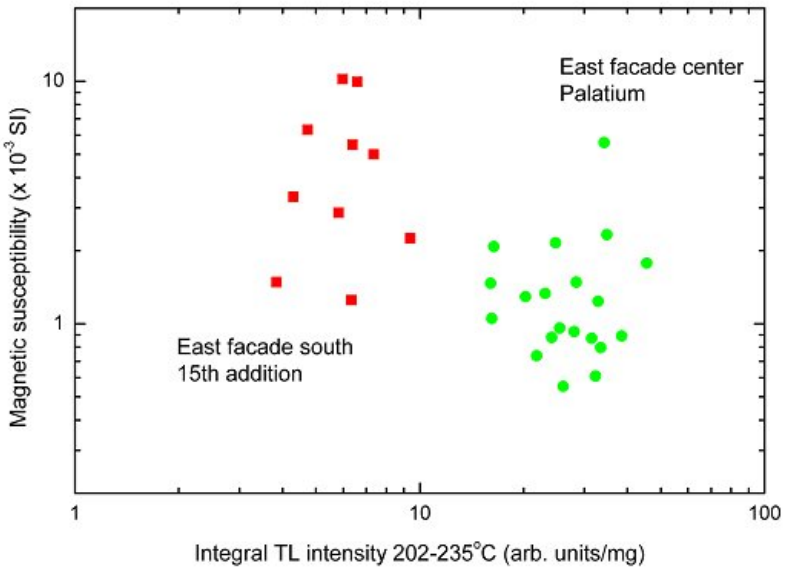

Figure 1. Samples from two different parts of the east façade of Nyborg Castle in Denmark. The squares are from the south part, presumably from 15th century AD, the circles are data for samples from the central part of the east façade presumably from the 14th century AD. The clay provenance of the two parts of the building is clearly different.

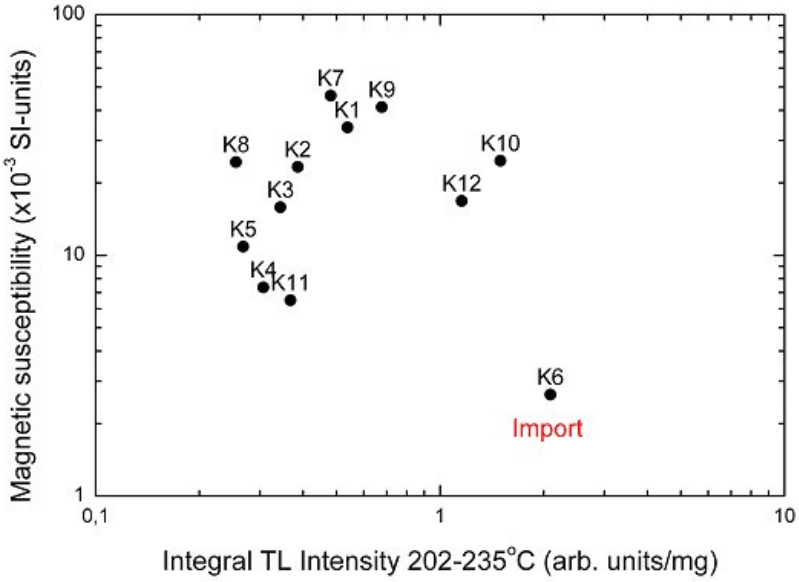

Figure 2. A small set of samples from Khirbet Qumran. K1-K5 are from Dead Sea Scroll jars, K6 is a known import piece and K7-K12 are local ware from Qumran. It seems that the jars were made from the same clay as the local Qumran pottery.

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RAMAN SPECTROSCOPIC STUDY OF ARCHAEOLOGICAL TEXTILE SAMPLES FROM THE 'CAVE OF LETTERS'

Peter Vandenabeele[1], Howell G.M. Edwards[2], Orit Shamir[3], Jan Gunneweg[4] and Luc Moens[1]

[1] Department of Analytical Chemistry, Ghent University, Belgium
[2] Department of Chemical and Forensic Sciences, University of Bradford, UK
[3] Israel Antiquities Authority, Jerusalem
[4] Institute of Archaeology, The Hebrew University of Jerusalem, Israel
E-mail: peter.vandenabeele@UGent.be

Abstract

Raman spectroscopy is a non-invasive molecular spectroscopic technique, which is gaining a lot of momentum in archaeometry research. This paper demonstrates the application of this technique to the study of Qumran textile samples, originating from the Cave of Letters. It is shown that dispersive as well as Fourier-transform (FT-) Raman spectroscopy reveals the proteinaceous nature of the fibres. The samples have undergone significant degradation that is reflected in their molecular spectra. On some fibres indigo has been identified using this non-destructive approach.

Keywords: Raman spectroscopy, Qumran textile, analysis of archaeological samples, textile, fibres, indigo, Cave of Letters.

Introduction

Due to several instrumental improvements, Raman spectroscopy has become increasingly important as an analytical tool in archaeometric research (Vandenabeele 2004). Several studies have been published on the analysis of paintings (Derbyshire and Withnall 1999, Soares 2001, Vandenabeele *et al.* 2000), mediaeval manuscripts (Gilbert *et al.* 2003, Smith *et al.* 2002, Edwards *et al.* 2001), pottery fragments (Colomban *et al.* 2004, Colomban 2004), etc. One of the most advantageous properties of this technique is its ability to study inorganic as well as organic compounds, and this is particularly valuable for an understanding of the particular interactions between the two types of material.

There are several reasons to investigate archaeological textile samples. People want to gather information on the nature of the materials that have been used. In addition to the materials identification, by studying the degradation of the textile samples the influence of different burial conditions on the remains can be examined. In a broader context, the analysis of historical textiles can discover which materials have been applied and what techniques that have been applied. Moreover, the study of archaeological remains and especially of textiles can provide valuable information on the interaction between different groups of people.

In this project, textile fibres have been analysed, originating from the Near East from the beginning of our calendar. This region was occupied by different groups of people, living in towns and villages and a part as nomads. Some groups of people were herdsmen; others were merchants, a fact that encouraged interaction between the different tribes. Moreover, important trade routes intersect the region of interest, contributing additionally to the interaction between groups of people. Therefore, this work, being part of a broader study on inter-human interactions in the Eastern Mediterranean region, examines the feasibility of Raman spectroscopy for the spectroscopic analysis of historical textiles.

Raman spectroscopy, being a molecular spectroscopic technique, has several advantageous features for this research. The ability to record spectra of minute areas of specimens (typical diameter a few micrometers) of organic materials as well as the non-destructive character make the technique well suited for these investigations. It is possible to obtain information on the composition of the fibres as well as on the dyes that have been used. From the literature, it is clear that Fourier-transform (FT-) Raman spectroscopy can be applied to identify historical textiles and to study degradation phenomena (Edwards and Munshi 2005, Edwards 2004, Edwards and Wyeth 2005). For instance, linens from mummies have been studied extensively using FT-Raman spectroscopy and some attempts have been

made to analyse natural dyes by means of Raman spectroscopy (Shadi *et al.* 2003, Andreev *et al.* 2001).

The aim of this work is to examine the feasibility of Raman spectroscopy for the examination of archaeological textile samples originating from the '*Cave of Letters*' (West Bank, *ca.* 2nd century AC). The samples have been studied by dispersive Raman spectroscopy (laser wavelength: 785 nm) as well as by FT-Raman spectroscopy. Fibres as well as natural dyes that were used are examined and considerations on the degradation of these samples are made. Finally, the results from this analysis will be compared with the analysis of the same samples using other techniques (Gunneweg *et al.* 2005).

Experimental

Samples

Eight textile samples, *ca.* 1-2 cm^2 each in area, have been analysed (*e.g.* the samples shown in Figure 1). Pieces were collected on the 14th of July 2000 in the Cave of Letters, at Locus 2 HH41 B 166, located near the Niche of Skulls. The samples were dyed (Abrahams and Edelstein 1963) in different colours: blue, black, red, green, and brown while one was described as 'discoloured'. In some textile samples it was rated that the warp and weft threads have different colours.

Fig. 1

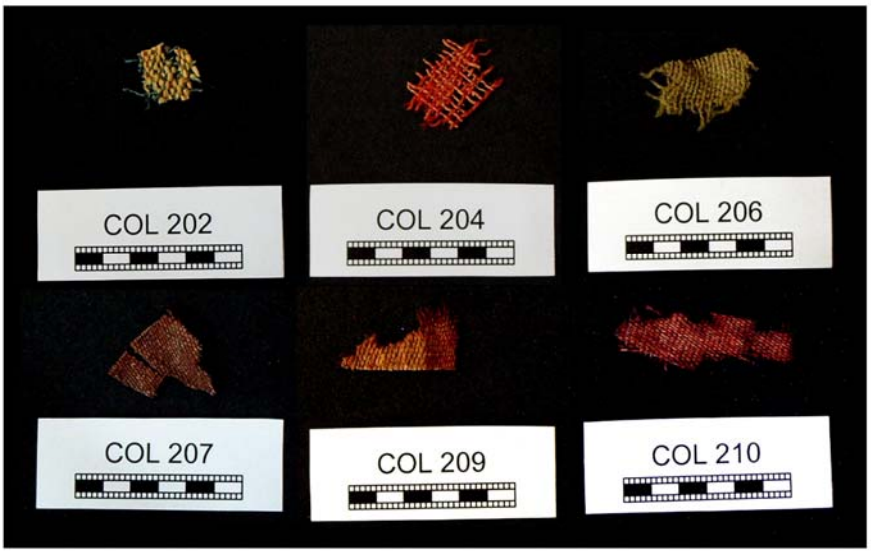

Figure 1. Some typical examples of the textile samples from the Cave of Letters, as analysed with Raman spectroscopy.

Raman Instrumentation

Dispersive Raman spectroscopy was performed on a Renishaw System-1000 (Wotton-Under-Edge, UK). This system is equipped with a low-power diode laser with a laser wavelength of 785 nm (laser power at the sample: less than 5 mW). An Olympus BH-2 research grade microscope (50X objective) is used to focus the laser beam on a single fibre of the sample and to collect the backscattered Raman radiation. The instrument is equipped with a 1200 grooves/mm dispersion grating and a Peltier-cooled CCD, allowing the recording of Raman spectra with a spectral resolution of *ca.* 1 cm^{-1}. Raman spectra were recorded between 300 and 1800 cm^{-1}, with a typical accumulation time of 300 seconds.

FT-Raman spectra were obtained using a Bruker IFS66/FRA106 system with Nd^{3+}/YAG laser excitation at 1064 nm. The spectral resolution was 4 cm^{-1} and approximately 2000 scans were made of each specimen region selected for study. In the macromode the spectral footprint was about 100 μm whereas with a dedicated Raman microscope and 100X objective lens, this was reduced to 8 μm. Typical accumulation times were 30 min – 1 hour and several spectra were recorded of each sample over the wave number range 200-3500 cm^{-1}.

Historical background

The Cave of Letters is located in Nahal Hever and is called so because the cave contained the Bar Kochba's letters exchange dated to the end of the second revolt of the Jews against the Romans in 135 A.C. The cave is 150 meter long and was inhabited by Jews who fled the Romans. It is located three kilometres west of the Dead Sea in a spot that is about $1/5^{th}$ the distance between 'En Gedi and the famous Masada fortress that had already fallen into Roman hands in 74 A.C. The cliffs in which the cave is situated may be called the continuation of the cliffs near the Dead Sea in which the Dead Sea scrolls have been found.

When the textiles of the Qumran caves contained mainly scroll wrappings of the 2^{nd} Century A.D., the Cave of Letters is special because of the finds of wool and linen and all kind of garments sometimes even intact mantles and tunics.

The importance of having the Cave of Letters' textiles analysed lies in the fact that it helps to understand what people wore at various parts in the Roman Empire and perhaps that we are pioneering in setting up a part of a database on textiles in the Eastern part of the Mediterranean to be enlarged as others join.

Results and discussion

FT-Raman spectroscopy has been performed on these samples to identify their nature; a first indication is that all these textile specimens have suffered significant and extensive fibre degradation. This is demonstrated by band broadening and the background noise in the spectra, probably caused by a fission of the biopolymer chains at the glycosidic centres and changes in conformations. It is possible that this occurred from a combination of mechanical stress that occurred during the use of textiles and molecular damage in the burial environment.

This degradation has undoubtedly complicated the microscopic identification of the nature of the fibres. This survey has revealed that the spectra are indicative of degraded wool. The FT-Raman spectra of these fibres are shown stack plotted in Figure 2. Although the spectra suffer from serious broadening of the Raman bands due to the degradation, it is still possible to observe the proteinaceous Raman bands near 1660, 1450 and 1300 cm^{-1}, which is highly supportive of degraded amide linkages. These features can be attributed to the amide I band (ν(CONH)), $\delta(CH_2)_{scissoring}$ and the amide III band (δ(NH)), respectively. Although the samples are badly damaged, these Raman spectra suggest an assignment to wool, as opposed to silk, both being proteinaceous textile fibres. This can be observed from the relative positions of the amide I and III bands, since these are highly indicative for the presence the keratotic α-helix structure, opposite to β-sheets as observed in silk fibroin.

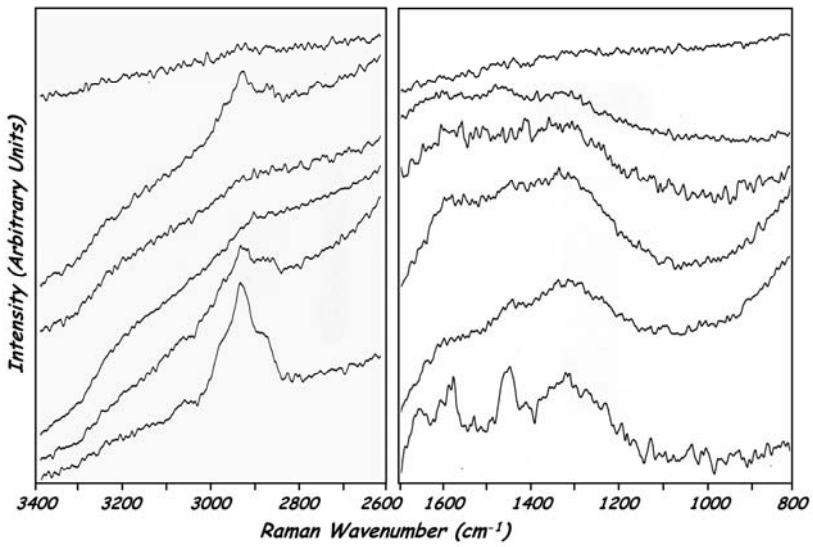

Figure 2. Typical FT-Raman spectra (800-1700 cm^{-1} and 2600-3400 cm^{-1}) from the Cave of Letters textile samples.

The spectra recorded on the dispersive spectrometer (laser excitation wavelength of 785 nm) suffer in general more from a high fluorescence background continuum, but nevertheless confirm the identification of wool (Figure 3). In some cases, calcite ($CaCO_3$) is identified along with the organic material in the Raman spectrum, and this is attributed to the rock cleft site.

When recording dispersive Raman spectra from some of the coloured textile fibres, it was possible to observe some Raman bands originating from the dyes that were used to stain the textile. In general, the red-pigmented samples suffered severely from fluorescence. However, the dark blue and almost black samples clearly revealed some distinct features (Figure 4), which correspond to the Raman spectrum of indigo, which has been studied and described in several papers (Tatsch and Schrader 1995, Vandenabeele and Moens 2003). It has to be noted that the Raman spectrum of indigo is highly dependent on the laser wavelength used for recording the Raman spectrum (in this case 785 nm); indeed, resonance Raman excitation may strongly enhance certain Raman bands. It is to be noticed that the dispersive Raman spectrum of indigo overwhelms the Raman features originating from the fibre. Based on these spectra it is not possible to determine the indigo source (synthetic (Not at this period), indigo (*Indigofera tinctoria*) of Asian origin or Woad (*Isatis tinctoria*) of local origin), however, the presence of haloindigo compounds (from marine sources) can be excluded.

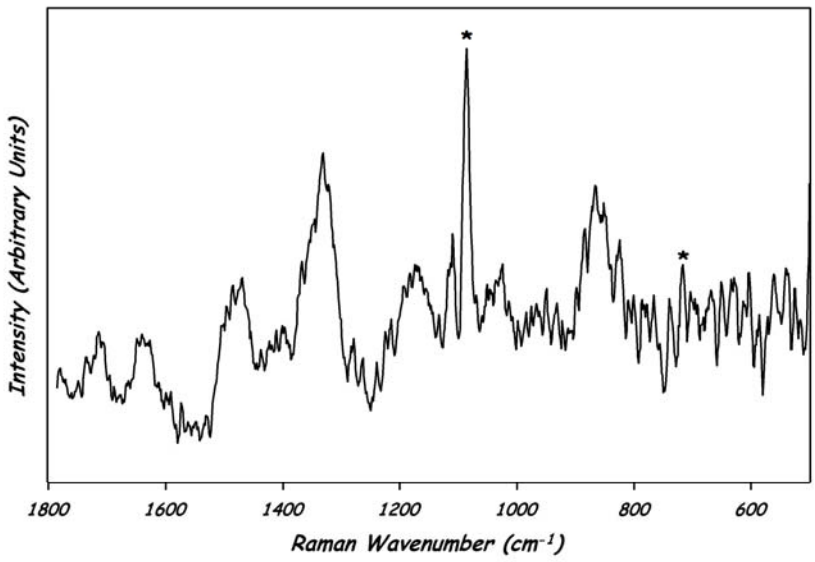

Figure 3. Baseline-corrected dispersive Raman spectrum (785 nm laser; 500-1800 cm^{-1}) from textile fibre originating from the Cave of Letters. The presence of calcite is identified by the observation of the two Raman bands, marked with *.

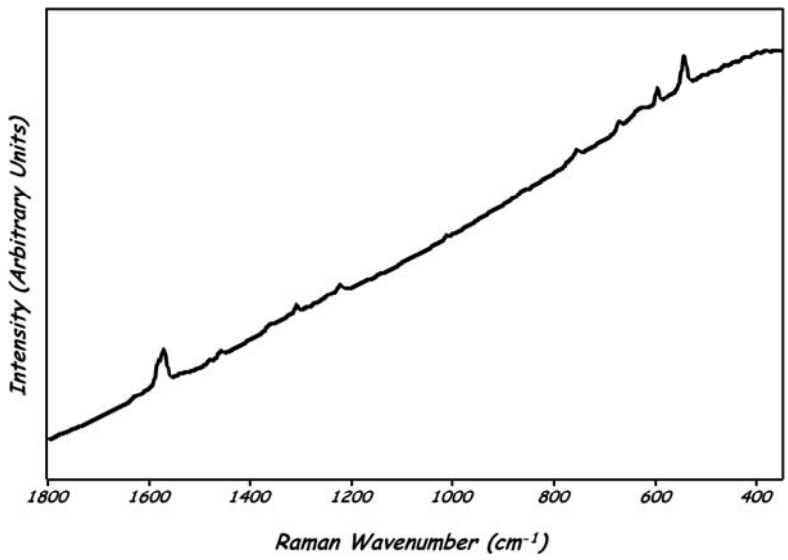

Figure 4. Dispersive Raman spectrum (785 nm laser; 350-1800 cm^{-1}) of a blue thread from a Cave of Letters textile sample, showing the presence of indigo.

Conclusions

In this work it has been demonstrated that Raman spectroscopy has great potential in the field of textile analysis. Despite its non-invasive nature, the technique is able to provide information concerning the nature of the fibres that are present in historical textile samples. However, with the exception of indigo, the identification of dyes on the textile fibres still seems to be problematic. Possible reasons for the occurrence are the occurrence of fluorescence, which overwhelms the spectrum even at 1064 nm in the near infrared region, the lack of spectral reference databases with spectra from dyes and the fact that dyes are generally weak Raman scatterers. Therefore in the field of textile analysis, because of its non-destructive character, Raman spectroscopy is valuable in a first non-destructive approach, providing information on the fibre nature as well as an indication for the dyes, which are present. A second, invasive, step the use of chromatographic techniques such as HPLC would be advised to provide more specimen details.

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CLEANING AND RADIOCARBON DATING OF MATERIAL FROM KHIRBET QUMRAN

Kaare Lund Rasmussen[1], Jan Gunneweg[2], Gregory Doudna[3], Joan Taylor[4], Mireille Bélis[5], Johannes van der Plicht[6,7], Jean-Baptiste Humbert[8], Helge Egsgaard[9]

[1] Department of Chemistry, University of Southern Denmark, DK-5230 Odense M, Denmark

[2] Institute of Archaeology, The Hebrew University of Jerusalem, Israel

[3] 1928 18th St. Apt. H101, Bellingham, WA 98225, USA

[4] Department of Philosophy and Religious Studies, University of Waikato, Hamilton, New Zealand

[5] 13, bd. Maréchal de Lattre de Tassigny, 88000 Épinal, France

[6] Centrum voor Isotopen Onderzoek, 9747 AG Groningen, The Netherlands

[7] Faculty of Archaeology, Leiden University, The Netherlands

[8] École Biblique, Jerusalem, POB 19053, Jerusalem, Israel

[9] Plant Research Department, Risø National Laboratory, DK-4000 Roskilde, Denmark
Email: klr@chem.sdu.dk

Abstract

A new battery of radiocarbon dates of linen, wood, and parchment excavated at Khirbet Qumran and in the caves at Qumran by Farther Roland de Vaux from École Biblique et Archéologique Français in 1951-1956 are presented. The data consist of two series of dates. One series was conducted on samples treated only by the standard AAA pretreatment procedure. In the other series, in which some of the items overlap, the samples were cleaned for contaminants prior to AAA and radiocarbon dating. From comparison of the two series,

several samples can be identified as contaminated, probably with conservational fluids, whereas some were found not to be affected by contamination. Based on our results we recommend that samples from Khirbet Qumran and the caves residing in museums should be analysed and/or cleaned prior to the AAA pretreatment and radiocarbon dating.

The majority of the dates fall in the time period ranging from 2nd century BC to 1st century AD, but several samples showed older dates, several were Byzantine/medieval, and two were dated to recent times. These results stipulate the need to treat the archaeological evidence from Khirbet Qumran and the caves with great care and to have an open mind concerning occupation of the site at other times.

Introduction

The archaeology of Qumran

The samples in the present paper were selected by J. Gunneweg and M. Bélis in 2001, when the former decided to try to identify textile yarns and the dyes used to tint them and submit them to radiocarbon dating intended for the publication in Volume II (Humbert and Gunneweg 2003). The primary question was whether the finds from the caves were contemporary with those of the settlement and cemetery in keeping with the hypothesis that they are from the same occupation periods. Before the collaboration on this Qumran project started, J. Gunneweg had doubts that all ceramics and textiles were of the same age. M. Bélis, specialist on textiles, was already aware that not all textiles identified as among the Qumran materials dated from the same period, and recommended further radiocarbon datings of textiles. Only a relatively small number of Qumran textiles had previously been analyzed, so consequently it was thought that a large batch would provide greater credibility in the dates obtained.

Most of the samples are from caves 8 and 11, where scrolls have been found. We wanted to investigate whether the textiles from Cave 8, located on the premises of the Qumran settlement, are similar in date to those of Cave 11 that is on the cliff, farther removed from Qumran.

An additional objective was to observe whether the enigmatic "SPI" lot of textiles (nobody knows what the abbreviation stands for) is of a similar or different date than the Qumran material of the 1st century before and after Christ (Bélis 2003, 220-221). Also the finds that were taken from the so-called "Christmas Cave" (designated QCC, QUM 543-546)

were checked to see whether they are of an earlier or later date than other charcoal and textiles found in the caves of Qumran. When the textiles from the Christmas Cave were sampled, it was immediately seen that there was a great difference in the use of dyes. The dyes varied from green to black to red and yellow. If the textile and wood analyses result in similar dates as those from other caves, then one should have a second look at the Christmas Cave material which once, that is to say, between 1997 and 2000 at least, was located among materials in the vaults of the Rockefeller Museum that have not yet been published. Even the location of the "Christmas cave" seems to be a long preserved secret since the time King Hussein of Jordan visited J. Allegro who found the cave on Christmas eve, fifty years ago (Bélis 2003, 211 & 220-21).

Sampling and cleaning

No one suspected any contamination on the initial series of samples, as no records in the Rockefeller Museum reported attempts at conservation of these samples. As will be shown below the content of the stable carbon isotope ^{13}C from this initial run led to the suspicion that some of the samples were indeed contaminated, probably but not conclusively by conservational fluids applied at some stage in the museum curation or during handling of the samples by experts in other fields than radiocarbon.

Therefore a second batch of samples were selected, seven of them overlapping with the first batch. This second batch was decontaminated prior to radiocarbon dating.

J. Gunneweg personally supervised the opening of the paper sheets containing the textiles and after M. Bélis had told him the importance of every single textile fragment, a piece of the untouched (*i.e.* sometimes dirty) textile was removed and placed in a thin rice-paper sheet after which it was send to K.L. Rasmussen in Denmark. The textiles were not treated by either one of these two people.

By analyzing Qumran pottery by INAA it was concluded that pottery found in the settlement has the same provenances as that in the caves (Gunneweg and Balla, 2003). The question was, could there be other evidence that would corroborate this? We thought that textiles might be just such material to compare dates for both the caves and the Qumran site.

Therefore, besides the various textiles that have been sampled from Caves 8, 11 and the Christmas Cave, there are two particular textile samples that are of the utmost importance since they might chronologically link the settlement, the caves, and perhaps the cemetery. QUM-503 is a linen sample from the settlement (Locus 96), and QUM-524 is linen from

Tomb 1 of the southern cemetery (described by Sheridan 2003). If these flaxes provided similar dates, they would also corroborate the pottery assemblage provenance.

Cleaning techniques

In 1960 Willard Frank Libby received the Nobel Price in Chemistry for his discovery of the radiocarbon method for dating archaeological artefacts. The radiocarbon method has been developed into a technique which is more or less standard for the large majority of samples from archaeological sites.

For sample preparation, a standard chemical pretreatment method has been developed: AAA – Acid/Alkaline/Acid (Mook and Streurman 1983). This is the standard procedure applied in order to select the proper datable fraction and remove contaminants, *e.g.* soil carbonates, from a sample. It consists of the following three steps. First a treatment in 4% hydrochloric acid (the first A). This acid removes any carbonate, most resins and sugars, and some infiltrated humic acids present in the sample. (Such carbon-containing compounds are usually considered contamination.) Second the sample is subjected to an alkaline (second A) treatment in a ca. 2% NaOH solution in order to remove tannic acids, compounds that are often deposited on the sample by groundwater. Finally the sample is again subjected to 4% hydrochloric acid (third A) in order to remove any carbon dioxide absorbed from the atmosphere during the alkaline treatment step.

Although this method has proven very effective for a variety of contaminants, there are contaminants that will not be removed by the AAA pretreatment procedure. Examples of such contaminants are castor oil applied to parchment (Rasmussen *et al.* 2001) and other unknown contaminants on parchment (Donahue *et al.* 2002).

In the present work it is shown that a more thorough decontamination procedure is called for on samples from the Qumran excavations, even for samples that were not considered likely to have been contaminated, and for which there exist no known conservation records.

Radiocarbon measurements

The samples were dated by Accelerator Mass Spectrometry (AMS) in Groningen. AMS is one of three different methods of measuring the $^{14}C/^{12}C$-ratio of a sample. In all three methods some material is consumed in the process, but for AMS the amount of sample consumed is by far the smallest: only about 1 mg of carbon is needed. Therefore AMS is the ideal technique for samples of which it is desirable to use as little as possible. The details of the Groningen AMS system are described in Gottdang *et al.* (1995) and van der Plicht *et al.* (2000).

After the chemical pretreatment, the samples were combusted and turned into CO_2 by an Elemental Analyzer (EA), coupled on-line with a stable isotope Mass Spectrometer (MS). The EA is also capable of purifying the CO_2, thus getting rid of compounds that could otherwise compromise the results. The EA/MS system enables precise measurements of the $\delta^{13}C$-values. The $\delta^{13}C$-value is necessary in order to correct the ^{14}C-measurement for any possible isotopic fractionation - that is, the preferential removal (or addition) of certain isotopes relative to the others, *i.e.* an artificial shift in isotopic ratios such as $^{13}C/^{12}C$ or $^{14}C/^{12}C$ - that may have taken place before or during the sample preparation procedure. The principle is that if a substance, *i.e.* the sample, is subjected to isotopic fractionation the $\delta^{13}C$-value is shifted only half that of the $\delta^{14}C$-value, as $\delta^{13}C$ is essentially the $^{13}C/^{12}C$-ratio whereas the $\delta^{14}C$-value is essentially the $^{14}C/^{12}C$-ratio.

The $\delta^{13}C$-value is expressed in ‰ VPDB (per mille deviation from the Vienna Pee Dee Belemnite standard) and the carbon content of the sample is measured in weight % by the EA/MS. The radiocarbon age is subsequently corrected for isotopic fractionation to the standard reference value of $\delta^{13}C$ = -25 ‰ VPDB, which is the average value for unfractionated terrestrial plant material.

Possible contamination in the first series

The results of the first series can be seen as the right half of Table 1. No contamination by conservational fluids or any other agents was suspected, and these samples were subjected only to normal AAA pretreatment procedure prior to analysis.

The radiocarbon ages themselves cannot be used as an indicator of the reliability of the dates. But the carbon content and the $\delta^{13}C$-values can, because these values usually lie within certain ranges independent of age, depending somewhat on the history of the samples. As can be seen from Table 1, the linen, wool, and wood samples all show carbon contents between 40 and 50%, which is in the normal range. Only the parchment sample 922 from cave 4 exhibited a somewhat large carbon content of ca. 60%. This is also not unexpected. The only extraordinary carbon content found is for the linen sample D057 (KLR-3322, GrA-17632). Here the yield was only 4.9 % or about 1/10 of the other samples. This is so different from the normal range that it can be suspected some foreign object was enclosed in the sample. This supposition is supported by the fact that the rest of the parameters for this sample, including the radiocarbon date, fall within the expected ranges.

Table 1.

		Second series (decontaminated)						First series (not decontaminated)					
Sample	**Type**	**KLR**	**GrA**	**BP**	**σ**	**$\delta^{13}C$**	**%C**	**KLR**	**GrA**	**BP**	**σ**	**$\delta^{13}C$**	**%C**
QUM-531 SPI 8: C075	Cotton	5450	24251	175	40	-24.78	41.7						
QUM-532 SPI 8: C076	Cotton	5451	24281	165	40	-22.89	42.1						
QUM-533 D037 Cave 11Q 35 (old QUM-513)	Cotton	5452	24282	1115	40	-25.30	41.3	3325	17408	1115	40	-25.71	41.7
QUM-534 D053 Cave 4Q (old QUM-501)	Linen from scroll jar	5453	24266	1975	40	-25.17	41.1	3320	17403	2040	40	-25.28	41.2
QUM-535 KhQ 3650 Loc.96 (old QUM-503)	Linen, charred	5454	24284	1965	40	-23.98	57.5						
QUM-536 cave 8Q (old QUM-504)	Linen	5455	24390	2135	40	-24.55	40.5						
QUM-537 cave 8Q-1 D013 (old QUM-505)	Linen + violet	5456	24257	2020	40	-25.76	40.4						
QUM-538 Cave 8Q D 009 (old QUM-506)	Marl+ linen+ violet	5457	24404	2090	35	-20.79	36.0						
QUM-539 Cave 8Q D009 (old QUM-507)	Olive pit	5458	24256	1875	40	-19.35	45.2	3321	17404	2110	40	-21.78	41.9
QUM-540 Cave 11Q D033b (old QUM-510)	Linen	5459	24285	2060	40	-25.24	42.0						
QUM-541 Cave 11Q DO43 (old QUM-512)	Linen, black and brown staining	5460	24287	2010	40	-24.66	36.9	3324	17407	2015	40	-25.08	41.6
QUM-542 Cave 11 (old QUM-514)	Wood	5461	24258	3415	40	-26.92	46.4	3326	17409	2375	40	-22.56	43.6
QUM-543 QCC 230 (old QUM-528)	Green wool	5462	24260	1905	40	-20.39	44.8	3334	17424	1900	50	-20.70	44.1
QUM-544 QCC 184 (old QUM-530)	Red wool	5463	24411	1940	40	-20.39	46.9	3336	17423	1885	40	-19.05	44.8
QUM-545 QCC 174 CC III	Charcoal	5464	24261	5230	45	-21.71	69.1						
QUM-546 QCC 174, Tr III	Charred wood	5465	24265	5845	45	-9.22	42.0						
QUM-508 D057 "Ain Feshkha"[1]	Linen							3322	17632	2030	80	-23.80	4.9
QUM-509 D052 Cave 4Q	Linen							3323	17405	2055	40	-25.35	40.5

[1] The box in which this linen was kept bore the mention in French *Ech. Tissus 3 Ain Feshkha.* Before the digging at Qumran and the discovery of the other scroll-caves, "Ain Feshkha" was the name used to describe the approximate location of the "Manuscript Cave" by archaeologists and all the authors (afterwards, it became "1Q"). It was also once called the "cave in the neighborhood of Jericho".

Table 1.

		Second series (decontaminated)						First series (not decontaminated)					
Sample	**Type**	**KLR**	**GrA**	**BP**	**σ**	**$\delta^{13}C$**	**%C**	**KLR**	**GrA**	**BP**	**σ**	**$\delta^{13}C$**	**%C**
QUM-515 D024b Cave 11Q	Wood, wooden root							3327	17412	1105	40	-10.62	43.8
QUM-516 D024c Cave 11Q 22	Wood							3328	17413	1125	40	-24.43	47.3
QUM-518 C060 SPI 23	Linen with fringe							3329	17414	1245	40	-23.94	42.3
QUM-520 C062 SPI 25	Linen weft faced cloth							3330	17415	1490	40	-24.12	41.7
QUM-521 C063 SPI 26	Linen 2 pieces sawn together							3331	17417	1255	40	-24.14	40.6
QUM-524 B003 Tomb 1 Southern cemetery	Linen with green stains of bronze							3332	17418	1470	40	-24.23	40.6
QUM-527 QCC 230	Textile, red and black							3333	17419	1850	40	-19.65	42.9
QUM-529 SPI	Wood							3335	17421	2060	40	-22.51	44.1
QUM-601 Cave 4Q 922	Parchment							3337	17633	2040	80	-21.45	59.9

The $\delta^{13}C$-values did, however, constitute a warning of contamination. As an example we can consider the wood sample D024b (KLR-3327, GrA-17412). This sample showed a $\delta^{13}C$-value of -10.62 ‰ VPDB, which is a completely unrealistic value for a normal wood sample. An intact uncontaminated wood sample under normal conditions will exhibit a $\delta^{13}C$-value close to -25 ‰. Values ranging between -24 to -26 ‰ cannot, however, be considered anomalous. If the $\delta^{13}C$-value of a wood sample is more negative than -25 ‰ it could be a sign that the wood is somewhat degraded by various processes of decomposition, like bacteria, for instance. A $\delta^{13}C$-value of -10.62 ‰ is a certain sign that either the sample is contaminated, and that the radiocarbon date produced therefore cannot be trusted, or the sample has undergone an extraordinary tough pretreatment process, possibly involving heating above say 60^{o}C at some point. If the cause of the anomalous $\delta^{13}C$-value is due to a tougher than usual pretreatment process then the radiocarbon date produced can still be fully trustworthy.

The wood sample 542 from cave 11 (KLR-3326, GrA-17409) showed a $\delta^{13}C$-value of -22.56 ‰VPDB, which is also a slightly unlikely number for a normal wood sample, indicating either that contamination might be present, or that the sample has undergone an unusual pretreatment process. Similarly the $\delta^{13}C$-value of -22.51 ‰ of wood sample 529 SPI (KLR-3335, GrA-17421) is suspicious.

The $\delta^{13}C$-values of linen and cotton samples, which are manufactured from plant fibers, are expected to fall in the same range as wood samples centered around -25 ‰. This indicates that there are no problems with the dates of cotton samples D037 (KLR-3325, GrA-17408) and linen sample D053 (KLR-3320, GrA-17403). Even the linen sample with the exceptionally low carbon content of 4.9 %, sample D057 (KLR-3322, GrA-17632), shows a $\delta^{13}C$-value of – 23.80 ‰ which is within the expected range. This supports the hypothesis that D057 included some foreign carbon-free heavy material.

For samples made from animal tissue, such as wool, the $\delta^{13}C$-values are expected to center around -21 ‰. Therefore samples like 543 QCC 230 (KLR-3334, GrA-17424) with a $\delta^{13}C$-value of -20.70 ‰ and 544 QCC 184 (KLR-3336, GrA-17423) with a $\delta^{13}C$-value of -19.05 ‰ VPDB must be considered quite normal, and there is no reason to suspect contamination on the basis of the $\delta^{13}C$-values of these samples.

When samples are just characterized as “textile” there remains a great uncertainty in judging the degree of contamination from the $\delta^{13}C$-values, as we do not know whether the sample consists of plant fibers (*e.g.* cotton) or is made from animal tissue *i.e.* wool. Therefore it is highly desirable that future analyses reveal the true nature of the material for these samples. However, our data can be used to predict the nature of the textile, e.g. for sample

QUM-527, QCC-230 from the Christmas Cave we suspect from the $\delta^{13}C$-value of -19.65 ‰ (KLR-3333, GrA-17419) that it is made of wool (also now confirmed by M. Bélis).

It should be stressed that this way of using the $\delta^{13}C$-values as an indicator of possible contamination is not a foolproof method. As explained above we measure the $\delta^{13}C$ in order to monitor changes in isotopic composition that might come from two processes: either some process in ancient times, between ca the time of the growth of the plant or the cutting of the sheep's wool and the time of analysis, *or* a process induced during the pretreatment and cleaning of the sample in the laboratory. If the isotopic ratio is shifted in a process of the latter type, *i.e.* in the laboratory, it is not a sign of contamination. So at best this method functions as an indicator or a red flag warning, but is not in itself decisive.

Cleaning for organic contaminants

When the potential for contamination was realized, a second series of samples from Qumran was selected for dating. Seven of these were second samples on items included in the first series. It was decided to attempt to remove any organic contaminant present, such as *e.g.* conservational fluids.

The samples were subjected to a cleaning procedure conducted at the Risø National Laboratory, Denmark. Each sample was placed in a stainless steel net, which was mounted in a Soxleth apparatus. Here the soluble organic compounds were extracted in a continuous reflux of 50 ml of 99.9 % ethanol for 8 hours, followed by a similar extraction in 50 ml hexane for 8 hours. After this the sample was subjected to the usual AAA pretreatment procedure at the AMS facility at Groningen, the Netherlands.

The results of the second series

The linen sample D037 showed precisely the same radiocarbon age, 1115 ± 40, in both the first (KLR-3325, GrA17408) and in the second series (KLR-5452, GrA-24282). Both the carbon content and the $\delta^{13}C$-values are almost identical in the first and the second series. We concluded there were no contaminating carbon compounds to be removed in D037.

Similarly no significant effects of the cleaning can be seen for the following samples: 541 linen from Cave 11 (KLR-3324, GrA-17407, and KLR-5460, GrA-24287), 543 QCC of green wool (KLR-3334, GrA-17424, and KLR-5462, GrA-24260), D053 linen (KLR-3320, GrA-17403, and KLR-5453, GrA-24266), and red wool 544 QCC 184 (KLR-3336, GrA-17423, and KLR-5463, GrA-24411). In all four cases there is no reason not to trust the radiocarbon

ages from both the first and the second series. In Table 2 the radiocarbon dates for each set are averaged and calibrated.

In two remaining items dated in both series there are, however, fairly large effects of the cleaning.

The wood sample 542 from cave 11 showed a slightly suspicious $\delta^{13}C$-value in the first series ($\delta^{13}C$ = -22.56 ‰). After cleaning, this sample exhibited a less unusual $\delta^{13}C$-value of -26.92 ‰, a value which is not uncommon for deteriorated wood. At the same time the radiocarbon age changed dramatically from 2375 ± 40 BP (KLR-3326, GrA-17409) to 3415 ± 40 BP (KLR-5461, GrA-24258), a change of 1040 ^{14}C-years. We recommend that only the date from the second series be trusted on this item.

The other large deviation is for olive pit QUM-539 from cave 8. The $\delta^{13}C$-value for this sample was a bit off in the first series ($\delta^{13}C$ = -21.78 ‰). A value close to -25 ‰ would be expected. We therefore suspected that the sample might be contaminated. The $\delta^{13}C$-value from the second run was, however even further off (-19.35 ‰). The radiocarbon date was significantly different in the two series. The sample in the first series showed a radiocarbon age of 2110 ± 40 BP (KLR-3321, GrA-17404) whereas it was significantly younger in the second series, 1875 ± 40 BP (KLR-5458, GrA-24256). The somewhat unexpected $\delta^{13}C$-values for the two sub-samples could perhaps be connected to the fact that the olive pit contains both a woody part and an oily part. Degradation of the oily part through the millennia could conceivably shift the average $\delta^{13}C$-value of the entire sample. However we consider it likely that besides the woody component of the pit and the oily component, there was some sort of conservation agent present, probably derived from petroleum (*i.e.* with an infinite radiocarbon age). We recommend that only the date from the second series on this item be trusted.

Which dates are to be trusted?

From the above discussion it can be concluded that some of the radiocarbon dates are highly trustworthy, either due to the fact that decontamination has been performed or due to agreement within the statistical limits with a decontaminated sub-sample. These highly trustworthy radiocarbon dates are listed in Table 2. Averages (marked with bold in Table 2) have been taken for samples on which two reliable dates have been achieved.

The calibration has been done with the OxCal program (Bronk Ramsey 1995, 2001) using the recommended INTCAL04 calibration curves (Reimer *et al.* 2004). The calibrated date is listed both within ± 1 standard deviation and ± 2 standard deviations.

Table 2.

Sample	Type	KLR	GrA	BP	σ	$\delta^{13}C$	%C	Calibrated date within ± 1 std. dev.	Calibrated date within ± 2 std. dev.
QUM-531 SPI8 C075	Cotton	5450	24251	175	40	-24.78	41.7	1660 - 1960 AD	1650 - 1960 AD
QUM-532 SPI C076	Cotton	5451	24281	165	40	-22.89	42.1	1660 - 1960 AD	1660 - 1960 AD
QUM-533 D037	Cotton	3325 5452	17408 24282	1115 1115 **1115**	40 40 **30**	-25.71 -25.30	41.7 41.3	890 - 975 AD	860 - 1020 AD
QUM-534 D053	Linen	3320 5453	17403 24266	2040 1975 **2010**	40 40 **30**	-25.28 -25.17	41.2 41.1	45 BC - 25 AD	100 BC - 70 AD
QUM-535 KhQ 3650 L.96	Linen, charred	5454	24284	1965	40	-23.98	57.5	20 BC - 80 AD	50 BC - 130 AD
QUM-536 Cave 8Q	Linen	5455	24390	2135	40	-24.55	40.5	350 - 90 BC	360 - 40 BC
QUM-537 Cave 8Q1 D013	Linen + violet	5456	24257	2020	40	-25.76	40.4	90 BC - 50 AD	160 BC - 70 AD
QUM-538 Cave 8Q D009	Marl+ linen	5457	24404	2090	35	-20.79	36.0	170 - 50 BC	210 BC - 1 AD
QUM-539 Cave 8Q D009	Olive pit	5458	24256	1875	40	-19.35	45.2	50 - 210 AD	20 - 230 AD
QUM-540 Cave 11Q D033b	Linen	5459	24285	2060	40	-25.24	42.0	160 BC - 1 AD	190 BC - 30 AD
QUM-541 Cave 11Q D043	Linen	3324 5460	17407 24287	2015 2010 **2015**	40 40 **30**	-25.08 -24.66	41.6 36.9	50 BC - 25 AD	100 BC - 70 AD
QUM-542 Cave 11Q	Wood	5461	24258	3415	40	-26.92	46.4	1770 - 1640 BC	1880 - 1610 BC
QUM-543 QCC 230	Green wool	3334 5462	17424 24260	1900 1905 **1905**	50 40 **30**	-20.70 -20.39	44.1 44.8	65 - 130 AD	20 - 220 AD
QUM-544 QCC 184	Red wool	3336 5463	17423 24411	1885 1940 **1915**	40 40 **30**	-19.05 -20.39	44.8 46.9	60 - 125 AD	1 - 210 AD
QUM-545 QCC 174 CC III	Charcoal	5464	24261	5230	45	-21.71	69.1	4220 - 3970 BC	4230 - 3960 BC

Table 3.

Sample	Type	KLR	GrA	BP	σ	$\delta^{13}C$	%C	Cal. Within ± 1 std. dev.	Cal. Within ± 2 std. dev.
QUM-546 QCC 174, Tr III	Charred wood	5465	24265	5845	45	-9.22	42.0	4790 - 4610 BC	4830 - 4580 BC
QUM-508 D057	Linen	3322	17632	2030	80	-23,80	4.9	160 BC - 60 AD	360 BC - 140 AD
QUM-509 D052	Linen	3323	17405	2055	40	-25,35	40.5	160 BC - 1 AD	180 BC - 30 AD
QUM-515 D024b, 11Q	Wood	3327	17412	1105	40	-10.62	43.8	890 - 985 AD	820 - 1020 AD
QUM-516 D024c, 11Q	Wood	3328	17413	1125	40	-24.43	47.3	885 - 980 AD	770 - 1020 AD
QUM-518 C060 SPI 23	Linen	3329	17414	1245	40	-23.94	42.3	680 - 860 AD	670 - 880 AD
QUM-520 C062 SPI 25	Linen	3330	17415	1490	40	-24.12	41.7	540 - 620 AD	430 - 650 AD
QUM-521 C063 SPI 26	Linen	3331	17417	1255	40	-24.14	40.6	670 - 810 AD	670 - 880 AD
QUM-524, Tomb 1 B003 Southern cemetery	Linen	3332	17418	1470	40	-24.23	40.6	565 - 635 AD	460 - 660 AD
QUM-527 QCC 230	Textile (wool)	3333	17419	1850	40	-19.65	42.9	120 - 230 AD	60 - 250 AD
QUM-529 SPI	Wood	3335	17421	2060	40	-22.51	44.1	160 BC - 1AD	190 BC - 30 AD
QUM-601 Cave4Q 922	Parchment	3337	17633	2040	80	-21.45	59.9	170 BC - 50 AD	360 BC - 130 AD

In Table 3 the samples are listed that are possibly valid without the confidence associated with the dates in Table 2. None of the dates in Table 3 have been decontaminated (*i.e.* they are all from the first series). Some of them show anomalous $\delta^{13}C$-values, such as wood sample QUM-546 QCC-174, wood sample D024b, linnen sample QUM-524 Tomb 1, and linen sample D057. These anomalous $\delta^{13}C$-values may be caused by contamination, in which case the date cannot be trusted, or it may be caused by natural or laboratory induced fractionation processes, in which case the dates are reliable. We cannot tell the difference.

In Table 4 samples are listed whose radiocarbon dates we know are invalid.

Table 4.

Sample	**Type**	**KLR**	**GrA**	**BP**	**Σ**	**$\delta^{13}C$**	**%C**	**Cal. Within ± 1 std. dev.**	**Cal. Within ± 2 std. dev.**
QUM-539 Cave 8Q D009	Olive pit	3321	17404	2110	40	-21.78	41.9	190 – 50 BC	350 – 30 BC
QUM-542 Cave 11Q	Wood	3326	17409	2375	40	-22.56	43.6	510 – 390 BC	740 – 380 BC

Results

Cave 11 – farthest away from the settlement

Cave 11 is situated ca. 1.5 km to the north of the settlement Khirbet Qumran itself. Six samples were dated from Cave 11, QUM-533 (cotton, Mueller *et al*. 2003), QUM-540 & 541 (linen), QUM-542 (wood), QUM-515 (wood), and QUM-516 (wood). The first four dates are highly trustworthy, thus excluding the date of QUM-542 in the first series. An hypothesis that the dates of the two linen samples are contemporary will be accepted, and the average radiocarbon date will be 2031 ± 24 BP, which calibrates to 91 calBC – 24 calAD at ± 1 standard deviation, and 165 calBC – 53 calAD at ± 2 standard deviations. If the two samples are not considered contemporary, they span the calibrated age interval from 160 calBC to 25 calAD (at ± 1 standard deviation). Either way their dates are consistent with the known habitation at Khirbet Qumran.

The wood sample, QUM-542, is much older, 1770-1640 calBC at ± 1 standard deviation. Two possible interpretations can be applied to this date. One is that the sample reflects human activity in Cave 11 some 3700 years ago. The other is that old wood found in the desert was

used for some purpose in some later period. Such re-use of wood, being an important resource, is known to have taken place at numerous locations worldwide. Normally the limit of such re-use is the time of decomposition of the wood, which in desert environments can be quite long. Either interpretation can be supported by our data.

The cotton sample QUM-533 (identical to QUM-513 from the first series) shows a medieval age of 890-975 calAD at ± 1 standard deviation.

The last two dates from Cave 11 are the possibly trustworthy dates of wood from the first run, QUM-515 and QUM-516. QUM-515 showed a highly anomalous δ^{13}C-value, whereas QUM-516 exhibited a δ^{13}C-value within the expected range. However, both dates are almost simultaneous, dating to 890-985 calAD and 885-980 calAD at ± 1 standard deviation, both in accordance with the date of the cotton sample QUM-533.

Cave 4 – very near the settlement

Cave 4 is situated very near Khirbet Qumran – a stone's throw away just opposite the gorge. Three samples from Cave 4 have been dated. One sample of parchment was dated, QUM-601, 922. Even though we are acutely aware that contamination with castor oil or British Museum Leather Dressing might be present on samples of Dead Sea Scrolls (see Rasmussen *et al.* 2001), we did not initially consider it necessary to decontaminate this particular sample prior to AAA pretreatment, as it was uninscribed. The sample was, however, not included in the second series, and therefore, like most previous radiocarbon datings of Dead Sea texts done so far, is not known for certain whether it was indeed free of contaminants. However, judging from its δ^{13}C-value (-21.45 ‰ VPDB, KLR-3337, GrA-17633) which is quite normal, no contamination is suspected. The calibrated date became 170 calBC - 50 calAD at ± 1 standard deviation, which is consistent with the radiocarbon datings of other Qumran cave texts and habitation at Qumran.

Secondly, a sample of linen used as a scroll jar wrapper between the jar and the lid has been dated – QUM-501 in the first series and QUM-534 in the second series. The two dates were in statistical agreement, and are thus highly trustworthy. The calibrated date at ± 1 standard deviation was 45 calBC - 25 calAD.

The third sample, QUM-509 consisting of linen, was only dated in the first series and can therefore only be considered possibly trustworthy. It calibrates to 160 calBC - 1 calAD at ± 1 standard deviation.

All three samples dated from Cave 4 are in excellent accord with each other and can be regarded as contemporaneous.

Cave 8 – on the premises of the Qumran settlement

Cave 8 is situated right below Khirbet Qumran itself. Four samples have been dated from Qumran Cave 8, QUM-536,-537,-538,-539, the first three being linen samples and the last an olive pit. The dates fall in succession, almost like pearls on a string: 350 - 90 calBC, 170 - 50 calBC, 90 calBC – 50 calAD, and 50 – 210 calAD, all for ± 1 standard deviation. All four dates are highly trustworthy. The dates are compatible with the known habitations of Qumran.

Khirbet Qumran itself

Two samples have been dated from the settlement itself. One sample from locus 96 at Khirbet Qumran, QUM-535, KhQ-3650, consisted of charred linen. The date, which is highly trustworthy, comes out to 20 calBC – 80 calAD at ± 1 standard deviation, and 50 calBC – 130 calAD at ± 2 standard deviations. This is in very good agreement with the known habitation of Qumran. The other sample is from the southern Cemetery.

The Cemetery

An interesting result was obtained from the linen QUM-524 (as shown in PAM 42.791 and in Bélis 2003, 257, Plate IV, 3) from Tomb 1 of the small cemetery south of the Wadi Qumran at the foot of the marl terrace, where there were some 30 graves of varying orientations (de Vaux 1973, 58). Tomb 1 is oriented east-west. De Vaux recorded that the pit of this grave was narrow and deep, but there was no covering or loculus, unlike most other Qumran graves. The body lay on its left side, with the head to the west, the face turned to the north (de Vaux 1994, 352). It contained the remains of an adult female and 30 beads (KhQ 2670) found close to the feet, and either two earrings or an earring and ring (KhQ2671 and KhQ 3651; see Clamer 2003, 171-2). The other three opened tombs of this cemetery contained the remains of children. While the date for QUM-524 B003 (KhQ 3649) was not based on a decontaminated sample, the result of 565-635 AD at ± 1 standard deviation may well be valid. A Byzantine date coheres with the jewellery typological study made by Christa Clamer, where it was noted that the earrings from Tomb 33 in the southern arm of the main cemetery and Tomb 1 in the southern cemetery as well as a crumbled glass bead from Tomb 32 should be dated to the Late Roman or Early Byzantine periods. Given a sometimes long use of jewellery Clamer suggests that all the burials fell between the 4th and 8th/9th centuries (2003, 175-6). These conclusions, along with the new radiocarbon date, call into question the

proposition made by Joe Zias (2001) that the intrusive Qumran graves should be attributed to relatively modern Bedouin (and see Norton 2003, 118-22).

The dating of the Qumran cemeteries still remains imprecise, but it would appear that Tomb 1 and others of a similar type are still to be included within the parameters of late antiquity, and may best be considered within the Byzantine demography of the region. The random orientations of the burials in the southern cemetery may indicate that precise placement was not of concern to those who buried the bodies, which would rule out Muslim burials, in which the body was positioned east-west with the face turned to the south, to Mecca. In Tomb 1 the face is turned to the north. The possibility then arises that the tombs are in fact Christian, rather than Jewish or Muslim. It is likely that people continued to visit or encamp at Qumran or in its vicinity throughout the Byzantine period. Coins from the 4th century found at Qumran include two from the reign of Theodosius (379-95 AD) in loci 34 and 152, with 6 other coins of the 4th century in loci 7, 68, 88, 91, 96, 119. Two later Byzantine coins were found in loci 42 and 76 (De Vaux, Rohrhirsch and Hofmeir 1996, 127-8). Note also the three linen dates of the "SPI lot" of uncertain provenance discussed elsewhere in this study, dating 5^{th}-7^{th} centuries AD.

Caves in the vicinity were inhabited at certain times by anchorites (cf. Egeria, *Itin*. 10.9), such as a cave situated above 'Ain Turaba and near 'Ain el-Ghuweir (Blake 1966, 566). De Vaux noted Byzantine sherds in cave no. 23, which is located just above Qumran near the aqueduct route (DJD III, 23). At Ain Feshkha there was Byzantine period occupation in the north-east corner of the stable (locus 20), probably for just one anchorite. The Judaean wilderness was also home to numerous lauras and monasteries (Hirschfeld 1992). Anchorites, lauras and monasteries of the region are described in *The Spiritual Meadow* (*Pratum Spirituale*) by John Moschus (flourished *ca*. 600).

However, there was also secular occupation. At Khirbet el-Yahoud (=Kh. Mazin), 3 km. south of Ras Feshkha, there is evidence of Byzantine settlement. Sulphur, bitumen and salt were collected from the Dead Sea shore (Piacenza Pilgrim, *Itin.* 10; Adomnan, *De Loc. Sanct.* 2: 17) and the lake was used for transport of local resources, as we see in the depiction of ships on the Dead Sea in the Madaba mosaic map of the 6th century. There were thriving towns around the lake at Jericho, Livias, Zoara and En Gedi. In addition, pilgrims were attracted to the Dead Sea area. The ruins of Sodom and Gomorrah were identified in the 6th century as lying southwest of Jericho (Piacenza Pilgrim, *Itin.* 15).

<u>The Christmas Cave</u>

The dates from the elusive Christmas Cave (marked QCC for Qumran Christmas Cave) fall in three sets. The first set encompass two wool samples, QUM-543, QCC-230 consisting of green wool and QUM-544, QCC-184 of red wool. Both samples have been included in both the first and second series, with almost identical results in the two series, and are thus highly trustworthy radiocarbon dates. The two wood samples are of almost the same age, 1905 ± 30 and 1915 ± 30 BP, which are identical within the uncertainty of the dates, *i.e.* a hypothesis of identical ages will be accepted seen from a statistical point of view. If we assume that the dates are identical, we can calculate a common (average) age of 1910 ± 21 BP, which calibrates to 71-124 calAD at ± 1 standard deviation, and 31-131 calAD at ± 2 standard deviations.

The second set consists of only one sample, QUM-527, QCC-230, which is textile, probably wool judging from our isotopic data. Its date, which is based on a sample that has not been decontaminated, falls between 120-230 calAD at ± 1 standard deviation and 60-250 calAD at ± 2 standard deviations.

These three dates are compatible with Bar-Kochba era activity which is known in other sites and caves near the Dead Sea. As noted previously, the precise location of the Christmas Cave is not now known.

The third set comprises two very old wood samples. One highly trustworthy, QUM-545, QCC-174, CC III, consisting of charcoal, and the other QUM-546, QCC-174, Tr III, which is charred wood that had not been decontaminated. The two samples date between 3960 and 4830 calBC, which is very old by any standard. Whether these samples reflect cultural activity some 6000 years ago or the use of old wood found in the desert cannot be revealed by this study.

The SPI lot

Six samples of the unknown source "SPI" were dated: four samples in the first series and two in the second. Two cotton samples, QUM-531, C075, and QUM-532, C076, came out very young indeed. Both have a calibrated date of 1660-1960 calAD, which within the uncertainty is consistent with a modern pre-atomic bomb date (*i.e.* before 1962).

The third sample, QUM-529, a wood sample, was not decontaminated, and had a slightly off $\delta^{13}C$-value of -22.51 ‰ VPDB (KLR-3335, GrA-17421). This date could, however, be trustworthy. The calibrated date becomes 160 calBC – 1 calAD at ± 1 standard deviation, which is in good agreement with the habitation at Khirbet Qumran.

The last three dates, QUM-518, -520, and -521, all of linen, which were from the first series, all turned out with almost similar dates *ca.* 6th-8th century AD. At ± 1 standard deviation the calibrated dates turned out to be 680-860 calAD (for QUM-518), 540-620 calAD (for QUM-520), and 670-810 calAD (for QUM-521).

Thus the SPI lot is very mixed, consisting of two most likely modern samples, three from the *ca.* 6th-8th century AD, and only one from the 1st century BC.

Four periods of radiocarbon datings

Four periods emerged from the present datings. The first is the expected range from 300 BC to 200 AD. Dates in this range were found in Cave 11, 4, and 8, Khirbet Qumran itself, the Christmas Cave, and the SPI lot.

The second period is very old dates, ranging between 4800 and 400 BC. Such dates were found in the Christmas Cave and a single sample in Cave 11.

The third period is in the range from 500 – 1000 AD, and these samples were located primarily in the SPI lot, one from Cave 11, and the single sample from the cemetery.

The fourth period is modern from dates 1660-1960 AD, and are from the SPI lot.

Linen datings in the caves associated with scroll deposits

Of particular interest are the datings of linen from caves near Qumran which are likely associated with scrolls deposited in those caves. Taylor *et al*. (2005) argued that all of the large quantity of linen found in Cave 1 was associated with deposits of scrolls to that cave. While hypothetically scenarios could be imagined by which linen could end up in scroll-bearing caves near Qumran not associated with scroll deposits, it is highly plausible that all of the linen items dated in the present series from Qumran caves 4, 8, and 11 were associated with scrolls in each of those caves.

As further discussed in Taylor *et al*. (2005), the linen could be associated with scrolls in more than one way. Each scroll likely had its own linen wrapper. But also, in some caves the scrolls were placed in jars and the jars then sealed with linen wrapping and extra linen packed in the jars as stuffing (Crowfoot 1955, 19). Therefore the linen found in scroll-bearing caves near Qumran may have been associated with individual scrolls either prior to or at the time of their deposit in the caves.

As pointed out by Taylor *et al*. (2005) with reference to the early work of Grace Crowfoot on linen found in Cave 1: "Crowfoot notes how 'many of the [linen] cloths show signs of wear and tear, and have several repairs' and 'there are only one or two instances of cloths

whose fringe ends seem to show no signs of fraying caused by use'. The fact that so many of the cloths are cut down from larger pieces also means there may have been a separate period of use for the larger pieces … which may then mean that from the earliest probable radiocarbon date we should add a period of use before the employment of the linen for storing the scrolls in Cave 1."

The first Qumran linen radiocarbon date was Willard F. Libby's famous 1950 dating of Cave 1 linen—the second radiocarbon dating of any item in history. Libby reported this linen had an age of 1917 ± 200 "Before Present" (BP) (Libby 1951; Sellers 1951). Because the need for calibration of radiocarbon age measurements was not known and implemented until over a decade later, this was straightforwardly, though slightly erroneously, reported at the time as an age estimate for the Qumran Cave 1 linen of 33 AD ± 200 years, at one standard deviation. After calibration by today's standards, Libby's Cave 1 linen of 1950 dated to between 170 calBC and 340 calAD at one standard deviation (68% confidence), or an even wider 9-1/2 century range, between 400 calBC and 550 calAD, at two standard deviations (95% confidence). It can be seen that although the Libby radiocarbon date was compatible with human activity in Cave 1 contemporary with Qumran habitation of the Second Temple era, in itself this radiocarbon date did not prove a Second Temple era dating for the scroll deposits (as opposed to somewhat earlier or later by 1-2 centuries). And the Libby dating was worthless in weighing for or against individual decades or centuries within the time Qumran was inhabited—since the one standard deviation range alone extends to much greater than the entire range of Second Temple period habitation at Qumran. The only practical outcome of the Libby Cave 1 linen date was a rather compelling argument against a medieval dating of the scroll deposits, which effectively ceased to be an issue thereafter.

Only in 1994, when a series of radiocarbon datings were carried out on Dead Sea items at the University of Arizona in Tucson, was more useful radiocarbon information obtained on Qumran cave linen. A linen scroll wrapper from Qumran Cave 4 was dated at this time by Accelerator Mass Spectrometry (AMS). For the first time a high-precision radiocarbon date was obtained on such linen. This particular Cave 4 linen wrapper was attached to a leather thong of the type used to wrap scrolls (Jull et al. 1995, 16). This linen measured a radiocarbon age of BP 2069 ± 40, which after calibration by today's standards means between 170 and 40 calBC at one standard deviation, or between 200 calBC and 20 calAD at two standard deviations.

It took another decade for a second Qumran cave linen wrapper to be dated by high precision AMS. A sample from a linen wrapping from Qumran Cave 1 was obtained in 2001

by a coauthor of the present article (Taylor) from the Palestine Exploration Fund, London (Taylor *et al*. 2005, 6). This Cave 1 linen gave a radiocarbon age of BP 1984 ± 28, which after calibration is between 40 calBC and 55 calAD at one standard deviation, or between 50 calBC and 80 calAD at two standard deviations.

To these two high-precision radiocarbon datings of Qumran cave linen done up to 2005 the present series adds either six or eight more, depending on whether the two "possibly trustworthy" AMS datings of cave linen in the present study are included. However it should be noted that by the criteria used in the present study, the 1994 Tucson AMS linen dating would also be classified as "possibly trustworthy", as well as most of the radiocarbon datings of texts from the Qumran caves that have been done so far. The 2005 AMS linen dating obtained by Taylor did involve decontamination prior to the AAA pretreatment, however, and is "highly trustworthy". The total database therefore now consists of seven "highly trustworthy", or ten if the "possibly trustworthy" dates are included, high-precision AMS dates on linen from the Qumran caves, with each of these linen items apparently reflecting an association with scrolls deposited in those caves.

Even though still further radiocarbon datings of linen from the caves would give better information, some preliminary observations can be made. A first observation concerns the difference between the dating of the charred linen from Qumran's locus 96, and the datings of the linen from the caves surrounding Qumran.

Unlike the linen in the caves, there is no known basis for identifying the locus 96 linen as associated with scrolls. Nevertheless, the dating of the locus 96 linen when compared with that of the linen of the scroll-bearing caves is of chronological interest.

As noted earlier, the radiocarbon dating of the Qumran locus 96 charred linen was BP 1965 ± 40, which after calibration is between 20 calBC and 80 calAD at one standard deviation. The cause of the charring of the linen is not known. It could be from the fire at the site at the time of the First Revolt, or it could be from an earlier fire, or it could simply have blown into the open area of locus 96 from a cooking fire.

Seven or ten (depending on how counted) high-precision AMS datings of Qumran cave linen in every case gave radiocarbon dates that appear older than the age of the charred linen of locus 96. To see how striking this is, consider the data in Table 5, with particular focus on the pattern of the lab BP age measurements.

Ever since de Vaux's first excavation of Qumran in 1951, it has been assumed in Qumran scholarly discussions that the text deposits in the caves at Qumran either occurred or ended at the time of the First Jewish Revolt, immediately prior to a fire at Qumran of c. 68 AD. In the

introduction to the first volume of the Oxford University Press flagship series *Discoveries in the Judean Desert* published in 1955, the director of antiquities of Jordan, G. Lankester Harding, reported without equivocation, "Excavation of the settlement at Khirbet Qumran has established beyond doubt that all of the material was deposited in these caves in the late first century A.D." (Harding 1955, 4). Some Qumran scholars later allowed that some texts could have been deposited earlier, but without questioning that the text deposits continued through the 1st century AD and ended at the time of the First Revolt. This conventional schematic dating of the Qumran text deposits as occurring as late as the 1st century AD was challenged by Doudna in a series of studies as lacking secure evidence on archaeological, palaeographic, or radiocarbon grounds (Doudna 1998, 1999, 2001, 2004, 2006). For the first time since the excavation of Qumran the question was raised: whether any scroll deposits in the caves of Qumran can be known to have occurred as late as the 1st century AD, as distinguished from all being 1st century BC.

Table 5.

	Uncalibrated lab BP age measurement	**Calibrated conversion to calendar years at one standard deviation (68% confidence)**
From buildings of Qumran (AMS), current study		
locus 96 charred linen—*highly trustworthy*	1965 ± 40	20 BC – 80 AD
From caves near Qumran believed associated with scroll deposits (AMS)		
Previous		
Cave 4 (Jull et al. 1995)—*possibly trustworthy*	2069 ± 40	170 – 40 BC
Cave 1 (Taylor et al. 2005)—*highly trustworthy*	1984 ± 28	40 BC – 55 AD
Current study, highly trustworthy		
Cave 4, QUM-534	2010 ± 30	45 BC – 25 AD
Cave 8, QUM-536	2135 ± 40	350 – 90 BC
Cave 8, QUM-537	2020 ± 40	90 BC – 50 AD
Cave 8, QUM-539	2090 ± 35	170 – 50 BC
Cave 11, QUM-540	2060 ± 40	160 – 1 BC
Cave 11, QUM-541	2015 ± 30	50 BC – 25 AD
Current study, possibly trustworthy		
Cave 1(?), QUM-508	2030 ± 80	160 BC – 60 AD
Cave 4, QUM-509	2055 ± 40	160 – 1 BC

While any individual radiocarbon dating in Table 5 would be indecisive, considered in aggregate the pattern is interesting: seven out of seven (if the three "possibly trustworthy" AMS datings are excluded), or ten out of ten (if the three "possibly trustworthy" AMS datings are included) Qumran cave linen radiocarbon datings measured older than the date of the charred linen of Qumran locus 96. This is what would be anticipated on the hypothesis that the cave scroll deposits occurred earlier than the time of the First Revolt. But it is also what we would expect if the linen in the caves had a long use prior to its employment in the caves. There is no claim here that these radiocarbon dates prove the hypothesis correct that the Qumran cave text deposits date to the 1st century BC, earlier than commonly supposed. But we note that the data above are compatible with such an hypothesis. What we do not see is the radiocarbon date of the locus 96 linen at Qumran measuring more or less equivalent in date with many of the linen items found in the caves.

Of course there are many explanations for why cave linen samples could have radiocarbon dates c. 1st century BC without meaning scrolls were deposited in the caves 1st century BC. The radiocarbon dating of the linen establishes only *terminus a quo* information for the dating of scroll deposits. Nevertheless the present AMS datings on the cave linen leave the question of the dating of the scroll deposits open. Many, perhaps all, of the linen items associated with scroll deposits in the caves which have been radiocarbon dated appear to reflect a period earlier than that of the locus 96 linen. In light of these data, we believe both the "late dating" of scroll deposits to the 1st century AD time ending at the time of the First Revolt traditionally held by Qumran archaeologists and text scholars, and the alternatively proposed "early dating" of the Qumran cave scroll deposits as an exclusively 1st century BC phenomenon, merit closer study, to see whether either of these hypotheses can be falsified or shown correct.

Implications for Past and Future Radiocarbon Datings of Qumran Materials

Above all, our results show the importance of the cleaning process in the preparation of samples for obtaining trustworthy radiocarbon dates. This may entail reviewing previously published radiocarbon dates on similar items from Qumran and the surrounding caves in light of the importance of the cleaning process.

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NON-DESTRUCTIVE STUDY OF QUMRAN POTTERY

Valentin Vladimirov

Dept. of Mineralogy, Petrology & Economic Geology, Sofia University St. Kl. Ohridski, Sofia, Bulgaria
E-mail: valentin@gea.uni-sofia.bg

Abstract

A non-destructive study of Qumran pottery related to Dead Sea Scrolls jars of ~2000 years old is presented here. In the process of museum objects conservation is very important to be studied non-destructively their physical properties. From one hand these are pore – filtration parameters, which are so important for the defining of conservation way and processes. From other hand it is very useful to determine elastic properties before and after conservation and restoration with aim to define their quality. Qumran scroll jars were studied non-destructively with petrophysical methods. By free water saturation and determination of ultrasonic waves velocities more than 15 physical parameters were obtained: effective porosity; conditional momentary saturation - corresponds to liquid permeability; quantity of large, medium, small pores, saturation constant (corresponds to exponential part of the saturation and it is independent of total porosity); density; ultrasonic waves velocities; Poisson's ratio; Young's modulus; Shear modulus; Volume deformation coefficient; Acoustic impedance; Debye temperature etc. Presented method could be used also to define if the observed part belongs to investigated object or not. It also possible to received important information for it origin and provenance. Data analysis of physical properties of investigated Qumran pottery shows strong similarity between first and second samples which could be evident for the same origin. Similarity between third and forth samples is not so strong but also could show the same origin.

Keywords: physic-mechanical properties, museum objects, non-destructive, petrophysic, ceramic, Dead Sea Scrolls jars, Qumran, pottery, conservation, restoration, origin.

Introduction

Much of the religious and cultural heritage of the Western world is derived from events which occurred in Qumran (Gunneweg 2000). A cache of manuscripts dated to 300 BC-70 AD, which were found there have become one of the most important literary finds of the 20th century. These manuscripts, numbering over 1000, known today as the Dead Sea Scrolls, have over the last 55 years shed light on the origins of Judaism and Christianity as well as providing insight into the life style of the inhabitants of the sect called the Essenes who reportedly wrote them. This sect, along with the Pharisees and Sadducees, played an important part in the new movement known today as Christianity.

The Dead Sea Scrolls have been put, for safety reason, in ceramic vessels – jars. Therefore they have the same history. The ceramic jars are much more resistant, as material and better preserved than the scrolls.

Most of them nowadays could be found just broken. Their parts are dispersed and mixed which created a lot of problems. This fact and generally makes a petrophysic study very appropriate. It is necessary for the purposes of conservation, reconstruction, their origin, provenance, etc.

Our contribution to the Qumran problems could be mainly in the field of the Nnn-destructive (ND) physic-mechanical properties measurements of the ceramic vessels – jars.

The study is a part of more widespread non-destructive ceramic samples evaluation, with prospective aim to create museum objects physical properties database, for the needs of archaeology, museum sciences, conservation, origin, provenance, etc.

Some of these properties are well known in a qualitative sense, but modern research needs their quantitative values, which are rather scared in the scientific literature (Vladimirov and Petkova 2003, Vladimirov 2005).

Establishment of non-destructive museum objects physical properties database will be very appropriate and completely new and original.

Methodology and materials

The non-destructive physic-mechanical (petrophysical) investigation can be performed in the Ore-Petrophysical lab of the Sofia University St. Kliment Ohridski, Department of Mineralogy, Petrology and Economic Geology, and in close collaboration with the Laboratory of Mechanics, Diagnostics and Non-destructive Techniques of Solids, which is part of the Institute of Mechanics of the Bulgarian Academy of Science.

Our experience of more than 20 years in rocks non-destructive investigation is significant. It is important because they are heterogeneous media, very difficult for studding, with just approximately known formation conditions. Thousands of rock samples are physically investigated such as follows: volcanic (tuffs, tuff's sandstones, tuff breccias, volcanic breccias, riolites, latites, latite breccias, andesites, andesitobasalts, dolerites, basalts, trachybasalts) and plutonic (monzonites, syenites, gabbros, gabbro-porphyrys, monzogabbros), sediments (sandstones, limestones), metamorphic (amphibolites, marbles, gneisses, skarns) and many others. We have also experience in studying building ceramics, metals, synthetically materials (crystals, ceramics), etc.

The methodological approach is according to Starostin (1979) and involved two groups of experiments: measurements of the free water saturation and determination of ultrasonic wave velocities (Vladimirov 1990).

The quantity of water absorbed in the sample until saturation was reached, was measured in the turbulent and laminar flow of the liquid, and the absorbed fraction was recorded as a function of time. Processing the measured data, allows a number of physical parameters to be determined: Effective porosity P_{ef} is percentage of the total volume of the rock that consists of interconnecting voids. Conditional momentary saturation A is saturation in the first twenty minutes and in fact corresponds to the liquid permeability. The fractions of pore sizes are evaluated and distributed into three groups: The fraction P_1 contains pores larger than 10^{-2} mm. Medium sized pores P_2, spread between 10^{-2} and 10^{-4} mm. The fraction P_3 of small pores extends below 10^{-4} mm. The saturation constant B describes the exponential tail of the saturation curve, i.e. how fast the saturation is reached. The saturation constant appears independent of the total porosity. Weighting in water also provides the stone density ρ.

By ultrasonic wave velocities measuring of both push (longitudinal) and shear (transversal) waves (V_p and V_s, respectively), is possible to extract important physical (mainly elastic) parameters: The Poisson parameter μ is the ratio between the lateral and the longitudinal strain for the body exposed to the longitudinal stress. Young's modulus E and the

shear modulus G measure deformation of the elastic body exposed to the longitudinal and tangential stress, respectively. The volume deformation coefficient K describes the volume change of the body exposed to an increased pressure. Acoustic impedance Z is the ratio between the acoustic wave pressure and the variation of the instantaneous velocity of the material elementary particles; it is measured in units of ommom (hPa s, sometimes $g/cm^2.s$). The Debye temperature θ is related to the cut-off frequency of acoustic phonon modes; larger Debye frequency indicates greater structure stability and stronger connections between individual constituent elements etc.

Results and discussion

As a first attempt, four ceramic parts of Dead Sea Scrolls jars (see Figures 1 and 2) were studied and the results of physico-mechanical investigation are presented to Table 1.

Figure 1. Four storage jar shards found at Qumran. From left up to right down samples 1 through 4. The left up sample is probably a part of a scroll jar. Outer side of the jars is covered with a thin matte hard slip.

Figure 2. Same storage jars as in Figure 1, but this time the inside, without a slip.

The values for the first and second samples of effective porosity, conditional momentary saturation, the pore space structure, density, ultrasonic velocities of longitudinal and transversal waves and their ratio, the Poisson parameter, Young's modulus and the shear modulus and the Debye temperature are almost identical. This strong similarity between first and second samples could be evident for the same origin. Not so strong but significant similarity between third and forth samples also could be evident for the same origin.

These data could be also used to define if the observed part belongs to investigated object or not. The strong but significant similarity between first and second samples, and third and forth samples show that they represent different vessels – jars. The effective porosity varies between 12 and 25 % of total sample volume and significant quantities of large pores characterized them as very favorable for the conservation and restoration.

Table 1. Physical properties of Qumran scroll jars samples

Physical characteristics (Dimension)	**1st sample**	**2nd sample**	**3rd sample**	**4th sample**
Pef - effective porosity (%)	22.14	25.59	12.66	14.06
A - conditional momentary saturation (%)	5.03	4.61	3.89	5.04
P_1 - quantity of large (>10^{-2} mm), pores (%)	23	18	31	36
P_2 - quantity of medium (10^{-2}-10^{-4}mm) pores (%)	32	34	19	40
P_3 - quantity of small (<10^{-4}mm) pores (%)	46	48	50	24
B - saturation constant (h^{-1})	0.03	0.05	0.03	0.07
ρ - density (t/m^3)	1.80	1.83	1.98	1.90
Vp - push waves velocities (m/s)	3403	3443	3392	3435
Vs - shear waves velocities (m/s)	2072	2077	2165	2120
Vp/Vs - push/shear waves velocities ratio	1.642	1.657	1.567	1.62
μ - Poisson's ratio	0.21	0.21	0.16	0.19
E - Young's modulus (x10GPa)	1.82	1.88	2.10	2.00
G - Shear modulus (x10GPa)	0.76	0.78	0.91	0.84
K - Volume deformation coefficient (x10GPa)	1.03	1.10	1.02	1.08
Z - Acoustic impedance (ommom)	6.11	6.32	6.71	6.52
θ - Debye temperature (K)	250	253	269	261

Conclusions

Data analysis of physical properties of investigated Qumran pottery shows strong similarity between first and second samples which could be evident for the same origin.

Similarity between third and forth samples is not so strong but also could come from the same origin.

The presented method could be used to define if the observed part belongs to investigated object or not. In this connection first and second samples, and also third and forth samples show that they represent different vessels.

They are very favorable for the conservation and restoration.

The aim of the study is to see how this method could work and help to Qumran case. It is obvious, that this approach could be very useful and effective.

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ARCHAEOLOGICAL GLASS FROM KHIRBET QUMRAN: AN ANALYTICAL APPROACH

Helena Wouters

Royal Institute for Cultural Heritage, Laboratories, Brussels, Belgium
E-mail: leen.wouters@kikirpa.be

Abstract

Two complementary X-ray emission techniques (SEM-EDX and μSR-XRF) were applied to fragments of glassware explored in Qumran to determine the major/minor and trace composition. Bulk analysis of the unaffected regions of the glass showed that all glass fragments are related to the low Mg / low K soda-lime-silica glass type what indicate the Roman/Byzantine glass. The use of Natron as alkali source and Belus-type sand to produce the glass could be established. In order to elucidate the major variations in the set of obtained compositional data, the multivariate statistical technique of Hierarchical Cluster Analysis was performed. The resulted dendrograms show no straightforward correlation between the substructure and the object typology but distinct groups, especially regarding to the antimony content, could be revealed. So either the glass was made locally by using different but closely related primary batches of bulk glass or it was ready-made imported glass of different kind.

Keywords: Glass, Roman, Qumran, Dead Sea, Composition, Production, SEM-EDX analyses, μSR-XRF, Archaeometry

Introduction

The archaeological exploration of the Khirbet Qumrân settlement, on the West bank of the Dead Sea, started almost half a century ago. The first excavations in the Qumrân "khirbeh" (i.e. "the Ruin") took place in November-December 1951 by a small team lead by G. Lankaster Harding for the Department of Antiquities of Jordan and Father Roland Guérin de Vaux for the "Ecole Biblique et Archéologique Française de Jérusalem" (EBAF), with the technical assistance of the Palestine Archaeological Museum of Jerusalem. Five other campaigns followed regularly between 1953 and 1958. Beyond the discoveries are more than hundred glass fragments, most of them were excavated at the *loci* of the central quadrangle of the site, next to the tower as shown in Figure 1.

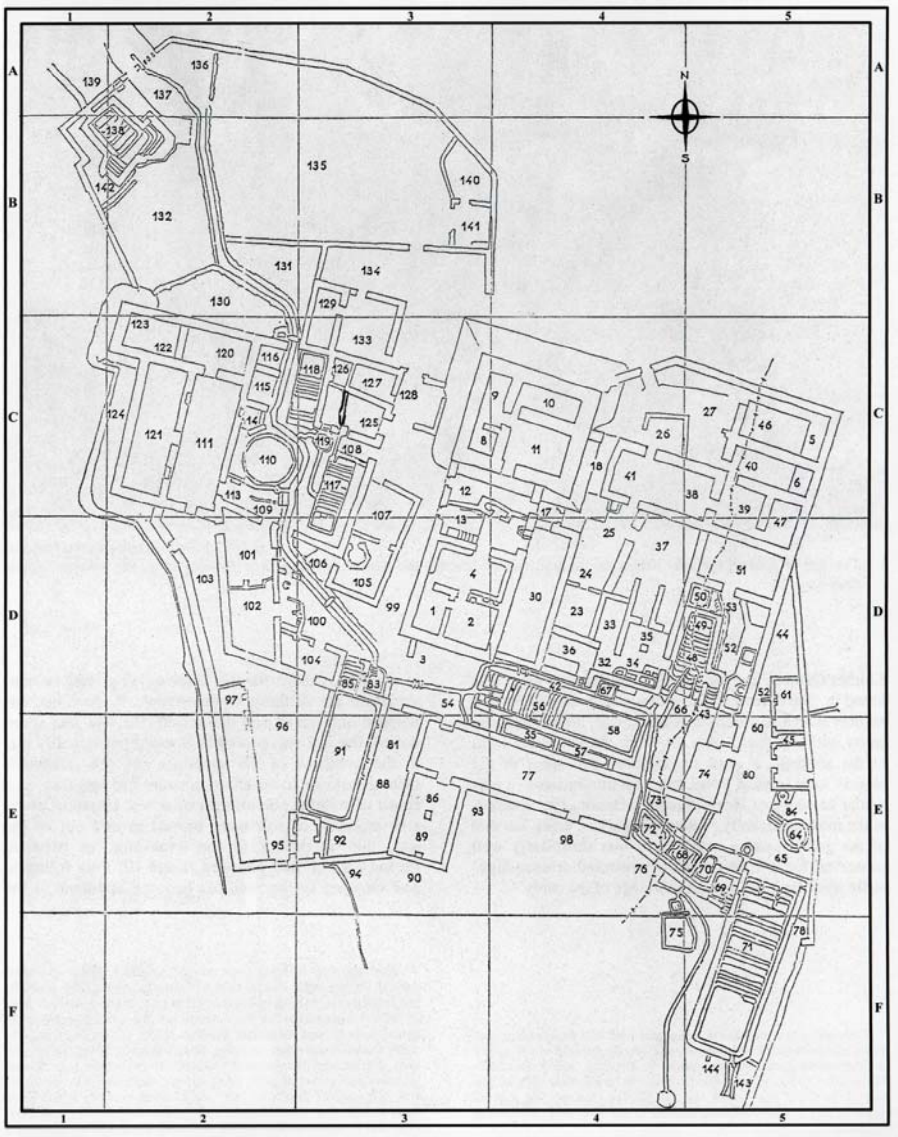

Figure 1. Plan of the Khirbet Qumran settlement locating the loci (after De Vaux, 1973, pl.XXXIX)

Proposed by De Vaux (1973) the chronology of the settlement started back to the end of the 2nd century BC and after many reoccupation periods abandoned in 73 AD with the fall of Masada.

The study of the glassware from Qumran is likely to provide interesting results in two fields of research: one is the history of the site itself, as described by Donceel (1990, 1994 and 1996) and another is the evolution of glass-making techniques. The fact that the glass artefacts originated from Syria (in the broad sense of the term) and from the first centuries before and mostly after J.C. justified an in-depth study of their material. It is clear that here, on the shores of the Dead Sea, one is fairly close to the areas of glass fabrication whose products found their way throughout the Roman Empire, at precisely that period in history which is characterised by the introduction of innovative techniques which, most probably, were developed in the north of Egypt or in the Syro-Phoenician coastal area (Forbes 1966).

The analysis attempted to determine both the chemical composition of the glasses and their degradation products. Within this article, only the composition will be discussed, while the morphology and degradation of the glass artefacts take part of other publications as Aerts (1998) and Wouters *et al.* (2002). The number of reports, found in the literature, on the chemical analysis of glass from the Roman/Byzantine period, excavated at various locations in Europe, describe however, in most cases only a few objects analysed per site. In the present study, an extensive series of objects was available. This was a unique opportunity to evaluate to what extent detailed investigations on the composition of the various glass objects could reveal information on the provenance and history of the objects and/or the excavation site.

The glass artefacts

In November 1988, R. Donceel brought about 150 glass fragments, originating from the Khirbet Qumrân settlement, to the Royal Institute for Cultural Heritage (IRPA-KIK) for restoration and examination. The uncovered glass pieces were marked, with Chinese ink and stored in a box in the basement of the Rockefeller Archaeological Museum. Almost all the glasses are in a state of advanced decomposition and are, as a consequence extremely fragile with partial or total loss of transparency. Fontaine (1993,1994) undertook the sorting, cleaning and consolidating of the fragments as a first step in the project. Almost ninety different vessels were identified: unfortunately most were fragmentary. Some fragments were regrouped and glued together as demonstrated in Figure 2 for one of the greatest bottles

(inventory number IRPA 22) of the recovered glassware. Figures 3a till 3j show all the objects as obtained after conservation.

Figure 2. Fragments of bottle N° IRPA 22: (left and middle) before conservation, (right) after conservation. (Height = 21.6 cm)

Figure 3. Glass from Khirbet Qumrâm: (a) nos. IRPA 1-6 ; (b) nos. IRPA 7-13 ; (c) nos. IRPA 14-20 ; (d) nos. IRPA 21 and 23-25 ; (e) nos. IRPA 26-31 ; (f) nos. IRPA 32-39 ; (g) nos. IRPA 40-48 ; (h) nos. IRPA 49-56 ; (i) nos. IRPA 57-64 ; (j) nos. IRPA 65-71 , 73 , 74 and 76.

Parallel to the restoration, a descriptive computerized database was established[1]. Whilst of unpacking of the splinters, each presumed vessel (sometimes a whole set of fragments grouped together in the same bag) received an inventory number (no. IRPA x). However, in the course of restoration, it become clear that some splinters had been erroneously grouped, necessitating further sub-numbering (no. IRPA x, 1; no. IRPA x, 2; ...). Each vessel was classified individually using eighteen fields including shape (with a proposed identification when the form is not clear), dimensions, manufacturing techniques, material condition, conservation treatment and references to IRPA-KIK negatives. Of all eighty-nine identified objects, only four recipients presented a complete profile after restoration. The database proved to be a useful reference tool during the study. Before setting out the whole study, it is very important to remark that in most cases the determination of the shape of an object is extrapolated from a single preserved fragment (a base, a fragment of the body, a neck, a handle or a lip). Table 1 summarize the first sorts of the vessels into eight large categories of identified shapes (goblet, ointment vessel, cup, bottle, flask, biconical recipient and chalice on foot) and a ninth category that regroups the analyses of the fragments unconnected with any certainty to any particular aforementioned category.

Table 1. Typological classification of the glasses presented in the card-index (Aerts, 1998)

TYPE	SUBTYPE	NUMBERS
Ointment vessels		4, 9, 11, 13, 15, 16, 26, 28, 31, 37, 36, 38, 41, 42, 45, 47, 51, 56
Goblets	With flat base Ribbed With widened lip Moulded With fluted body Decorated with glass strings Incised With vertical flattening With band at the top	6, 20, 29, 40 3, 49 10, 21b, 23b, 44, 54 12, 60, 65, 66, 73, 74 14 39 43, 68 75 21
Cups	Ribbed with flat base Moulded ribbed With decoration (?) Ribbed with rounded base (?)	2, 18, 30, 49b, 55 35 8, 48, 63, 76 7 17, 53, 69
Flasks		27, 32, 50, 62
Biconical recipients		5, 23, 34
Bottles		19, 22, 25, 27b, 33, 59, 61
Chalice on foot		24
Indeterminable shapes		52, 70, 71, 72, 77

[1] See dossier IRPA 2L/123 - 88/4139 where some technological observations, as probable manufacturing processes, decoration technique, difference in shaping of the lips and the bases.

Subgroups are introduced in the classification of the goblets and the cups. However, the differentiation is sometimes based on scanty information and/or the selection criteria are perhaps not always exclusive. For instance, for the goblets the proposed subgroup is sometimes determined by a type of foot or lip, a decoration (e.g. ribbed goblets), a shaping and decoration technique (e.g. moulded goblets), and sometimes only on one decorative style (e.g. incised goblets or goblets decorated with a glass-string).

Analytical methods and sample preparation

A selection of micro-analytical techniques was made based on the availability of the instruments and their respective requirements. In addition, the application was proposed by the author and implemented as part of the Ph.D. thesis of Ann Aerts (1998). Out of the great amount of glass artefacts 75 samples were analysed using conventional Electron probe X-ray micro-analysis (EPXMA) (Reed 1993) to determine the major and minor elements. Trace elements of the glass fragments were identified using Microscopic Synchrotron Radiation Induced X-ray Fluorescence Analysis (µ-SR-XRF) (Janssens *et al.* 1996). µSR-XRF was applied only to a selected set of 64 Qumrân glass samples. Sometimes the glass was too badly altered that an adequate analyses was not possible and furthermore for some fragments no sampling was done to avoid critical damaging, as was the case for the only complete ointment vessel (Figure 4).

Figure 4. Only entire ointment vessel (height = 10 cm)

Samples of 1-5 mm^2 in size were taken from each of the glass fragments. These glass samples were mounted into a butyl-methylacrylate resin block and polished down with diamond paste to 1 µm grain size to obtain a cross-section perpendicular to the corroded glass surface. For the EPXMA measurements, the resin blocks were carbon coated to avoid charging; for the µSR-XRF analyses, no such additional preparation was necessary.

EPXMA or SEM-EDX measurements were performed on a JEOL JSM 6300 Scanning Electron Microscope equipped with a PGT energy-dispersive X-ray detector. This type of measurement involves the irradiation of the glass with an energetic electron beam that ionises some of the atoms in the material, causing the latter to emit characteristic X-rays. The spectrum of X-rays emitted by the sample permits qualitative and quantitative elemental analysis of the irradiated material. In this study, an electron beam current of 1nA and a voltage of 15 kV were employed; a low magnification setting of the instrument (300X) and a limited analysis time (200 s) were used to ensure that no significant diffusion of Na occurred during the irradiation. The X-ray intensities obtained were quantified by means of a standardless ZAF scheme (correction factors for atomic number, Z, absorption A and fluorescence, F).

µSR-XRF measurements were executed at the NSLS (National Synchrotron Light Source, Brookhaven National Laboratories, Upton, NY, USA) X26A beamline using a 8x8 µm white synchrotron X-ray beam and at the DORIS III (Hasylab, Hamburg, Germany) beamline L-station. For each sample, a spectrum collection time of 200 to 1000 seconds was used. Quantification of the obtained µSR-XRF spectra was done using a Monte Carlo simulation model (Vincze *et al.* 1995).

Results

In Table 2, the major/minor element composition in weight % (as obtained by EPXMA from 75 samples) and the trace composition in ppm (as obtained by µSR-XRF from 64 samples) are listed. The data pertaining to each sample are organised according to the different typological categories: (a) ointment vessels (18 objects), (b) different types of goblets (23 objects), (c) cups (14 objects), (d) biconical recipients (3 objects), (e) bottles (7 objects), (f) flasks (4 objects), (g) chalice (1 object) and (h) indeterminable shapes (5 objects). The average major/minor composition per category is also indicated, although some outliers

(numbers 31, 32 and 33) are left out from the calculation of the average concentrations for the trace composition. Taking the accuracy of the EPXMA method into account (Wouters 2002), these averages initially appear to be almost identical and only convey the information that all glass samples were of the typical low magnesium/low potassium soda-lime-silica type, in common with most glass from the Roman period (Sayre *et al.* 1961, 1965; Wedephol 1998).

Instead of distributing the samples *a priori* into typological categories, we have found it more useful to keep all data together and to employ the multivariate statistical technique of Hierarchical Cluster Analysis (HCA) to emphasise the structure in the data. The result of HCA is a dendrogram, showing in a graphic form the similarity of the composition of the various Qumrân samples. In Figure 5, the dendrogram obtained on the basis of the major/minor element composition alone (75 samples analysed by EPXMA) is shown. A clear distinction between a large group comprised of 64 objects (group I) and a small group of 11 samples (group II) can be observed.

In the histogram, the typological category corresponding to each of the samples is also indicated. It can be observed that the small group of objects is exclusively composed of the types “O” and “G”, respectively ointment vessels and goblets. In the last category, the “moulded goblet” type is particularly well represented. Although in the dendrogram the large group displays a definite structure and is further divided into sub-groups, no straightforward correlation between this substructure and the object typology can be made.

If also trace element abundances are taken into account (only 64 samples analysed by μSR-XRF), the obtained dendrogram reveals that the situation is in fact more complicated than suggested by just the two groups mentioned. Within the large group of objects (group I), another small subset (group IB, 5 objects) can be distinguished. The remaining objects of the first group I form part of group IA (45 objects). Table 3 gives the average major, minor and trace compositions of the glass objects as obtained by EPXMA as well as by μSR-XRF within the three groups (IA, IB and II). The compositional differences between the glasses of the latter group IB and group IA is mainly due to the antimony, copper, lead and tin concentrations, which are all lower for group IB artefacts. Within all the glasses belonging to group IA, some antimony is found as constituent, while in the objects of group IB no antimony is detected. Next, it can be noticed that also the manganese content in the glass of group IB is significantly lower than for those in group IA and II. Group II artefacts have a lower CaO concentration than glass of groups IA and IB.

Table 2. Composition of different types of objects in the Qumran series (concentration in weight% in top part of each table; in ppm in bottom part)

a) Ointment vessels (18 objects)

Oxides \ Object number	4	9	11	13	15	16	26	28	31	36
Na_2O	16.44	16.89	16.15	16.25	16.07	17.36	16.53	16.55	16.12	17.04
MgO	0.54	0.40	0.36	0.32	0.55	0.01	0.21	0.32	0.10	0.01
Al_2O_3	2.53	2.53	2.52	2.54	2.54	2.13	2.57	2.64	2.49	2.10
SiO_4	68.17	68.98	69.20	69.72	68.63	71.73	69.97	69.36	69.80	71.66
P_2O_5	0.12	0.07	0.06	0.11	0.05	0.01	0.07	0.14	0.08	0.03
SO_3	0.13	0.16	0.15	0.18	0.18	0.26	0.13	0.17	0.14	0.19
Cl	0.68	0.73	0.75	0.79	0.69	1.17	0.78	0.82	0.86	1.01
K_2O	0.92	0.80	0.84	0.82	0.87	0.47	0.88	0.92	0.85	0.60
CaO	9.23	8.33	8.74	8.15	9.34	5.36	7.86	8.19	8.44	5.82
TiO_2	0.07	0.04	0.07	0.05	0.03	0.05	0.03	0.05	0.05	0.04
MnO	0.47	0.42	0.45	0.47	0.45	0.94	0.43	0.40	0.49	1.20
Fe_2O_3	0.57	0.52	0.56	0.55	0.58	0.37	0.52	0.51	0.50	0.35
Cr_2O_3	26	26	29	29	24	34	0	0	0	0
NiO	10	7	8	7	10	11	14	0	0	26
CuO	126	110	146	124	138	8	215	292	2901	552
ZnO	29	24	33	28	33	23	28	37	170	57
Br	3	3	4	7	4	4	9	12	0	36
Rb_2O	11	9	14	12	16	10	16	14	284	15
SrO	571	489	670	614	663	564	616	411	13700	339
Y_2O_3	9	9	13	10	9	6	9	7	304	2
ZrO_2	96	76	106	99	101	71	72	69	1750	62
Mo_2O_3	4	4	3	1	3	3	1	1	57	6
SnO_2	165	94	146	100	138	42	92	158	6600	165
Sb_2O_5	360	269	496	318	371	0	335	221	11300	12
BaO	212	172	310	179	188	160	306	110	19200	64
PbO	113	103	154	152	139	5	77	280	1119	45

Oxides \ Object number	37	38	41	42	45	47	51	56		Mean
Na2O	17.46	16.43	16.62	16.49	15.69	15.70	17.72	16.37		16.55
MgO	0.02	0.14	0.15	0.01	0.01	0.05	0.02	0.13		0.18
Al_2O_3	2.09	2.44	2.52	2.55	2.42	2.34	2.15	2.46		2.42
SiO_4	71.56	70.36	70.05	71.06	72.96	71.43	71.04	69.37		70.29
P_2O_5	0.04	0.07	0.06	0.02	0.01	0.04	0.01	0.14		0.06
SO_3	0.18	0.10	0.09	0.21	0.13	0.23	0.16	0.12		0.16
Cl	1.13	0.73	0.85	1.05	1.13	0.96	1.13	0.81		0.89
K_2O	0.56	0.77	0.83	0.69	0.43	0.67	0.56	0.88		0.75
CaO	5.74	7.90	7.87	7.26	7.02	8.03	6.20	8.81		7.68
TiO_2	0.05	0.07	0.04	0.04	0.01	0.04	0.04	0.05		0.05
MnO	0.82	0.52	0.42	0.19	0.01	0.17	0.65	0.37		0.49
Fe_2O_3	0.36	0.50	0.49	0.37	0.25	0.40	0.34	0.47		0.46
Cr_2O_3	0	0	24	13	11	19	0	0		14
NiO	31	125	7	6	4	6	20	4		17
CuO	124	104	136	6	3	8	67	277		143
ZnO	37	53	24	9	10	18	27	56		31
Br	3	12	4	5	4	13	17	4		8
Rb_2O	13	6	13	12	9	11	6	26		12
SrO	656	183	624	614	511	520	287	1030		551
Y_2O_3	7	1	10	9	5	9	5	13		8
ZrO_2	59	34	96	78	56	63	33	91		74
Mo_2O_3	2	16	3	0	0	1	2	1		3
SnO_2	40	70	100	34	36	55	10	85		90
Sb_2O_5	76	102	497	0	0	1	44	391		205
BaO	187	36	192	198	76	64	70	309		167
PbO	16	181	143	5	6	9	16	143		93

Table 2. Composition of different types of objects in the Qumran series (concentration in weight% in top part of each table; in ppm in bottom part)

b) Goblets (23 objects)

Oxides \ Object number	6	20	29	40	3	49	10	21b	23b	44	54	12
Na_2O	16.67	16.64	17.03	16.52	16.47	16.41	16.52	17.58	16.23	16.50	16.30	17.33
MgO	0.34	0.16	0.27	0.20	0.64	0.13	0.33	0.08	0.22	0.15	0.26	0.01
Al_2O_3	2.55	2.45	2.41	2.56	2.53	2.52	2.54	2.64	2.41	2.53	2.43	2.50
SiO_4	68.53	69.92	69.34	69.80	67.86	69.73	68.59	66.54	69.83	70.24	69.63	71.84
P_2O_5	0.11	0.06	0.12	0.10	0.01	0.02	0.10	0.02	0.08	0.09	0.02	0.03
SO_3	0.15	0.20	0.22	0.12	0.14	0.07	0.16	0.22	0.10	0.09	0.10	0.22
Cl	0.75	0.85	0.83	0.86	0.68	0.83	0.71	0.92	0.86	0.82	0.85	1.23
K_2O	0.86	0.79	0.85	0.85	0.89	0.83	0.93	0.90	0.84	0.85	0.81	0.56
CaO	8.75	7.94	7.88	7.99	9.45	8.50	8.87	8.03	8.44	7.79	8.41	4.94
TiO_2	0.04	0.06	0.05	0.07	0.07	0.05	0.04	0.10	0.05	0.04	0.03	0.04
MnO	0.48	0.37	0.44	0.40	0.48	0.42	0.48	3.89	0.37	0.41	0.39	0.87
Fe_2O_3	0.57	0.45	0.54	0.53	0.63	0.48	0.57	1.19	0.52	0.49	0.52	0.29
Cr_2O_3	26	19	0	0	19	26	26	0	16	26	0	39
NiO	8	7	0	0	8	7	10	0	7	7	0	14
CuO	134	176	437	243	130	149	138	208	181	148	332	10
ZnO	31	28	35	36	30	25	33	40	138	26	22	20
Br	18	6	28	3	5	4	9	0	4	3	2	3
Rb_2O	11	16	17	12	11	11	11	11	10	10	15	12
SrO	553	896	647	566	564	658	599	345	499	479	662	503
Y_2O_3	9	13	13	10	9	10	8	5	6	8	10	6
ZrO_2	89	112	101	65	95	99	83	23	69	68	68	71
Mo_2O_3	9	4	1	1	5	4	4	0	3	0	2	3
SnO_2	12	77	85	132	137	127	96	37	152	146	116	42
Sb_2O_5	294	418	896	619	364	414	233	91	281	182	673	3
BaO	164	226	228	376	190	178	120	754	121	118	351	122
PbO	156	152	152	139	131	108	170	64	118	99	159	9

Oxides \ Object number	60	65	66	73	74	14	39	43	68	75	21	Mean
Na_2O	17.07	17.18	16.91	17.07	16.48	16.50	16.97	17.21	16.45	15.76	16.34	16.70
MgO	0.03	0.02	0.01	0.01	0.02	0.12	0.01	0.03	0.21	0.23	0.17	0.16
Al_2O_3	2.48	2.46	2.80	2.52	3.10	2.57	1.99	2.18	2.46	2.54	2.60	2.51
SiO_4	70.57	72.23	72.35	72.11	72.13	70.07	71.90	71.52	70.28	70.12	70.25	70.32
P_2O_5	0.04	0.02	0.01	0.01	0.05	0.05	0.01	0.06	0.02	0.10	0.08	0.05
SO_3	0.26	0.14	0.05	0.12	0.12	0.19	0.16	0.14	0.06	0.13	0.18	0.14
Cl	1.08	1.24	1.03	1.24	1.06	0.85	1.17	1.07	0.80	0.77	0.84	0.94
K_2O	0.63	0.53	0.60	0.56	0.84	0.81	0.44	0.62	0.79	0.92	0.82	0.76
CaO	7.47	4.97	5.03	4.99	4.93	7.77	6.41	6.18	7.91	8.42	7.79	7.34
TiO_2	0.03	0.03	0.05	0.03	0.09	0.07	0.04	0.02	0.02	0.03	0.03	0.04
MnO	0.01	0.88	0.67	0.99	0.91	0.43	0.65	0.67	0.49	0.43	0.42	0.68
Fe_2O_3	0.32	0.27	0.37	0.34	0.33	0.51	0.28	0.33	0.52	0.57	0.49	0.48
Cr_2O_3	0			9	53	24	0	69		14	0	18
NiO	1			10	14	7	13	6		8	73	10
CuO	321			31	11	163	85	24		131	832	194
ZnO	40			16	23	29	22	33		26	119	38
Br	9			5	4	5	6	23		3	9	7
Rb2O	14			11	17	11	13	13		11	46	14
SrO	421			562	493	548	747	557		496	1860	632
Y_2O_3	4			8	8	6	6	4		8	20	9
ZrO_2	36			68	88	77	56	71		76	193	80
Mo_2O_3	0			4	5	3	3	1		3	0	3
SnO_2	71			51	33	143	82	125		11	226	95
Sb_2O_5	1			70	9	257	1	51		291	1050	309
BaO	133			166	197	115	179	52		183	726	235
PbO	19			50	14	120	6	26		105	406	110

Table 2. Composition of different types of objects in the Qumran series (concentration in weight% in top part of each table; in ppm in bottom part)

c) Cups (14 objects)

Oxides \ Object number	2	18	30	49b	55	35	8	48
Na_2O	16.80	16.57	16.84	16.54	16.56	18.42	16.62	16.37
MgO	0.23	0.23	0.16	0.15	0.21	0.33	0.12	0.18
Al_2O_3	2.51	2.54	2.42	2.51	2.41	2.27	2.53	2.46
SiO_4	70.21	69.53	69.68	70.15	69.91	68.48	68.86	69.83
P_2O_5	0.09	0.08	0.06	0.06	0.10	0.01	0.10	0.08
SO_3	0.16	0.14	0.18	0.08	0.14	0.24	0.18	0.11
Cl	0.91	0.79	0.86	0.88	0.88	0.97	0.78	0.85
K_2O	0.82	0.84	0.78	0.81	0.80	0.67	0.92	0.80
CaO	7.06	8.13	8.05	7.73	7.99	7.93	8.63	8.41
TiO_2	0.03	0.04	0.07	0.07	0.04	0.02	0.07	0.07
MnO	0.44	0.41	0.39	0.43	0.43	0.12	0.48	0.36
Fe_2O_3	0.53	0.58	0.47	0.51	0.50	0.59	0.49	0.50
Cr_2O_3		29	0	0	0	0	26	13
NiO		8	14	4	0	21	10	8
CuO		176	342	319	348	76	93	266
ZnO		26	44	47	37	16	34	36
Br		3	5	9	5	5	12	9
Rb_2O		13	16	15	20	17	14	12
SrO		607	739	698	834	783	647	451
Y_2O_3		9	9	10	11	13	9	6
ZrO_2		94	64	70	88	63	82	57
Mo_2O_3		3	0	3	1	0	4	1
SnO_2		90	61	118	102	15	100	85
Sb_2O_5		402	337	476	792	1	109	108
BaO		190	207	278	406	286	103	53
PbO		165	177	174	212	26	122	108

Oxides \ Object number	63	76	7	53	69	17		Mean
Na_2O	16.48	16.78	17.66	16.49	16.46	16.46		16.64
MgO	0.17	0.15	0.46	0.26	0.36	0.15		0.23
Al_2O_3	2.39	2.55	2.22	2.37	2.51	2.41		2.44
SiO_4	70.34	69.27	69.47	69.49	69.12	69.89		69.59
P_2O_5	0.08	0.01	0.16	0.05	0.16	0.06		0.08
SO_3	0.11	0.14	0.30	0.09	0.10	0.21		0.15
Cl	0.88	0.88	0.92	0.83	0.79	0.86		0.87
K_2O	0.79	0.74	0.97	0.84	0.88	0.79		0.82
CaO	7.86	8.46	6.34	8.66	8.52	8.10		7.99
TiO_2	0.05	0.19	0.06	0.03	0.08	0.04		0.06
MnO	0.40	0.41	0.59	0.39	0.47	0.40		0.40
Fe_2O_3	0.46	0.47	0.61	0.55	0.55	0.48		0.53
Cr_2O_3		14		0		24		11
NiO		7		13		7		9
CuO		180		436		164		240
ZnO		21		47		26		33
Br		6		7		5		7
Rb_2O		16		16		10		13
SrO		791		802		594		694
Y_2O_3		9		10		8		9
ZrO_2		88		80		89		78
Mo_2O_3		4		1		3		2
SnO_2		173		78		70		89
Sb_2O_5		90		553		356		322
BaO		169		266		207		217
PbO		151		228		107		147

Table 2. Composition of different types of objects in the Qumran series (concentration in weight% in top part of each table; in ppm in bottom part)

d) Biconical recipients (3 objects)

Oxides \ Object number	5	23	34	Mean
Na_2O	16.94	16.06	16.31	16.44
MgO	0.19	0.26	0.12	0.19
Al_2O_3	2.45	2.61	2.52	2.53
SiO_4	69.38	69.78	69.80	69.65
P_2O_5	0.08	0.11	0.10	0.10
SO_3	0.17	0.16	0.12	0.15
Cl	0.83	0.80	0.84	0.82
K_2O	0.82	0.86	0.87	0.85
CaO	8.02	8.49	8.36	8.29
TiO_2	0.06	0.07	0.05	0.06
MnO	0.37	0.36	0.47	0.40
Fe_2O_3	0.45	0.53	0.48	0.49
Cr_2O_3	20	0	0	7
NiO	7	11	0	6
CuO	160	270	768	399
ZnO	24	41	69	45
Br	6	7	30	14
Rb_2O	10	15	71	32
SrO	493	611	3090	1400
Y_2O_3	8	9	44	20
ZrO_2	73	65	420	186
Mo_2O_3	4	2	14	7
SnO_2	56	77	1380	504
Sb_2O_5	241	318	905	488
BaO	132	181	946	420
PbO	91	230	607	309

e) Bottles (7 objects)

Oxides \ Object number	19	25	27b	33	61	22	59	Mean
Na_2O	16.40	16.16	16.54	16.42	16.22	16.24	16.33	16.32
MgO	0.14	0.44	0.12	0.27	0.15	0.07	0.11	0.19
Al_2O_3	2.50	2.49	2.52	2.48	2.41	2.46	2.50	2.49
SiO_4	69.15	69.21	70.36	70.08	69.88	70.02	69.93	69.80
P_2O_5	0.14	0.06	0.02	0.11	0.05	0.04	0.11	0.07
SO_3	0.20	0.16	0.07	0.15	0.11	0.19	0.14	0.15
Cl	0.80	0.78	0.83	0.90	0.83	0.85	0.87	0.85
K_2O	0.96	0.81	0.80	0.80	0.84	0.81	0.88	0.84
CaO	8.70	8.86	7.69	7.62	8.34	8.25	8.29	8.25
TiO_2	0.03	0.03	0.04	0.05	0.08	0.06	0.06	0.05
MnO	0.46	0.47	0.47	0.56	0.38	0.43	0.39	0.46
Fe_2O_3	0.45	0.50	0.51	0.54	0.58	0.49	0.46	0.51
Cr_2O_3	26	0		0		0	0	6
NiO	10	0		0		5	18	8
CuO	83	302		879		244	237	217
ZnO	29	41		98		33	46	37
Br	3	1		1		2	3	2
Rb_2O	16	16		52		20	15	17
SrO	658	571		2381		996	632	714
Y_2O_3	10	8		13		16	8	11
ZrO_2	76	57		326		94	50	69
Mo_2O_3	1	2		10		2	2	2
SnO_2	95	221		835		220	106	161
Sb_2O_5	97	441		1481		359	136	258
BaO	97	250		1797		451	155	238
PbO	106	186		371		341	235	217

Table 2. Composition of different types of objects in the Qumran series (concentration in weight% in top part of each table; in ppm in bottom part)

f) Flasks (4 objects)

Oxides \ Object number	27	32	50	62		Mean
Na_2O	16.64	16.35	16.30	15.91		16.30
MgO	0.28	0.28	0.06	0.16		0.20
Al_2O_3	2.61	2.54	2.48	2.47		2.53
SiO_4	69.21	68.61	69.37	70.12		69.33
P_2O_5	0.12	0.15	0.06	0.02		0.09
SO_3	0.17	0.04	0.07	0.05		0.08
Cl	0.79	0.61	0.79	0.76		0.74
K_2O	0.88	1.13	0.84	0.84		0.92
CaO	8.25	9.25	8.97	8.50		8.74
TiO_2	0.06	0.06	0.05	0.04		0.05
MnO	0.42	0.44	0.47	0.46		0.45
Fe_2O_3	0.54	0.55	0.54	0.58		0.55
Cr_2O_3	0	0	29			15
NiO	0	0	10			5
CuO	291	2380	94			191
ZnO	39	10800	31			35
Br	2	0	3			3
Rb_2O	25	0	13			19
SrO	948	2474	700			824
Y_2O_3	15	156	9			12
ZrO_2	102	19600	88			95
Mo_2O_3	1	105	3			3
SnO_2	129	739	189			159
Sb_2O_5	518	49	161			339
BaO	279	377	192			235
PbO	328	267	136			232

g) Chalice (1 object)

Oxides \ Object number	24
Na_2O	16.24
MgO	0.26
Al_2O_3	2.58
SiO_4	70.01
P_2O_5	0.09
SO_3	0.13
Cl	0.76
K_2O	0.82
CaO	8.05
TiO_2	0.06
MnO	0.49
Fe_2O_3	0.54
Cr_2O_3	0
NiO	5
CuO	222
ZnO	42
Br	0
Rb_2O	16
SrO	626
Y_2O_3	9
ZrO_2	69
Mo_2O_3	2
SnO_2	169
Sb_2O_5	447
BaO	333
PbO	13

Table 2. Composition of different types of objects in the Qumran series (concentration in weight% in top part of each table; in ppm in bottom part)

h) Indeterminable shapes (5 objects)

Oxides \ Object number	52	70	71	72	77		Mean
Na_2O	17.09	16.54	15.64	18.20	15.89		16.67
MgO	0.12	0.10	0.43	0.08	0.04		0.15
Al_2O_3	2.57	2.55	2.52	2.54	2.55		2.55
SiO_4	69.38	69.80	68.10	68.38	69.35		69.01
P_2O_5	0.01	0.01	0.12	0.01	0.11		0.05
SO_3	0.14	0.01	0.08	0.30	0.11		0.13
Cl	0.90	0.78	0.65	0.86	0.77		0.79
K_2O	0.72	0.88	1.02	0.82	0.88		0.86
CaO	8.20	8.24	10.27	7.84	9.41		8.79
TiO_2	0.04	0.04	0.05	0.03	0.07		0.05
MnO	0.31	0.46	0.50	0.66	0.32		0.45
Fe_2O_3	0.48	0.54	0.67	0.33	0.51		0.51
Cr_2O_3	0		16	0	13		7
NiO	10		10	22	8		12
CuO	410		144	139	101		198
ZnO	42		30	25	24		30
Br	5		3	4	18		7
Rb_2O	14		12	17	12		14
SrO	676		582	735	548		635
Y_2O_3	11		9	9	8		9
ZrO_2	65		89	55	76		71
Mo_2O_3	2		1	3	4		3
SnO_2	79		100	48	91		80
Sb_2O_5	334		265	203	20		206
BaO	304		159	313	66		211
PbO	282		163	103	71		155

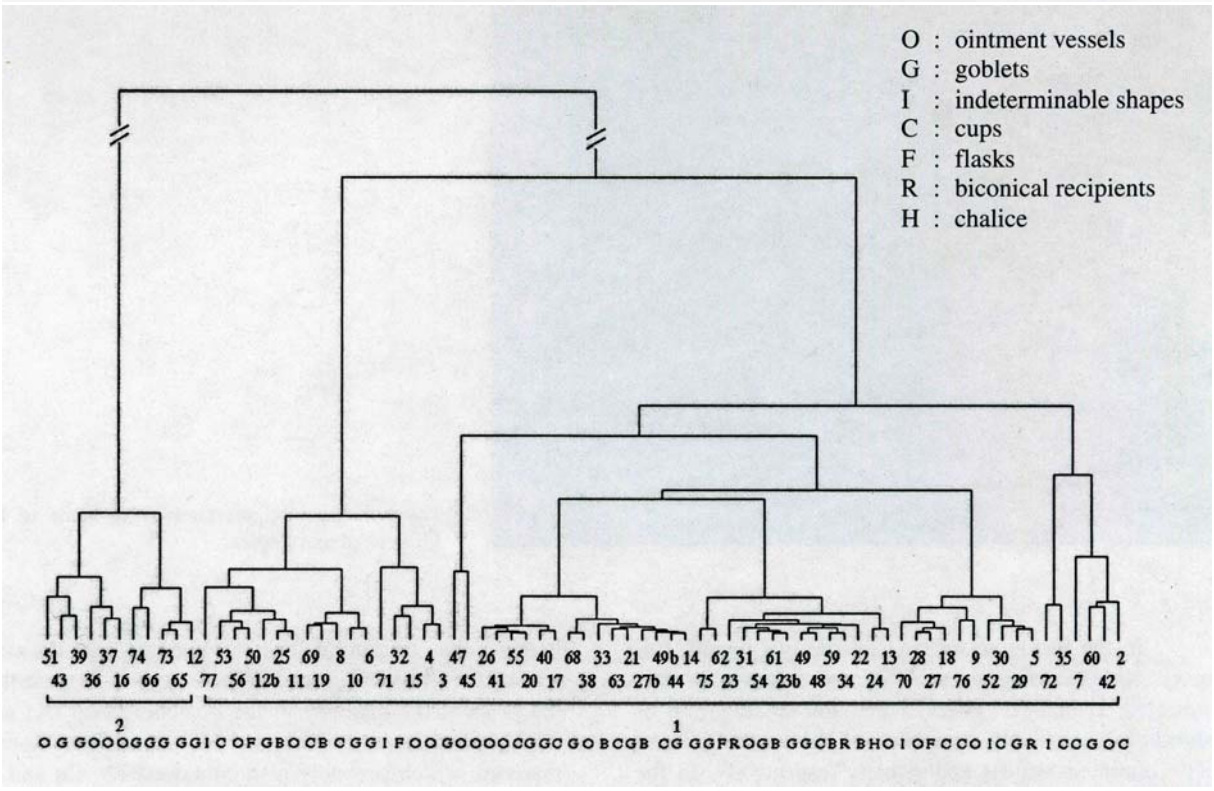

Figure 5. HCA dendrogram obtained using major/minor elements composition of the samples

Table 3. Average concentration and standard deviation for oxide concentration of major, minor and trace elements in the glass fragments belonging to the three statistical determined groups of Qumran objects (concentrations above the horizontal line are given in weight%, below it in ppm).

Oxides	Group IA (n=45)	Group II (n=9)	Group IB (n=5)
Na_2O	16.48±0.40	17.20±0.35	16.28±0.60
MgO	0.23±0.13	0.01±0.01	0.07±0.13
Al_2O_3	2.51±0.07	2.35±0.34	2.42±0.10
SiO_4	69.46±0.62	71.69±0.42	70.92±1.62
P_2O_5	0.08±0.04	0.02±0.04	0.01±0.01
SO_3	0.16±0.11	0.17±0.07	0.20±0.07
Cl	0.82±0.07	1.16±0.05	1.06±0.05
K_2O	0.84±0.06	0.58±0.12	0.61±0.11
CaO	8.41±0.55	5.52±0.61	7.54±0.42
TiO_2	0.05±0.04	0.04±0.04	0.02±0.02
MnO	0.43±0.06	0.84±0.13	0.09±0.09
Fe_2O_3	0.52±0.06	0.33±0.04	0.39±0.13
Cr_2O_3	12±12	23±27	9±8
NiO	7±5	15±7	8±8
CuO	209±95	50±43	83±137
ZnO	35±19	26±7	18±13
Br	7±11	8±7	7±4
Rb_2O	14±4	13±3	13±3
SrO	637±145	534±130	570±137
Y_2O_3	9±2	6±1	8±3
ZrO_2	79±17	63±16	59±15
Mo_2O_3	3±2	3±1	0±0
SnO_2	113±49	56±34	42±21
Sb_2O_5	354±190	29±31	1±1
BaO	234±127	151±59	151±92
PbO	156±64	17±14	13±9

Discussion

In general, glass produced in early times and up to the 9th century AD was made by melting together a siliceous constituent (e.g., quartz sand), a fluxing agent (e.g., natural soda or sodium-rich plant ashes) and one or more colorant, decolorant and/or opacifying substance(s). It is logical to assume that the use and type of these constituents varied, depending on the manufacturing centres and the historical period. But on the contrary, the major composition of Roman vessel glass from the period 1st-6th century A.D. is very similar, and irrespective of the geographical location or time period of production.

Recent investigations of the remains of large-scale glassmaking in Israel & Egypt (Freestone 2000, 2002; Nenna 2000) are leading to a re-evaluation of our concepts of early glass production. Instead of a model whereby fresh glass was produced from its raw materials in the same workshops that produced glass vessels, a division of production appears to have existed whereby large quantities of glass were made from alkali and sand in a relatively

limited number of locations. These centres of primary glass production were located close to the favoured sources of sand, such as that at the mouth of the Belus River, or close to sources of alkali, such as the Natron of the Wadi Natrun in Egypt. The freshly made primary glass was then broken up into lumps or chunks and distributed to glass workshops for fabrication into vessels, the so called secondary glass production sites.

So the bulk glass used to produce the glass found in the Qumran settlement was either manufactured (in the form of ingots) in one or in a few locations in the Middle East. A Middle Eastern source seems to be the most logical explanation for the calcareous sand used, as for example coming from the mouth of the river "Belus" on the Syrian coast. The sand of the "Belus" river appears to be of a remarkable quality and not yet found outside the Syria-Palestine area. The relative proportions of calcium oxide (CaO), about 9%, magnesium oxide (MgO), typical around 1%, aluminium oxide (Al_2O_3), around 2.5%, iron oxide (Fe_2O_3), less than 1% and titanium oxide (TiO_2), a trace amount, make the "Belus" sand so extra ordinary (Foy 2000). The research work of Foy and co-workers (2000) demonstrate that slightly different proportions in the five constituents were found in Middle Eastern glass ingots, so that different sand sources besides the "Belus" sand were in use during Roman times, most probably also originating from the same Syria-Palestine coastal region.

Trace elements like Strontium (Sr) and Zirconium (Zr) found in the Qumran glass indicates the use of coastal sand since they all have higher Sr than Zr content. Shells (Aragonite) in the beach sands have higher capacity to incorporate Sr than calcite of the limestone (inland Egyptian sands).

The very low concentration of potassium oxide (K_2O found between 0.4 and 1.1%) and the trace level of phosphorous oxide (P_2O_5 concentrations found between 0.01 and 0.2%) suggest that the soda used for making the glass must have been of mineral origin[2]. The mineral soda (the so called "natron", which is a naturally occurred sodiumsesquicarbonate $Na_2CO_3.NaHCO_3.2H_2O$) might have been obtained from salts produced by evaporation of the water of the Nile delta, especially from the "Wadi Natrun", North-West of Cairo (Newton *et*

[2] The same argumentation about the use of natron in Roman Glass production was brought forward during a discussion of two mosaic-glass cups from Hollogne-aux-Pierres (1st century A.D.): Ch. FONTAINE-HODIAMONT, *Une technique particulière pour la fabrication des coupes en verre de Hollogne-aux-Pierres (Belgique). Le témoignage de Pline l'Ancien (Histoire Naturelle, XXXVI, 199)* in *Bulletin des Musées Royaux d'Art et d'Histoire*, 65, 1994, p. 60-61; When sea-plant ashes were used as sodium source for the flux of the glass, a higher proportion of the potassium content is observed in the composition of the glass, see M. VERITA, *L invenzione del cristallo muranese: una verifica analitica delle fonti storiche*, in *Rivista della Stazione Sperimentale del Vetro*,vol. 1, 1985, p. 23-25; and also the research notes of A. GASPARETTO, L. ZECCHIN and T. TONINATO in *Rapporti CNR, Roma, Murano*, 1983 and 1986.

al. 1989). The composition of natron is complex and variable: the sodiumcarbonate content varies from 22.4 to 75.0%, sodium bicarbonate from 5.0 to 32.4%, sodium chloride (which explains the presence of chlorine, between 0.7 and 1.2%, in the glass under discussion) from 2.2 to 26.8%, sodium sulphate from 2.3 to 29.9%, plus water and insoluble material (Turner 1956).

As suggested in the discussion regarding the source of the sand, the difference in CaO content in the observed subgroups in the Qumrân samples could be the use of different sand, although certainly originated from the Syria-Palestine region (Foy *et al.* 1999). On the other hand, the lead, copper and tin content of group IB is lower than in group IA but comparable with the content of the glass of group II. These results suggest that the glass of the majority of the objects (group IA) was decolourised by the intentional addition of an Sb-rich material, which probably also contained Pb, Cu and S, as for example the natural mineral Bournonite ($CuPbSbS_3$) (Aerts 1998). However, the existence of such a mineral in the Near East is not established (Healy 1978). Velde (1996) investigated the correlation between the antimony, manganese and iron content in Gallo-roman glass but came to the conclusion that there is no clear correlation between these three constituents and that the use of antimony was dependent upon the desires and working methods (oxidation-reduction and possibly temperature) of the individual roman glassmaker. Because the trace fingerprints of the three groups differ only significantly in a relatively limited number elements, one can reasonably assume that all the objects from the Qumrân site were either made from batches of bulk glass which were closely related (Davidson 1988) or else they were manufactured using different procedures, each introducing slightly different concentrations of some trace elements.

Conclusions

By using two complementary X-ray emission techniques (SEM-EDX and µSR-XRF) respectively the major/minor and trace composition of a series of 75/64 glass objects of different types was determined.

The results show that all glass fragments are related to the low Mg / low K soda-lime-silica glass type what indicate the Roman/Byzantine glass. The use of Natron as alkali source and Belus-type sand to produce the glass could be established.

Regarding the question of the provenance of the objects, the above-discussed composition information suggest that almost all objects found at the Khirbet Qumrân site were made from the same or closely related batches of bulk glass[3]. Either they were made locally in a glass workshop (e.g., by remelting and working of a large stock of bulk glass) or they were imported ready-made in large quantity from elsewhere. The hypothesis of local or quasi-local production should not be neglected, since, according to R. Donceel, the nearby site "Ain Feshka" might have procured remains of the first material and glass-working residues.

It is hoped that this research will stimulate further analytical studies, including the analysis of trace elements in glass artefacts from other regions of the Roman Empire, in particular of those sites located in the Near East. More reference studies treating the detection of subtle differences in glass composition – on well-defined, dated objects with secure provenances – would certainly help establish series' of productions and refine our hypotheses on the origins and manufacture of Roman/Byzantine glass.

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Section III

CONSERVATION

Jan Gunneweg[1] and Charles Greenblatt[2]

[1] Institute of Archaeology, The Hebrew University of Jerusalem, Israel

2 Kuvin Centre and Department of Parasitology, The Hebrew University of Jerusalem, Israel

E-mail: jan.gunneweg@huji.ac.il; greenbl@cc.huji.ac.il

Conservation is one of the final steps in caring for our cultural relics, and especially the organic artifacts. Yet even before we “lay hands on” we must attempt to assess the damage. Of prime concern in the Qumran Project are the Dead Sea Scrolls themselves. Adolfo Roitman, Director of the Shrine of the Book, detailed for us the loving care, which they now receive. Here the stress is on “now” in their new refurbished home. In an "ideal" preventive environment, the Scroll’s integrity would be long lasting, but accessibility, early attempts at preservation, smuggling, transport, exposure to natural disasters, as well as acid rain, air pollution and other adverse environmental conditions have been stressful. Humans having created the texts on these biopolymers also contributed to their degradation.

Other biological agents also add to the damage. Insects, fungi, and bacteria all take their toll. Itzhak Polacek described one of the threats to ancient documents – fungal attack. He discussed some of the methods of both prevention and cure. Polymer integrity can be assessed for damage with new physical tools. Kennedy and Wess analyzed parchment deterioration through microfocus X-ray diffraction. This technique allows one to describe the microstructure of parchment, not only in terms of the collagen, but of the lipids, the minerals and ink. Damade can be detected and described. Abraham Domb then told how polymer science can offer new insights into the preservation of these items without extreme methods and arrives at sustainable preservation. The chains of the biopolymers can be protected and stabilized by subtle cross linkages, and protective chemicals can be inserted which prevent bacterial and fungal attack. New insights from polymer chemistry and biotechnology can help

modern society conserve and protect its cultural heritage. Biological control may afford pest management to protect our cultural heritage.

These faded and damaged documents at first perusal may seem to hide their content. Hain and Dorica gave examples of the optical methods that can assist us in reading them. Near infrared reflectography and ultraviolet fluorescence distinguish processes unseen by the eye. Libman, Bitler and Shor described the consortium of interest, which have cooperated in making sense from the translation of the text of the *Hodayot* (Thanksgivings) Scroll. An original reconstruction of Stegemann put fragments into their proper order. However poor restoration methods required the aid of Berman of NASA to read the fragments by infrared. This is also a story of the advancement of conservation science in the recent years. Pantos and his colleagues demonstrated the power of Synchrotron Radiation analysis in understanding the pigments in ancient pigments. Orit Shamir put other artifacts such as the textiles, and the clothing made from them, into their proper perspective. These technologies of manipulating natural polymers along with the work presented in earlier sessions on the agricultural endeavors of growing grapes and olives, the even earlier discoveries of domestication of plants and animals are all a rich part of the bio-cultural context of the life of Qumran. The Pfanns, father and son, have attempted to integrate these many strands into a rich computerized construct, which visualizes life in ancient Qumran, no matter what the people who lived there were called. Together, we hope, we can come to understand how these people in their many aspects of life and work, struggled to put food on their table and maintain their community and culture. Our only clues to this understanding are the archaeological finds, both organic and inorganic. We are certain as we learn to analyze these documents and artifacts and understand what they teach us of our rich cultural heritage, we will strive even harder to conserve them.

When the study of the material culture explains the relation of the local population with that from further remote sites, as well as the technology that was employed, the research of the bio polymers of organic relics will provide a clue as how to preserve organic as well as inorganic materials and artifacts for the next generations.

New scientific tools in the future will be used to postpone the daily degradation of various substances, which is only possible when we preserve them today so that future research can be performed on them.

PRESERVATION AND ANALYSIS OF NATURAL POLYMERIC MATERIALS

Abraham J. Domb

Department of Medicinal Chemistry and Natural Products, School of Pharmacy - Faculty of Medicine, The Hebrew University of Jerusalem, Israel
E-mail: adomb@md.huji.ac.il

Abstract

Natural polymeric materials based on proteins and polysaccharides are the main building blocks of common utilities used in ancient times as well as today. Papers, parchments, fibres, sticks and other commonly used materials are all made of polymeric materials produced from natural sources including plant, animal tissue, and animal and insecticide produced products. Methods for the characterization and stabilization of proteins and polysaccharides have been extensively studied as a main source for materials used in various applications. The characterization methods include: chemical structure, surface morphology, mechanical strength, thermal properties, chain molecular weight and stability under various conditions. While these natural polymers have reasonable physical stability at time of production, it is desirable to have products produced from these polymeric materials that are stable and preserve their properties for years under out-door conditions. These polymers are sensitive to bacterial and fungal attack, light and moisture degradation, and other outdoor conditions. Preservation and stabilization of proteins and polysaccharides include chemical modification (crosslinking, increasing hydrophobicity, surface modification, and blending), incorporation of stabilizers (antifungal and antimicrobial agents, radical scavengers), and storage under proper conditions. This article discusses in brief the various structures of natural polymeric materials, methods for their characterization, stabilization and long-term preservation.

Keywords: biopolymers, parchment analysis, polysaccharide, collagen, material stabilization, crosslinking

Natural polymeric materials

Materials from natural origin can be divided into three main groups, polysaccharides, polypeptides and polyesters (Figure 1). These groups of materials are produced by cells in plants, animals, fungi and bacteria. Polysaccharides and polypeptides (proteins) are the most common polymers that have been used by humans, polyesters made from hydroxy acids produced by bacteria have essentially been discovered in the past century and have found limited use as biodegradable plastics. Protein based materials that have been used by humans include: gelatine, collagen, fibrin, serum albumin and full tissues made from proteins. Polysaccharides include cellulose, amylose, arabinogalactan, galactomannan, plant gums, alginates, hyaluronan, chitin, and others extracted from plants. Such materials are often complex and difficult to characterize. Various polymers in this group have been studied and utilized to date (Figure 1).

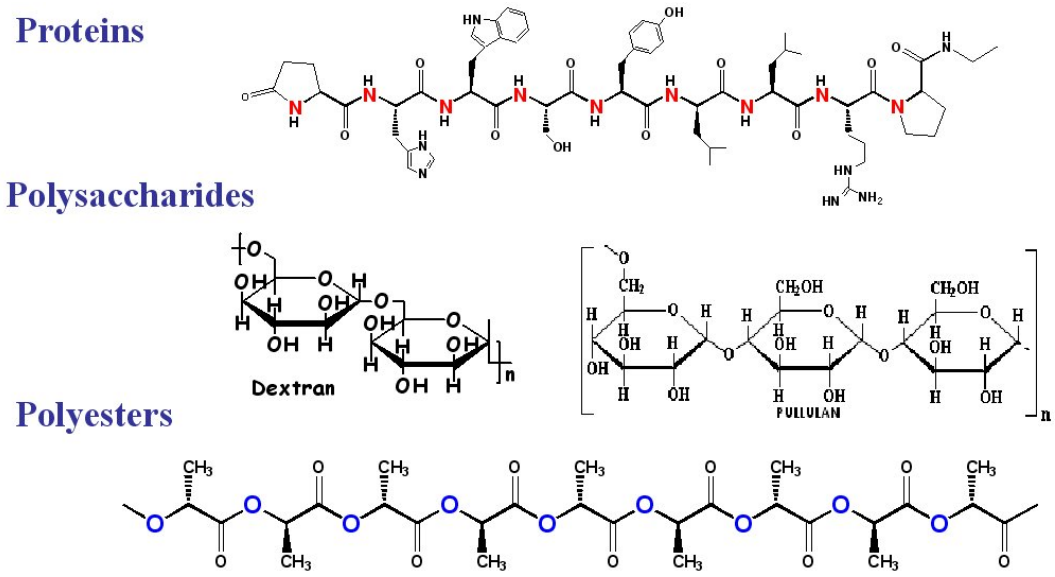

Figure 1. Biopolymers derived from natural origin

Proteins: Collagen is the most widely used tissue derived natural polymer and it is a main component of extracellular matrices of mammalian tissues including skin, bone, cartilage, tendon and ligament. Physical formed collagen gels are thermally reversible and offer a limited range of mechanical properties. Chemical cross-linking of collagen using diphenylphosphoryl azide or glutaraldehyde can improve the physical properties. However, these gels are still short of physical strength, potentially immunogenic if used in the human body and can be expensive. Furthermore, there can be variations between batches. Collagens

are composed of specific combinations of amino acid sequences that are recognized by cells and degraded by enzymes secreted from cells (i.e. collagenase). Collagen has been used as a tissue culture scaffold or artificial skin due to the ready attachment of many different cell types and its cell based degradation. The attachment of cells to collagen can be altered by chemical modification, including the incorporation of fibronectin, chondroitin sulfate or low levels of hyaluronic acid into the collagen matrix. Collagen gels have been utilized for reconstruction of skin, blood vessel and small intestine.

Gelatine is a derivative of collagen, formed by breaking the natural triple helix structure of collagen into single strand molecules. There are two types of gelatine, A and B. Gelatine A is prepared by acidic treatment before thermal denaturation, while gelatine B is processed by alkaline treatment that leads to a high carboxylic content. Gelatine forms gel by changing the temperature of its solution. It has been used in many tissue-engineering applications due to its compatibility and ease of gelation. Gelatine gels have also been used for delivery of growth factors to promote vascularization of engineered new tissue. However, the weakness of the gels has been a problem and a number of chemical modifications have been investigated to improve the mechanical properties.

Fibrin has been used as a sealant and an adhesive in surgery as it plays an important role in natural wound healing. Fibrin gels can be produced from the patient's own blood and used as an autologous scaffold for tissue engineering. No toxic degradation or inflammatory reactions are expected from this natural component of the body. Fibrin forms gels from enzymatic polymerization of the fibrinogen at room temperature in the presence of thrombin. An interesting feature of fibrin is the degradation and remodelling by cell associated enzymatic activity during cell migration and wound healing.

Fibrin gels may promote cell migration, proliferation and matrix synthesis through the incorporation of platelet derived growth factors and transforming growth factor. Fibrin gels also have been used to engineer tissues with skeletal muscle cells, smooth muscle cells and chondrocytes. However, fibrin gels are limited in mechanical strength and this prevents their use in certain applications.

Polysaccharides: Celluloses have been used extensively for various applications. Cellulose derivatives yielding materials with various mechanical and physical properties have been developed and are in use for a wide range of applications from construction and paints to drug delivery systems and food additives. Carboxymethyl-cellulose (CMC) is an example of derivative that swells in water. It is prepared by swelling cellulose in sodium hydroxide

solution, followed by reaction with monochloroacetic acid. The acid can react with hydroxyl on C2, C3 and C6 on each glucose unit to give a maximum degree of substitution. Presence of ionisable side groups disrupts the cellulose crystal structure and hence making CMC water-soluble. The polymer forms high viscosity solution. CMC also forms insoluble ionic complexes with cationic polymers such as chitosan, polyethyleneimine and diethylaminoethyl dextran.

Glycosaminoglycans (GAGs) are linear heteropolysaccharides consisting of disaccharide units with the general structure of uronic-amino sugar. In their native form, several GAG chains are covalently linked to a central protein core and the protein-polysaccharide conjugates are termed proteoglycans.

There are six different types of GAGs – chondroitin sulphate, dermatan sulphate, keratan sulphate, heparin sulphate, heparin and hyaluronic acid. Heparin and hyaluronate are interesting candidates for development of implantable biomaterials. Heparin is being examined for tissue regeneration and wound healing.

Alginic acids or alginates are isolated from several species of brown algae (e.g. *Macrocystis pyrifera*). Alginates are block copolymers of α-L-guluronic acid (G) and β-D-mannuronic acid (M) with average molecular weight of 200,000 to 500,000. G blocks are linked by α(1→4) and M blocks are linked by β(1→4) glycosidic bond. Simple gelation will be obtained from adding divalent cation such as Ca^{2+} into a solution of alginates. Despite its advantages features, alginate itself may not be an ideal material because it degrades via a process involving loss of divalent ions into the surrounding medium and subsequent dissolution. This process is generally uncontrolled and unpredictable. Therefore, covalent cross-linking with various types of molecules has been attempted to precisely control the mechanical and swelling properties of alginate gels.

Chitosans are partially or fully deacetylated derivatives of chitin, the primary structural polymer in arthropod exoskeletons. Primary source of chitin and chitosans is shells from crab, shrimp and lobster. Shells are ground, demineralized with HCl, deproteinized with a protease or dilute NaOH and then deacetylated with concentrated NaOH. Structurally, chitosans are very similar to cellulose, except for their amino or acetylamido substitute. The polymer is linear, consisting of β(1→4) linked d-glucosamine units with a variable number of randomly located N-acetyl-glucosamine groups. Molecular weight of chitosan is in the range of 50,000 - 1,000,000. Commercially, available preparations carry 10-30% acetylamido residues.

Crystallinity is maximal when the polymer is fully acetylated with varying crystallinity at intermediate deacetylation. Chitosan is normally insoluble in aqueous solution above pH 7 but is readily soluble in dilute acid (pH < 5) where free amino groups are protonated.

Dextran is a nontoxic biodegradable polymer and is widely used in many biomedical areas. It is primarily based on 1→6-α-D-glucopyranose and carries an average of 3 hydroxy groups per anhydroglucose unit. Solution of Dextran has been used as surgical aids for reducing tissue adhesion. Derivatization of dextran with maleic anhydride gives the dextran-maleic acid half ester, followed by UV crosslinking and formation of dextran-maleic acid hydrogel. Swelling of dextran-maleic hydrogel increased with increasing the degree of maleic substitution over a wide range of pH. Dextrans have been in used for drug conjugation, via reductive amination, to obtain large molecular weight drug derivatives for the purpose of altering drug distribution after intravenous injection and accumulation of the drug conjugates in cancer or in flamed tissues, where large molecules leak out from broken blood vessels. Also conjugation of water insoluble drugs to the water-soluble dextran provides a water-soluble derivative, which can be injected to a patient.

Stabilization of natural polymers

To improve and preserve articles made of proteins from being deteriorated by weather changes or microbial activity, protein based materials should be modified by chemical and physical means so that the article body or its surface is protected from the environment (Figure 2). Such modifications include: crosslinking of the protein chains by reacting the lysine amino side groups of the proteins with reactive bifunctional molecules such as glutaraldehyde or adipoyl chloride that connect protein individual chains into a stable network. Another possibility is to denaturate the protein by heat or immersion in solvent so that the protein structure is no longer in its natural form. Blending or mixing the proteins or coating of protein surfaces with protecting materials such as waxes, fats, modified polysaccharides and inorganic materials my protect them from physical and microbial deterioration. Microbial protection may include the incorporation of antimicrobial agents that are inert to the proteins such as broad-spectrum antibiotics and antifungal agents such as gentamicin, chloramphenicol, amphotericin B, nystatin and herbal extracts with known antimicrobial activity. These agents can be either embedded within the protein material or chemically bound to the protein chains via reductive amination, esterification or amidation.

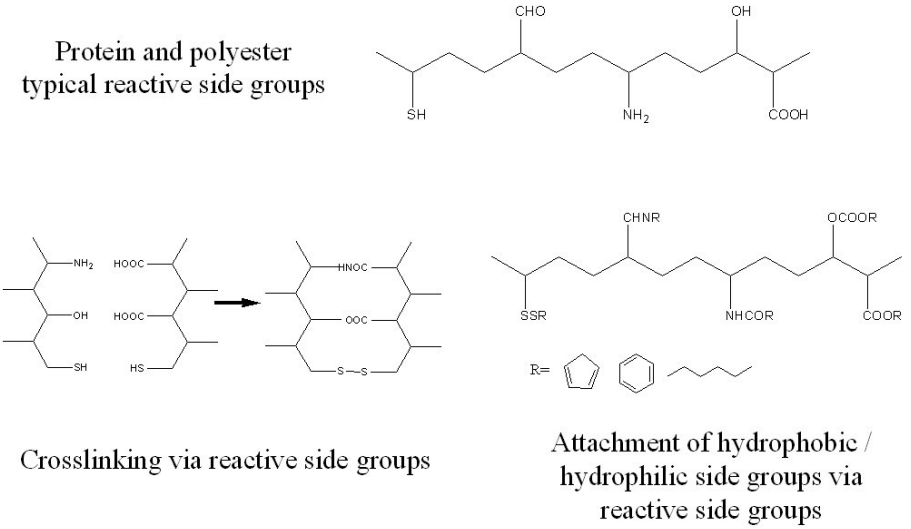

Figure 2. Modification of proteins and polysaccharides by crosslinking or attachment modifier via reactive side groups along the protein or polysaccharide chain

Chemical binding is preferred as it reduces evaporation of leach-out of the active agent as well as deposition of the agent on animal and humans body upon contact. Similarly, polysaccharides can be crosslined through the hydroxyl, amino or carboxylic acid groups along the polymer chain using a bifunctional reactive molecule that can react with either reactive group on the polymer. Modifications can also be applied by attachment of various groups along the polymer chain. Polysaccharides can be oxidized to form the highly reactive polyaldehyde that is water-soluble and react with amines at room temperature in high yields. Typical crosslinking of oxidized polysaccharides is shown in Figure 3.

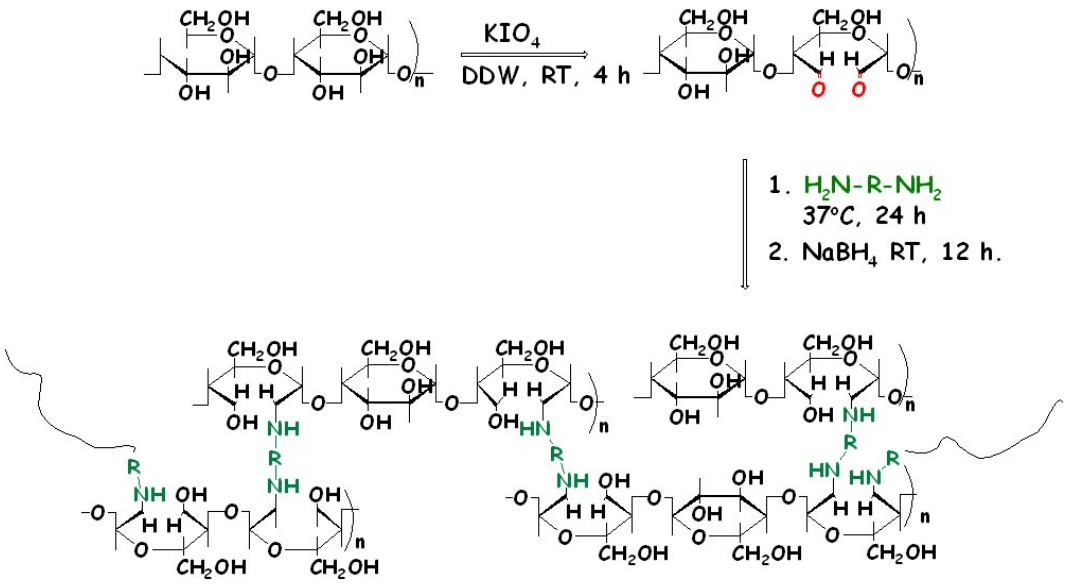

Figure 3. Typical crosslinking of polyesters or proteins by imine or amine bond formation

Polymer characterization

Various instrumentations have been developed in the past two decades to better characterize polymeric materials and organic materials. This includes determination of polymer chain length, i.e. molecular weight analysis, chemical structure identification (spectroscopy), thermal properties, visualization of polymeric materials by microscopy, diffraction, and determination of mechanical properties. Polymer molecular weight is commonly determined by size exclusion chromatography where a polymer mixture is passed through a column loaded with particles of different pore size and the polymer chains are separated based on their length. Longer polymer chains elute first while short chains stay longer in the column and are excluded last. Statistical analysis of the obtained chromatogram using a calibration curve provides an average molecular weight and distribution. Light scattering of polymer solutions and mass-spectrometry are the most updated accurate methods for absolute polymer molecular weight determination. Chemical structure of polymers is usually determined by infrared, ultraviolet and nuclear magnetic resonance. Thermal properties of polymers and polymer compositions are determined by differential scanning calorimetry (DSC) where the sample of polymer is heated at a constant rate while the heat provided is changing with the polymer thermal transitions, which are indicated in a thermogram output. The main thermal transitions are the Tg – the temperature where the polymer chains change from a glass like stiff organization to moveable chains, the Tm which is the melting temperature, and the temperature where the polymer starts to thermally degrade or react with air or oxygen and burn. The thermal stability of a polymer can be determined by monitoring the weight loss with temperature using Thermal Gravimetric Analysis (TGA) system. The mechanical properties of polymer samples are determined using a tensiometer where a polymer sample is either pulled at a constant rate or pressed at a constant rate using variable force. The crystallinity of a polymer sample can be determined by X-ray, and surface chemical structure and elemental analysis are determined by various X-ray tools such as XPS, WAXS, SAXS, SIMS and SANS. Surface morphology is determined by electron optical microscopies, TEM, SEM, and scanning tip microscopies (AFM).

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TIME AND SPACE:
ARCHAEOLOGICAL LANDSCAPES AT QUMRAN

Shimon Gibson

Albright Institute of Archaeological Research, Jerusalem, Israel
E-mail: Jafudigs@hotmail.com

Landscape Archaeology is an all-inclusive and highly flexible method for studying the development through time and space of a continuous distribution of large and small man-made features across a given landscape. In using this method, one is attempting to explain how and what one sees today came to look the way it does and to interpret the spatial patterns and structures created in the past in terms of social and economic behavior. The object of Landscape Archaeology is to examine the extent to which landscapes have been modified by human agencies from antiquity to the present day. Landscape Archaeology can be combined with existing regional surveys and excavation projects and can provide data on land exploitation systems, e.g. the study of ancient field systems.

Although early landscape work was first undertaken by nineteenth century explorers, particularly with the work of the Survey of Western Palestine, proper archaeological field surveys were only made in the 1920s, with the intention of identifying and mapping "biblical" sites. During the "golden age" of biblical archaeology, numerous tells were excavated and surface surveys were made on various types of settlements: towns, villages, farms and even individual installations (e.g. wine presses). Today building upon site catchment analysis and regional surveys one can really begin to speak of landscape archaeology. In my presentation I will apply these concepts to Qumran and the surrounding area. The following questions will be addressed: (1) what environmental data has emerged from the excavations at Qumran since the 1950s? (2) what archaeological information exists regarding the landscapes surrounding the Qumran settlement? (3) what methodologies are there that might help in extracting the maximum of information about the economy and function of the site during the various stages of its existence?

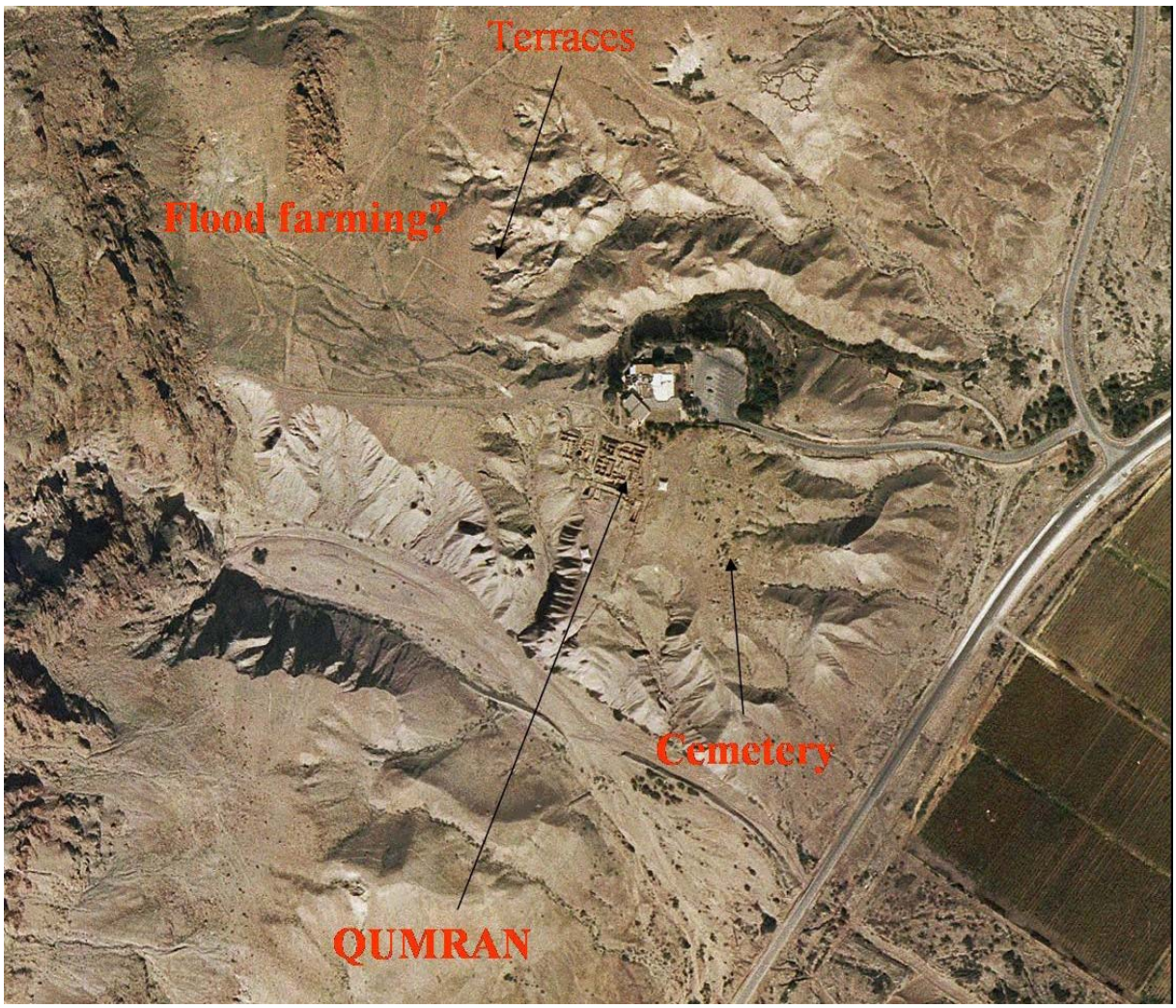

Figure 1. Arial photograph of the Qumran excavations (in center), the cemetery (to the right of center) and landscape architecture consisting of "flood farming" agriculture, northwest of the settlement.

FORENSIC PRACTICES - SCRIBAL ACTIVITIES

Azriel Gorski

The Kuvin Centre for the study of Infectious and Tropical Diseases, Hebrew University - Hadassah Medical School, Jerusalem, Israel
E-mail: AGorski@newhaven.edu

Abstract

Inductive inference is basic to forensic science. The forensic scientist logically infers information on cause, history, individuals or place involved in a human event from items found at a crime scene. Many times this involves hypothesis testing. These analyses can center on the items themselves or on the form and/or the pattern they present. Examples of the use and application of forensic science analyses to archaeological samples will be presented. Case studies involving a shroud, scrolls and population shifts will be used to illustrate the information contained in microscopic detail and the use of the habitual nature of some activities, such as sewing, the spinning of threads and writing. A sub theme of communication, the understanding of disparate requirements and capabilities and the need for an integrated and step-by-step approach encompassing the archaeological and the scientific will be stressed.

Keywords: Dead Sea Scrolls, Forensic Science, Stitching, Habitual Activities, Anthropogenic

Introduction

What is called Forensic Science came into being in the late 1880's when practitioners of several scientific disciplines applied their discipline to the questions of identification, guilt and innocence (Saferstein 1977). But legend provides an earlier example of Forensic Science, namely Archimedes using the principle of buoyancy to uncover a fraud against King Hieron II of Syracuse (c. 278-276 BC). It is perhaps fitting that the earlier example is in ancient times.

A simple definition of Forensic Science is the use of physical and chemical methods in the investigation of crime. For the most part the methods are accepted and well defined in their parent discipline, but for forensic purposes special modifications of the procedures are generally required in order to give results that are acceptable to legal authorities as proof of some specific point (Lundquist 1962). A basic tenet in the forensic sciences is the Locard Exchange Principle that states, "Every contact leaves traces. Whenever any two objects come into contact with one another they affect one another in some way" (Robertson and Vignaux 1995). The nature of the effect and the particles exchanged or deposited will depend upon the nature or the contact and the nature of the objects. Following on the Locard Principle, forensic scientists have developed an arsenal of techniques to obtain data from small and microscopic amounts of material that will yield interpretable information that can shed light on an event or series of events. Most of these events have human actions at their core.

Evett (1966) suggests that one of the central activities of Forensic Science is inductive inference. Inman and Rudin (2001) go further and state the following as a basic tenet of forensic science, "Inductive inference is a primary tool for evaluating physical evidence gathered from a criminal event." The aim of inductive inference, in many cases, is reconstruction, which Inman and Rudin define as "The ordering of events in relative space and time based on physical evidence." This ability to reconstruct human actions need not be limited to a crime scene or contemporary events. It is equally valid for those that left their trace in the archaeological record.

Habitual Activities

Forensic Analysis is not limited to the examination of materials. Document examiners use learned and habitual activities to compare handwriting. Learning to write normally involves trying to duplicate a standard of handwriting. In the early stages of this process the

handwriting of different individuals is very similar. As time passes we add to or subtract from the standard that we copied from as we learned. We develop our own individual style, which we unconsciously reproduce. These stylistic elements can be quantitated and linked to a writer.

Handwriting is only one of the habitual actions we perform. Spinning and hand sewing provide two other examples. In pre-technological tribes and culturally associated groups manual spinning methods were taught to the young who copied it. As they learned, they did, and then they taught it. Hand spinning and sewing are automatic, consistent and repetitive. Whether the fibers were twisted by pulling them up the leg or down the leg, or the hand spindle was spun to the right or left determine which of the two types of twist, one S and the other Z (Figure 1), are produced.

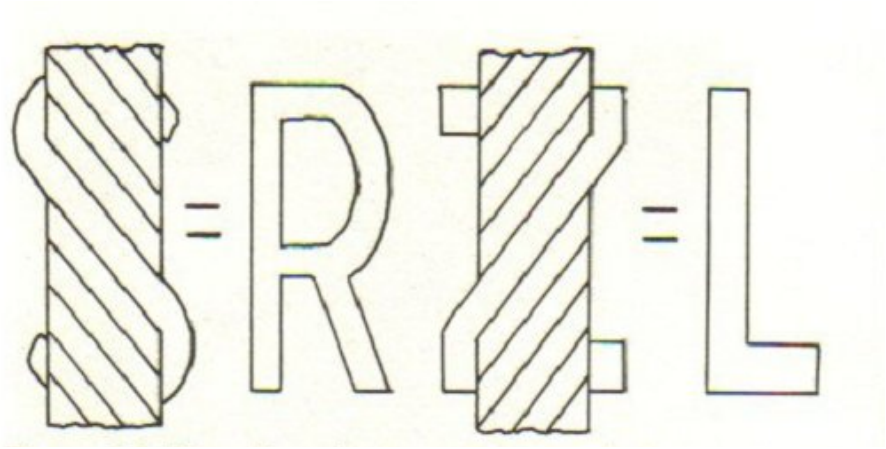

Figure 1. S and Z twist

This twist direction can be seen either in the cordage itself or the imprints it left on clay items such as pottery. The cultural association of twist direction is strong enough that it was used by Maslowski (1996) to detect cultural groupings and migrations between the middle and late Woodland periods (400 to 1100 CE) and the Late Prehistoric and Protohistoric periods (1000 to 1600 CE) along the Ohio Valley.

A Burial Shroud from 2000 BP

As part of a multidisciplinary analytical team of scientists and archaeologists, Orit Shamir (personal communication) of the Israel Antiquities Authority used the nature of the material and the fibers twist direction to discuss the origin of burial shroud fragments discovered by Dr. Shimon Gibson in a second temple period burial cave in the Hinnon Valley of Jerusalem.

A photomicrograph of a shroud fragment is shown in Figure 2. Based in part on identification of the fibers as wool fibers and their Z twist she arrived at conclusions as to the possible origins of the shroud textiles and the relative social status of the family. She wrote:

> *"Wool textiles from the Roman period in Israel are usually S-spun in both warp and weft. Z-spin suggests production probably outside of Israel and has formed only a small proportion of textiles of the Roman period recovered in Israel and the neighboring countries. The textile from the Ben Hinom Valley could, therefore, have been imported from Greece or Italy in which Z-spinning was the norm. Also some of the glass vessels at other tombs imported from Greece. This would indicate that the individual came from a wealthy family. Importing a special and "fine" burial cloth would entail time and expense and would not be done for the common man."*

Figure 2. Fabric of Burial Shroud – Wool in a Z twist

The Dead Sea Scrolls

With the kind permission of the Shrine of the Book of the Israel Museum, two Dead Sea Scroll Manuscripts, the *Habakkuk Commentary* and the *Isaiah Manuscript A* from Cave 1, were studied (Gorski 2001). The stitching joining several panels were analyzed using a hand

magnifier and a ruler in an attempt to derive information about the number of sewing events and whether they were sewn by more than one person. The data is presented in Table 1.

The stitching in seam 1 of the *Habakkuk Commentary* and seams 2, 3, 4 and 5 top and 5 bottom of the *Isaiah Manuscript* follow a "standard." The work is high quality, contains the same type of stitch and done so a minimal amount of each stitch is visible to the reader of the text. Looking only at the type, quality and number of stitches per inch, it can be seen that the *Habakkuk Commentary* with an average of 8 stitches per inch and the *Isaiah Manuscript* with an average of 5.4 stitches per inch were sewn by different people. In seam 1 of the *Isaiah Manuscript* no attempt was made to hide the stitching nor does it follow a repetitive pattern. The "repair" in seam 5 is extremely random and apparently done with little care for aesthetics. Thus we are there are at least 4 different sewing events, done by no fewer than two individuals. The data as to the number of strands and twist direction supports the above conclusions.

Table 1. Thread and stitching analyses of two Dead Sea Scroll Manuscripts

<table>
<tr><th colspan="2">Scroll</th><th colspan="3">Stitching</th><th colspan="3">Thread</th></tr>
<tr><th>Name</th><th>Seam No.</th><th>Direction</th><th>Count Range per inch</th><th>Count Average per inch</th><th>No. of Strands</th><th>Twist Direction of Strand</th><th>Strand Comp.</th></tr>
<tr><td>Habakkuk Commentary</td><td>1</td><td>Z</td><td>7 to 9</td><td>8</td><td>2</td><td>Z</td><td>Fibers</td></tr>
<tr><td rowspan="8">Isaiah Manuscript A Cave 1</td><td>1</td><td>S and Straight</td><td>—</td><td>—</td><td>1</td><td>—</td><td>Fibers</td></tr>
<tr><td>2</td><td>Straight</td><td>5 to 6</td><td>5.5</td><td>2</td><td>Z</td><td>Fibers</td></tr>
<tr><td>3</td><td>—</td><td>5*</td><td>5*</td><td>2**</td><td>Z**</td><td>Fibers**</td></tr>
<tr><td>4</td><td>Very Slight S "Straight"</td><td>5 to 7</td><td>5.5</td><td>2</td><td>?*** Perhaps S</td><td>Fibers</td></tr>
<tr><td>5 Bottom</td><td>Straight</td><td rowspan="2">5 to 6</td><td rowspan="2">5.5</td><td>?***</td><td>?***</td><td>?***</td></tr>
<tr><td>5 Top</td><td>Straight</td><td>2</td><td>Z</td><td>Fibers</td></tr>
<tr><td>5 Repair</td><td colspan="2">Random</td><td>2 or 4 Folded over?</td><td>S</td><td>Fibers</td></tr>
<tr><td colspan="2">Notes:</td><td colspan="3">Average count of 2, 3, 4 and 5 = 5.4
* Based on holes</td><td colspan="3">** Based on thread fragment
*** Thread hidden by seam</td></tr>
</table>

Conclusions

The above examples are presented here in abbreviated form. Each represents a continuum of analytical steps, considering and building subsequent analytical steps on the conclusions arrived at in previous steps. Further, they are the result of the contributions of various professionals, scientific and non-scientific, each contributing from their own specialty and knowledge base. Thus while scientific analyses, especially forensic scientific analyses, of archaeological or ancient samples can test archaeological hypotheses and allow for the reconstruction of past events, they are best done, and perhaps can only be productively done, in an interdisciplinary atmosphere. One in which there is an emphasis on strong bridges of communication between all the specialties and specialists involved.

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OPTICAL METHODS FOR THE VISUALISATION OF FADED TEXT IN ANCIENT DOCUMENTS

Miroslav Hain[1] and Jozef Dorica[2]

[1] Institute of Measurement Science, Slovak Academy of Sciences
[2] Chamber of Restorers, Slovakia
E-mail: hain@savba.sk

Abstract

Optical methods are powerful non-destructive tools to examine works of art (e.g. pictures), old scrolls and other objects. Examples include the exposure of underdrawings, the visualisation of faded text and other artefacts that are due to degradation processes invisible by the naked eye, distinguishing between authentic and retouched parts of work of art. In this contribution two selected optical methods, useful for examining old documents, will be described – ultraviolet (UV) fluorescence and near infrared reflectography.

Ultraviolet (UV) fluorescence

Fluorescence is a process by which a substance irradiated by electromagnetic radiation (ultraviolet light) is emitting light of a longer wavelength (visible colour). A UV fluorescence setup is shown in Figure 1 and consists of UV radiation source (e.g. lamp HQV 125, λ=365 nm), an excitation filter (short-wavelength-pass) which cuts off visible wavelengths overlapping the fluorescence, an emission filter (short-wavelength-cut) which cuts off reflected UV radiation (undesired fluorescence background) and an image sensor (e.g. CCD camera).

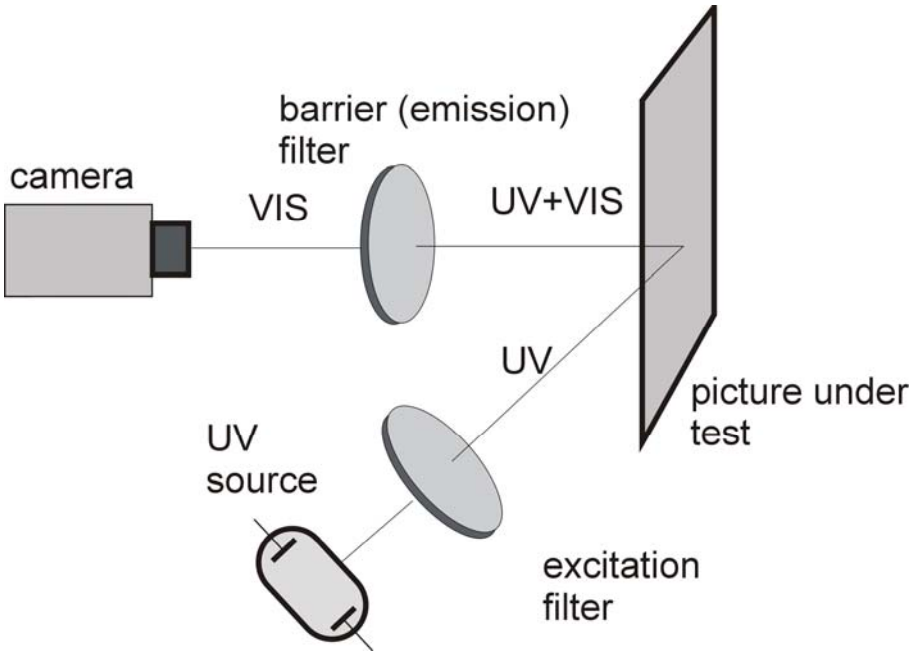

Figure 1. Basic configuration of UV fluorescence method

The UV fluorescence method can be used for visualization of old documents that have become invisible due to degradation processes (fading). This is based on the fact that UV fluorescence of the background (e.g. paper) in general strongly differs from the fluorescence of the text (e.g. ink). An example of a small fragment of a mediaeval document, visualized by UV fluorescence method, is shown in Figure 2.

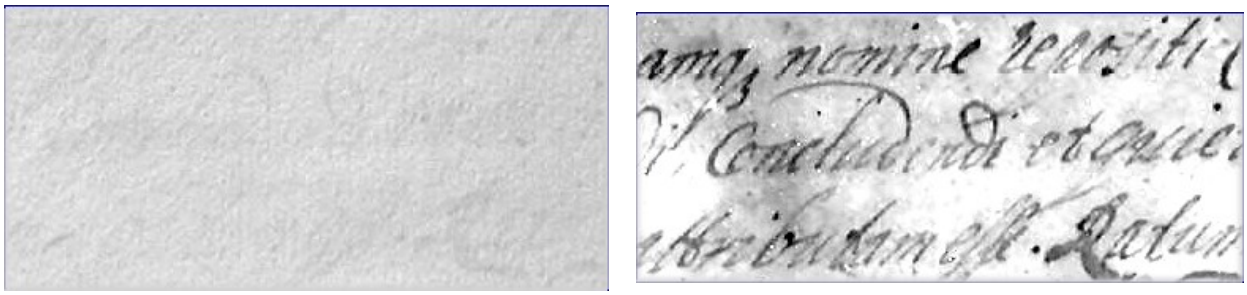

Figure 2. Fragment of mediaeval document in visible light, text is invisible to a human eye (left); Fragment of mediaeval document visualised by UV fluorescence method (right)

Another application of UV fluorescence method consists of distinguishing between old and newly repainted or retouched areas of the artefact, e.g. a picture. It is well known that old paint or varnish layers under UV emits more fluorescence light comparing to newly applied materials (repainted or retouched areas) and therefore retouched areas of a picture appear in a fluorescence image darker. UV fluorescence can also distinguish between pigments, which have similar colour in the visible band, but have a different fluorescence. An example is

shown Figure 3. It is clear that some parts of two little fingers on this picture were retouched (green areas on fluorescent image).

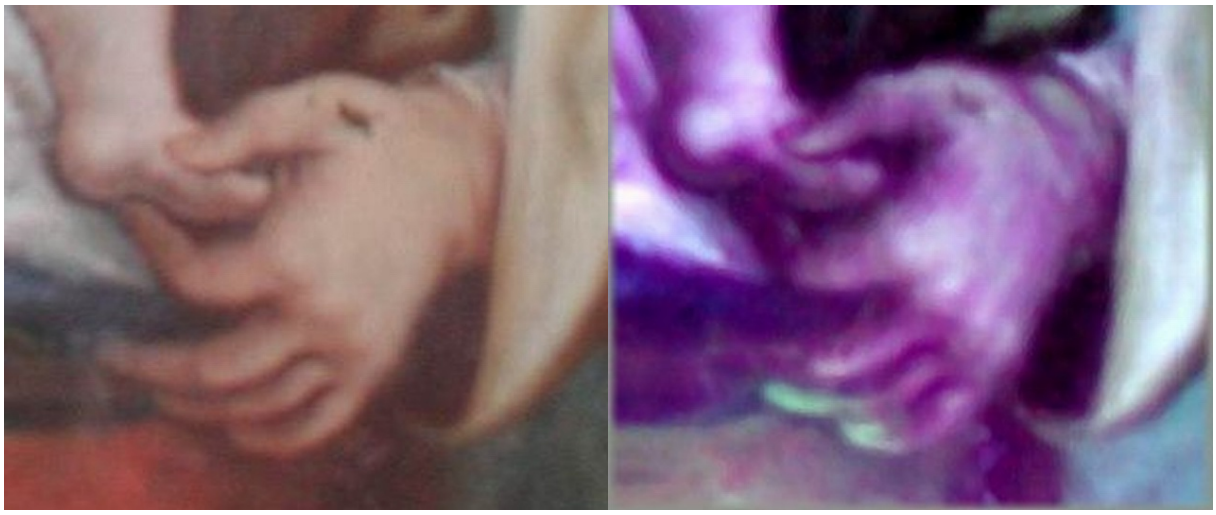

Figure 3. Fragment of the picture under test, image in the visible band (left) and as a UV fluorescence image (right)

Near infrared reflectography

NIR reflectography can be used to reveal hidden text, underdrawings or other artefacts covered by a thin layer, opaque in visible light (dust, pigment layer, paper). The method is based on the fact that near infrared radiation (IR) 0.8–2 μm is absorbed and scattered less in these layers than the visible radiation. A basic configuration of an IR reflectographic system is shown in Figure 4 and consists of IR radiation source, an IR camera, an image digitalisation electronic (frame-grabber) and a personal computer. The object which is examined is uniformly irradiated by the source of IR radiation (tungsten lamp); reflected radiation is scanned by a near infrared camera equipped with 800 nm short-wavelength cut filter (Schott UG8), digitised by a frame-grabber. The image is processed in personal computer in order to gain better contrast and readability of visualised information.

An example of an application of the IR reflectographic method is shown in Figure 5a which is taken in visible band and we can see part of a signature normally visible by a naked eye. Figure 5b shows the same fragment investigated by the infrared reflectography and we can see (after image processing) some hidden text or signature, invisible by naked eye.

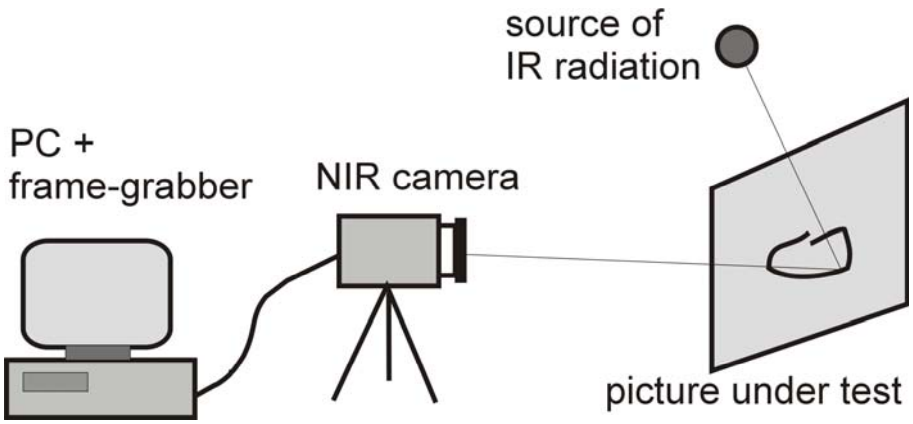

Figure 4. Basic configuration of an IR reflectographic system

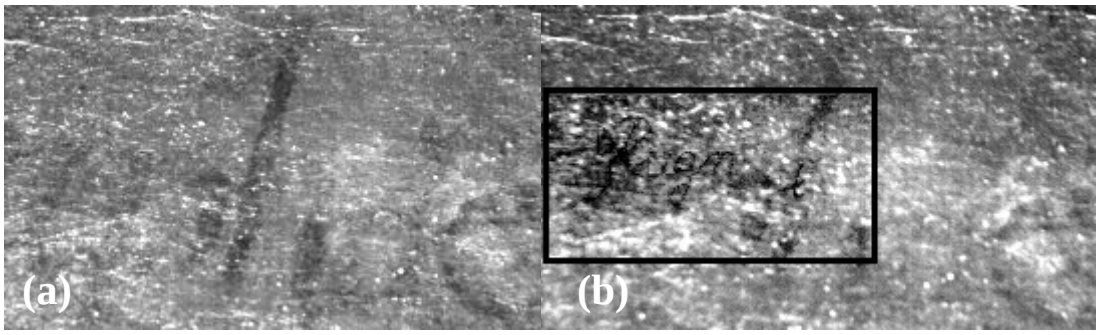

Figure 5. (a) Fragment of a picture - image in visible band and
(b) the same fragment with visualised hidden text - image in near infrared band

The typical application of infrared reflectography is the exposure of underdrawings in pictures. Very good results can be obtained in the case of carbon-based underdrawings e.g. underdrawings drawn by charcoal. Example of the IR reflectography application can be seen in Figure 6.

Comparing to classical IR photography the digital IR system has several advantages: (1) real-time information about presence of an underdrawing, (2) a better quality of IR images due to digital image processing and (3) the possibility to digitally compare infrared and visible images.

Figure 6. Medieval table oil painting (left) and infrared reflectography of the table oil painting with clear visible underdrawing (right)

Conclusions

Above described optical methods give possibility to visualise faded text in ancient documents, reveal hidden texts and signatures invisible for naked eye and in non-destructive way reveal underdrawings in paintings. Methods can also be helpful in testing of authenticity of various historical artefacts.

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PARCHMENT DEGRADATION ANALYSED BY X-RAY DIFFRACTION

Craig J. Kennedy and Tim J. Wess

Structural Biophysics Group, School of Optometry and Vision Science, Cardiff University, King Edward VII Avenue, Cardiff CF10 3NB, UK
E-mails: kennedyc1@cardiff.ac.uk; wesstj@cardiff.ac.uk

Abstract

Parchment is a collagen-based biomaterial that contains important information, from text written on the surface to the structure of the material itself. The degradation of historical parchments is often attributed to inappropriate storage conditions, although other factors may also accelerate the decay of the collagen within parchment, such as harsh cleaning or manufacturing techniques that involve extreme variations in pH or mechanical treatment. X-ray diffraction at small and wide angles is an ideal tool for analyzing the structure of the collagen, which gives the parchment its strength and durability over time. This chapter will describe how small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) can give a detailed account of the collagen structure within parchment in a manner that is not destructive to the material.

Key words: Parchment, collagen, X-ray diffraction, scattering

Introduction

Parchment has been used for millennia as a writing medium. Perhaps the most famous example of historical parchment is the Dead Sea Scrolls, a group of documents which date from 300 B.C. to A.D. 70, and were found in 1945 in a series of caves near the Wadi Qumran, approximately 2 km from the Dead Sea, (Burton *et al.* 1959). The religious texts displayed on the manuscripts have been of great importance to Middle Eastern historians. Over the centuries, many important documents have been written on parchment worldwide; to this day, all Acts of Law that pass through the British Parliament are written on parchment. Parchment is also used on musical instruments such as banjos and drums.

Parchment is a biological material processed from the skin of animals, usually cattle, sheep and goats (Reed 1975). As many of its structural features derive from skin, it is not a uniform structure in cross section, but made up of distinct layers (Horie 1990). As a biomolecular composite, parchment is subject to deterioration due to the effects of increasing atmospheric UV radiation, sulphur dioxide, cycling relative humidity and microbial attack (Bowden & Brimblecombe 2002, Strzelczyk & Karbowska 1994, Poglazova *et al.* 1988). This realisation has led to an awareness that important historical documents such as the Dead Sea Scrolls are under threat from increased pollution levels, damaging storage conditions, persistent humidity, and harsh methods of cleaning. This has led to a number of studies concerning the manufacture and degradation of parchment with the aim of producing techniques to slow or prevent parchment deterioration, or to regenerate the parchment structure (Larsen 2002, Fessas *et al.* 2000, Parry & Ricks 1996).

In recent years, large, multidisciplinary projects such as the EU projects Microanalysis of Parchment (MAP, Larsen 2002) and Improved Damage Assessment of Parchment (IDAP: www.idap-parchment.dk) have used X-ray diffraction in conjunction with other biochemical, mechanical, thermal, and visual techniques to provide a broad overview of the characteristics of a large number of historical samples from a number of European countries.

Collagen structure

Parchment is composed mostly of the protein collagen (Kennedy & Wess 2003). The loss of collagen structure is linked to the physical degradation of parchment over time. At the ultrastructural level, collagen exists in the form of fibres. The fibres are composed of fibrils, which are made up of collagen molecules, which are in turn comprised of individual peptide chains, providing collagen with a discrete structural hierarchy.

Collagen fibres are approximately 50-300 μm in diameter, and are composed of tightly packed collagen fibrils (Woo *et al*. 1993). In skin the fibres are arranged in a two-dimensional felt-like network (Kronick & Buechler 1986), lying at random orientations over the large area of the skin, providing tensile strength in the plane of the parchment (Hansen *et al*. 1992). Collagen fibres in skins taken from the spine or under the legs of an animal often display some preferential orientation.

Collagen fibrils are the principal, tensile strength-bearing components of connective tissues. They are long approximately cylindrical structures with diameters ranging between 10 and 500 nm (Hulmes *et al.* 1995), and range from 40-100 nm in skin (Kielty *et al*. 1993). Of the twenty-nine known types of collagen molecules, types I, II, III, V and XI are capable of self-assembling to form fibrils (Hulmes 1982).

In the axial direction, collagen fibrils exhibit a long-range order. The 300 nm long collagen molecules are staggered relative to their neighbouring molecules by a regular distance, d, which is typically ~67 nm in tendon, or ~65.5 nm in skin (Stinson & Sweeny 1980, Brodsky *et al*. 1980), comprising gap and overlap regions (Figure 1). In parchment, due to the dehydration of the collagen in the manufacturing process, the d period decreases to between 60 and 64 nm (Wess & Orgel 2000). The staggered arrangement of molecules is known as the Hodge-Petruska model (Hodge & Petruska 1962, 1963).

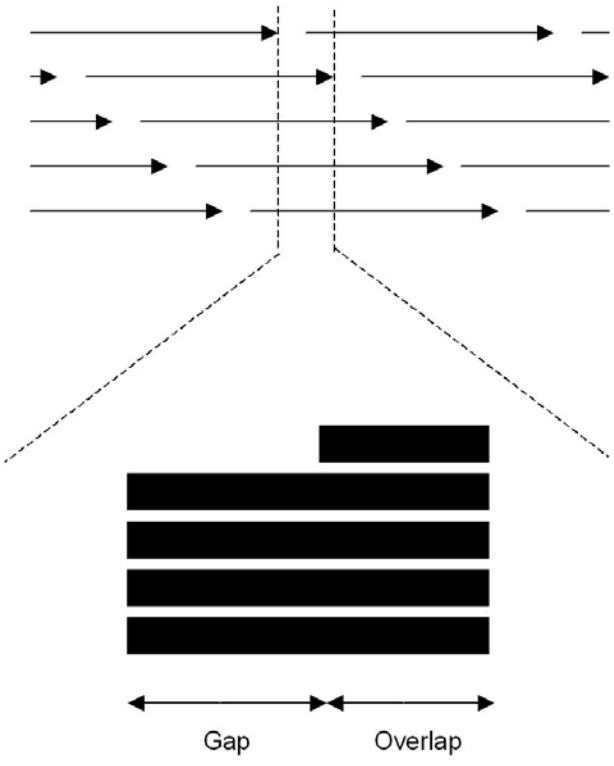

Figure 1. Representation of the arrangement of collagen molecules within a fibril and the gap/overlap function that is characteristic of the molecular packing of collagen. Each arrow (top) represents a collagen molecule in the staggered array. The d period (bottom) shows the five collagen molecules. The four complete segments are approximately 234 amino acids in length; the truncated segment that allows for the presence of the gap region is approximately 108 amino acids in length. The gap region comprises 0.54 of the d period, and the overlap makes up the remaining 0.46.

The collagen molecule comprises a triple-stranded rope-like structure formed by three interwound polypeptide α-chains. In skin the main collagen types present are types I and III; type I is the most common collagen type, and forms approximately 80% of the collagen in skin; type III collagen molecules have longer helical regions than type I collagen, and forms the remaining ~20% of skin collagen. The long central section of the polypeptide chains exist in a triple-helical conformation, and invariably has the amino acid sequence glycine-X-Y, where X and Y are any amino or imino acids, most commonly proline and hydroxyproline. Each molecule contains short non-helical regions at the N- and C- terminals, termed telopeptides. The telopeptide regions contain lysine residues, which are implicated in covalent cross-links between neighbouring collagen molecules, which play a vital role in maintaining the structure of the collagen fibrils (Orgel *et al*. 2000).

Collagen degradation

The processes of parchment manufacture and degradation alters the structure of the collagen, from an intact, fibrillar structure to a more disordered system. The rate of this process is determined by long-term factors such as storage conditions, and short-term factors, such as fire, flood or harshly applied cleaning techniques.

Collagen degradation in parchment can be initiated by biological agents such as bacteria, fungi and rodents (Strzelczyk & Karbowska 1994), as parchment is a source of nutrition for many microorganisms. Chemical degradation of collagen occurs through the processes of oxidation and hydrolysis; structural deterioration is brought about by gelatinisation (Derrick 1991).

Oxidation of the collagen molecules can occur in the side chains of individual amino acid residues, the main chain of the collagen molecule, or between the amino group of an amino acid residue and its associated Cα-atom. Side chain oxidation results in a reduction of the number of basic amino acids, and an increase in the number of acidic amino acids. The level of oxidation of collagen in parchment can be assessed by measuring the ratio of basic to acidic amino acids (B/A ratio). In fresh collagen this ratio is 0.69, but as the collagen undergoes oxidative change this ratio decreases to as low as 0.5 in historical parchments (Larsen 2002, Larsen *et al*. 1989). Free radical oxidation is capable of breaking the covalent bonds that link neighbouring amino acid residues, cleaving the polypeptide chains that comprise the collagen molecule. Oxidative cleavage of the collagen molecules occurs preferentially at tyrosyl residues on the collagen molecule (Larsen *et al*. 2002, Deasy & Michele sr. 1965) or in regions of charged residues (Larsen 1994).

Hydrolysis can be caused by acids, such as atmospheric SO_2 and water mixing to form sulphuric acid, cleaving in the main chain of the collagen molecule. Through both oxidative (Deasy 1967) and hydrolytic (Bowes & Raistrick 1967) breakdown processes, the large 300nm collagen molecules are broken into smaller fragments. Collagen molecules that have been cleaved no longer contribute to the strength of the collagen fibrils, reducing the stability of the collagen hierarchy overall.

Gelatinisation is the conversion from the fibrillar arrangement of collagen molecules in a triple helix form to a random conformation (Weiner *et al*. 1980). In moist conditions, water competes with the existing hydrogen bonds within collagen and attempts to form new bonds with the molecule. This occurs when hydrogen bonds are in a position within the molecule where they are open to attack from the water molecules. The action of heat makes water-induced gelatinisation more likely to occur (Hassel 2002). As the heat increases, the hydrogen bonds gain mobility, enhancing the chance of interaction with water. When this occurs, the three chains of the molecule are no longer held together and are free to form individual, less ordered structures. Gelatinisation is more likely to occur in partially degraded collagen molecules compared to native intact collagen, as the energy required to denature a shortened triple helix is lower than that of an intact one (Condell *et al*. 1988).

X-ray diffraction studies of parchment

Whilst many X-ray diffraction studies of native collagen (e.g. from rat tail tendon) have been done, relatively few have been carried out on parchment. The first major analysis came from wide angle X-ray diffraction (WAXD) of Dead Sea Scrolls samples by Weiner *et al.* (1980). WAXD is a technique capable of describing molecular-level details of samples, in the range of approximately 0.1 nm to 20 nm. In terms of collagen this provides information regarding the molecule-to-molecule interactions within a fibril, and the helical characteristic of the collagen polypeptides.

Following the work of Weiner *et al.* a number of advances were made in X-ray diffraction technology. For instance, photographic film has largely been replaced by charge-coupled devices (CCDs) as a means to collect diffraction images. This allows for easier computational analysis of the diffraction profiles. Improvements have been made to the dynamic range and the ability to avoid high count-rate saturation of detectors. The level of background scattering can be better estimated from CCD images; photographic film is more prone to saturation, making this estimation extremely difficult. Additionally, CCDs instantly produce X-ray diffraction images without the need to develop film, providing more reproducible readouts;

this development has led to rapid output of data, allowing more images to be taken in a given period of time.

Advances were also made in the field of photon production. In 1980, at the time of Weiner's work, the first second generation synchrotron radiation (SR) source was opened in Daresbury, UK. SR sources produce highly parallel, high brilliance X-ray beams, reducing experimental time and improving data quality. Since then, third-generation synchrotron radiation sources have been developed, such as the European Synchrotron Radiation Facility (ESRF), which came on-line in 1994. Third generation SR sources provide exceptionally high quality, high intensity X-ray beams, such that an X-ray diffraction image of parchment typically takes approximately one second, compared to five minutes from a second generation SR source, or five hours from a lab-based X-ray source such as the NanoSTAR facility at Cardiff University.

With these updated technologies, Wess *et al.* (2001) analyzed the structure of collagen within parchment and were able to determine that parchment was a more disordered structure than native collagen. This was followed by a high intensity micro diffraction analysis of parchment (Kennedy *et al.* 2004a), a study of the impact of laser cleaning on the structure of collagen within parchment (Kennedy *et al.* 2004b) and an investigation in to the effects of lipids on the degradation of collagen (Ghioni *et al.* 2005), using the latest technology offered by synchrotron radiation sources.

Materials & Methods

Parchment samples

The National Archives of Scotland, Edinburgh, UK, provided samples of historical parchment. Samples were dated from the 18th and 19th centuries and were mainly processed from cattle, goats and sheepskins.

To assess the impact of cleaning methods on historical parchment samples, one document, dated 1694, was cut into sections 5 cm x 5 cm and treated with cleaning and relaxing agents.

Small Angle X-ray Scattering

X-ray diffraction at smaller angles ($<6^{o}$ at λ = 0.154 nm) gives information concerning long-range order of structures. It is a process that is analogous to X-ray diffraction; however,

this technique uses a much greater sample-to-detector distance that allows longer periodicities and particle sizes in the nanometre range to be investigated.

In the case of collagen, the axial staggering of molecules is represented as the meridional series of reflections at small angles. Wess *et al.* (2001) analyzed the meridional series and demonstrated that in degraded samples the level of disorder present was higher. Crystalline lipids within a sample were also observed, as the head-to-head distance of phospholipids bilayers (typically 4-5 nm) falls in to the SAXS region.

For the samples discussed here, SAXS images were obtained from the NanoSTAR facility at Cardiff University. The sample-to-detector distance was 1.25 m, and the X-ray wavelength used was 0.154 nm. Samples were loaded in to the sample chamber, placed under vacuum and exposed for 6 hours per image; several images were taken from different areas of each sample to ensure reproducibility (Kennedy *et al*. 2002).

SAXS data were reduced to one-dimensional linear profiles in accordance with Wess *et al.* (2001). A parameter of sample ordering was measured by SAXS; from this, a ratio of crystallinity was devised. This involved taking the integral of the area of a linear profile corresponding to the 6^{th} to the 9^{th} orders of diffraction (I_1) and dividing that integral by the integral of the entire linear trace (I_2; Figure 2). This parameter is based upon the assumption that the meridional orders of collagen represent the crystalline component of the collagen fibrils, whilst the overall scattering is due to the total X-ray scattering from crystalline and non-crystalline regions. Crystallinity is measured in this manner in biological polymer systems such as cellulose and silk (Burghammer *et al.* 2003). The linear profiles are treated by removing the area near the centre of the diffraction image to remove any effects generated by the beam stop, removing the underlying background from the sample and normalising the profiles to account for sample density.

Microfocus X-ray Diffraction

The advent of microfocus X-ray technology has led to the development of intense micron sized X-ray beams (Snigirev *et al.* 1996), which can be used for X-ray microdiffraction experiments where small areas of textural variation can be probed in a sample. Small cross sections of parchment (0.3 mm x 5 mm) were analysed at beamline ID18F at the ESRF (Kennedy *et al.* 2004a). The sample to detector distance was 20 cm, allowing wide angle X-ray diffraction (WAXD) images of the parchment to be obtained. The X-ray beam was focussed using a compound refractive lens to 1.5 μm x 15 μm; up to 200 diffraction images can be taken in a single cross-sectional scan of a 300 μm thick sample. Microfocus technology

has allowed for surface-to-surface scans of parchment (Kennedy *et al.* 2004a) or X-ray diffraction images from the entire thickness of a sample.

In each diffraction image the main peaks occur at 2 nm^{-1} caused by amorphous scatter, and 0.85 nm^{-1}, from collagen. As described by Weiner *et al.* (1980), the relative intensities of these peaks can give an indication of the relative amounts of collagen and gelatine (denatured collagen) present in the sample, known as the collagen: gelatine (C:G) ratio. To determine the C:G ratios, Kennedy *et al.* (2004a) used a peak fitting program to determine the integrated intensities of both peaks, and divided the intensity of the 0.85 nm^{-1} (collagen) peak by that of the 2 nm^{-1} (amorphous) peak; values of 0 indicate complete degradation of the collagen structure.

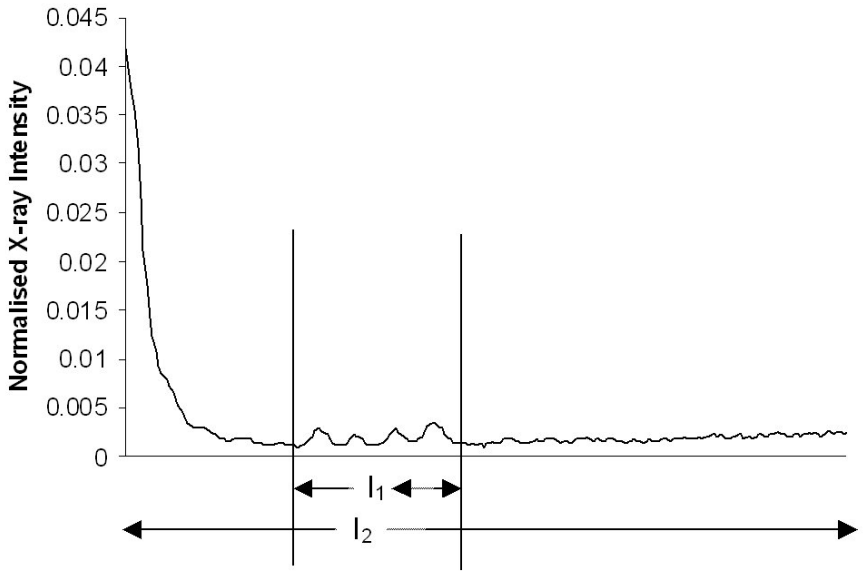

Figure 2. Linear profile from a parchment sample. I_1 denotes the area where the integral of the intensity is taken between the 6th and the 9th orders of collagen. I_2 denotes the area of the integral of the entire linear profile. These values are then used to calculate the ratio of crystallinity.

Results & Discussion

SAXS and WAXD analysis of parchment

Small angle X-ray scattering (SAXS) analysis of parchment is capable of describing the fibrillar crystallinity of the collagen; the retention of the staggered array of molecules that are characteristic of collagen structure. Wide angle X-ray diffraction (WAXD) on the other hand details the molecular breakdown of collagen. The relationship between fibrillar and molecular

degradation is clear; molecules that undergo scission will no longer contribute to fibrillar integrity. However, the pathway of this degradation is not yet clear.

The ratio of crystallinity from SAXS can be compared to the C:G ratio from WAXD to assess the fibrillar and molecular integrity of the samples. Figure 3 plots these values against each other. If a direct trend were observed, such as a low ratio of crystallinity from SAXS corresponding to a C:G ratio from WAXD, then the conclusion drawn may be that molecular and fibrillar degradation of collagen occur concurrently. However, a clear trend is not observed. One possible explanation for this is the existence of the pre-gelatinous state, whereby molecular degradation such as scission may have occurred but with the molecules remaining in roughly the same configuration as before damage; thus the electron density in the axial direction of the fibrils is not greatly altered and the meridional series of collagen remains strong, giving high crystallinity values.

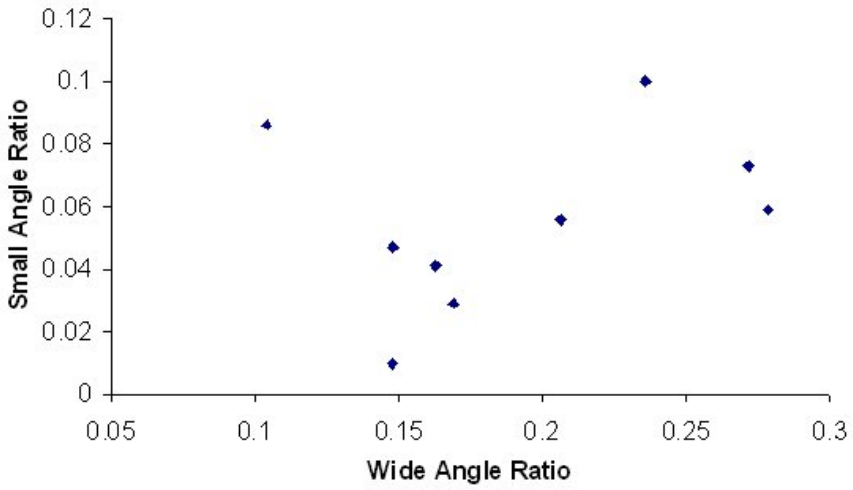

Figure 3. The ratio of crystallinity from small angle X-ray scattering versus the C:G ratio from wide angle X-ray diffraction. A clear linear trend is not observed from the sample set analysed, indicating that the degradation of the collagen molecules and fibrils does not necessarily happen concurrently.

Surface to surface analysis of parchment cross-sections

Using microfocus X-ray beams, surface-to-surface scans of parchment samples are possible. Depending on the thickness of the parchment, as many as 200 images may be taken in a single cross-sectional scan. Figure 4 displays the diffraction images from one such scan.

A detailed investigation of parchment structure in cross-section was given by Kennedy *et al.* (2004a, 32). In terms of collagen structure, this study showed that the alignment of

collagen fibrils were in the plane of the parchment, with little variation. Diffraction of non-collagenous components of parchment such as lipids and minerals were also observed by this method. Through a parchment cross-section, the d spacing of the lipids varies between 4.4 nm to 4.6 nm, suggesting variations in the hydration state or biochemical composition of the lipid; a multidisciplinary study of this phenomenon has recently been carried out (Ghioni *et al.* 2005). The presence of minerals in the parchment samples is shown by sharp peaks at very high angles of diffraction. Mineral phases were identified using PCSIWIN software and the International Center for Diffraction Data (ICDD) PDF-2 database. It was found that the minerals present were polymorphs of calcite such as aragonite and vaterite. These calcites probably originate from the parchment making process where skins are bathed in lime to remove hair, and often polished with chalk to alter the color and feel of the finished product.

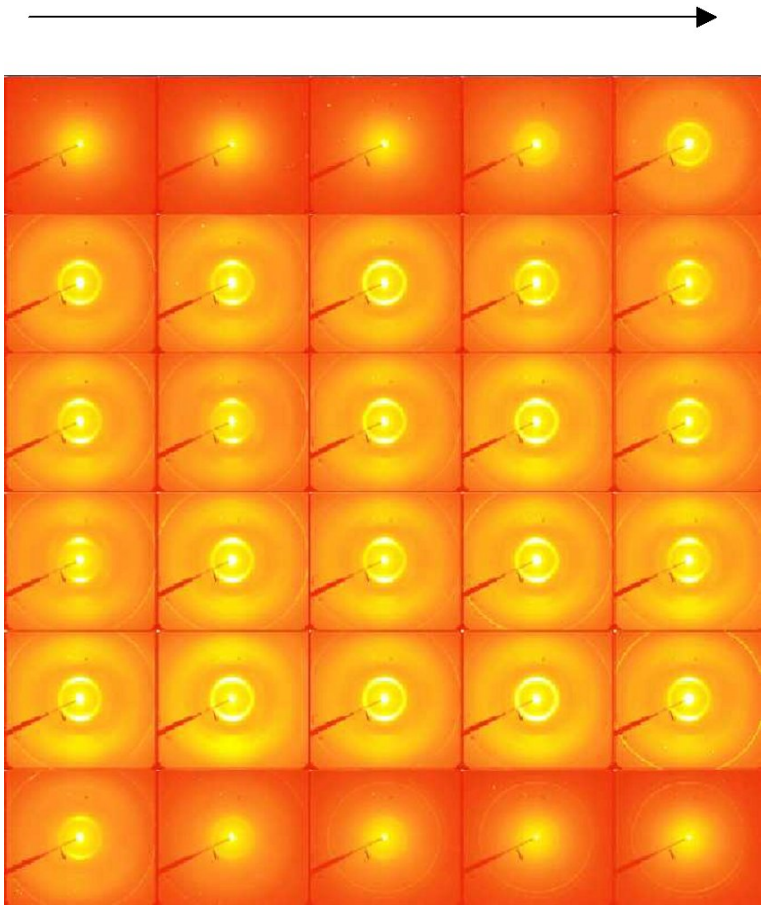

Figure 4. Composite of X-ray diffraction images from a scan through a cross-section of a parchment sample dated 1765. The images are organised into rows from top left to bottom right. Some images show sharp rings corresponding to minerals present in the sample. As the scan progresses towards the centre of the section, the collagenous component of the parchment sample becomes more apparent, and displays prominent reflections at 0.85 nm^{-1} and 2 nm^{-1} (inner and outer rings respectively).

The impact of cleaning parchment is an area of great importance to conservators, as using an inappropriate cleaning method may damage valuable historical documents. It may be the case that cleaning damages only a portion of the collagen in parchment near the surface; microfocus X-ray diffraction is a tool ideally suited to assess if this occurs with various cleaning techniques. Using the technique outline, cleaned parchment samples were analyzed from surface-to-surface, and the first point at which the C:G ratio is non-zero (i.e. not gelatin) was recorded. Cleaning the parchment with a sponge or an eraser alone do not appear to damage the collagen at the sample surface; however when cleaning is carried out in conjunction with relaxing agents such as ultrasonic humidifiers and isopropanol, damage to the collagen becomes apparent.

Conclusions

X-ray diffraction is a tool capable of providing a detailed insight in to the structure of parchment without the need for harsh sample preparation or destruction. Recent studies have allowed for characterization of the collagen in parchment, from degradation over time to the effect of cleaning methods. This technique may be an extremely useful tool in analyzing parchment from the Qumran; it has already been employed to assess textile fibres from the caves of the Qumran (Müller *et al.* 2004).

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CONSERVATION, SCIENCE AND SCHOLARLY COLLABORATION

Elena Libman, Tania Bitler and Pnina Shor

Israel Antiquities Authority, Jerusalem, Israel
E-mails addresses: libman@israntique.org.il; bitler@israntique.org.il; pnina@israntique.org.il

Abstract

Presented here is an interesting case of cooperation between conservators, scholars and scientists concerning the conservation, preservation and reading of 1Q Hodayot Scroll. Professor H. Stegemann provided the staff of the Dead Sea Scrolls (DSS) Conservation Laboratory of the Israel Antiquities Authority (IAA) with a copy of his invaluable reconstruction of the 1Q Hodayot scroll. The Thanksgiving Scroll consists of four substantial fragments and numerous small fragments, differing in shape and size, badly preserved and heavily gelatinized. These fragments were glued on paper, as a result of which they became rigid and cringed. After treatment their physical condition improved, but unfortunately, the process of gelatinization is irreversible, and some of the fragments still remain illegible. In the mid 1990's, Dr. Greg Berman, a scientist from NASA donated our lab a camera with an infrared lens which he developed especially for the decipherment of illegible scroll texts. The camera is attached to a computer, thus when placing the illegible fragments under the lens, the completely invisible texts come to life. The combination of Prof. Stegemann's reconstruction, together with Berman's infrared photos of the fragments enabled us to rejoin the broken fragments and then to incorporate them in their place within the larger four restored fragments. The treated and preserved fragments are now exhibited alternately in the Shrine of the Book among all of the other manuscripts restored by the Dead Sea Scrolls laboratory of Israel Antiquities Authority.

Keywords: Hodayot - Thanksgiving Scroll, Conservation DSS, Reconstruction, Infrared photos

This paper presents an interesting case of cooperation between conservators, scholars and scientists concerning the conservation, preservation and reading of 1Q Hodayot - the Thanksgiving Scroll.

In 1955, Professor Eliezar Lipa Sukenik of the Hebrew University first wrote the following: “The part which was opened first contains three sheets, each one with four columns, or a total of twelve columns… The second part of the “Thanksgiving Scroll” is a crumpled mass of about seventy detached fragments of leather of assorted sizes” (Sukenik and Avigad 1955). Sukenik published these fragments and the basic twelve columns separately. No attempt was made to deal with their sequence.

Professor Hartmut Stegemann began his reconstruction of the Scroll in the 1960's and succeeded to determine the sequence of numerous fragments. At the same time, Professor Emil Puech published his reading of the scroll. Both reconstructions coincided.

Professor Stegemann provided the staff of the DSS Conservation Laboratory of the IAA with a copy of his invaluable reconstruction of the scroll. The Thanksgiving Scroll consists of four substantial fragments (col. 1-4; 5-8; 9-12; 13-16) and numerous small and at times tiny fragments, differing in shape and size, badly preserved and heavily gelatinized. They are completely black, crumbled, stiff and very fragile pieces. A mass of substance that at times does no longer resemble parchment.

Professor Stegemann wrote that the: "… crumpled mass … was hidden for some time in some moist place, perhaps in the garden of Mr. Kando” (Stegemann 2000). In Professor Stegemann’s opinion Kando was the man who in 1947 sold to Professor Sukenik, three ancient scrolls, among them the Thanksgiving manuscript.

Later on these fragments were glued on paper. Once they dried out, both fragments and paper became rigid and cringed. The fragments were then placed in numbered envelopes, or wrapped up in the same paper they were glued to (Figure 1).

Unfortunately, this is how they were kept for many years until we began treating, one by one the scrolls housed in the Shrine of the Book, in the Dead Sea Scrolls Conservation Laboratory of the Israel Antiquities Authority (Figure 2).

When treatment began, we started to work on the four large fragments. First of all, in order to protect the fragment, the scroll's recto was reinforced by Japanese tissue paper with MC glue and a small quantity of distilled water. This procedure has an additional effect – the

slight moisturizing of the deformed convex areas of the parchment and the pressure exerted, enables us to flatten the fragments, facilitating further work with the parchment.

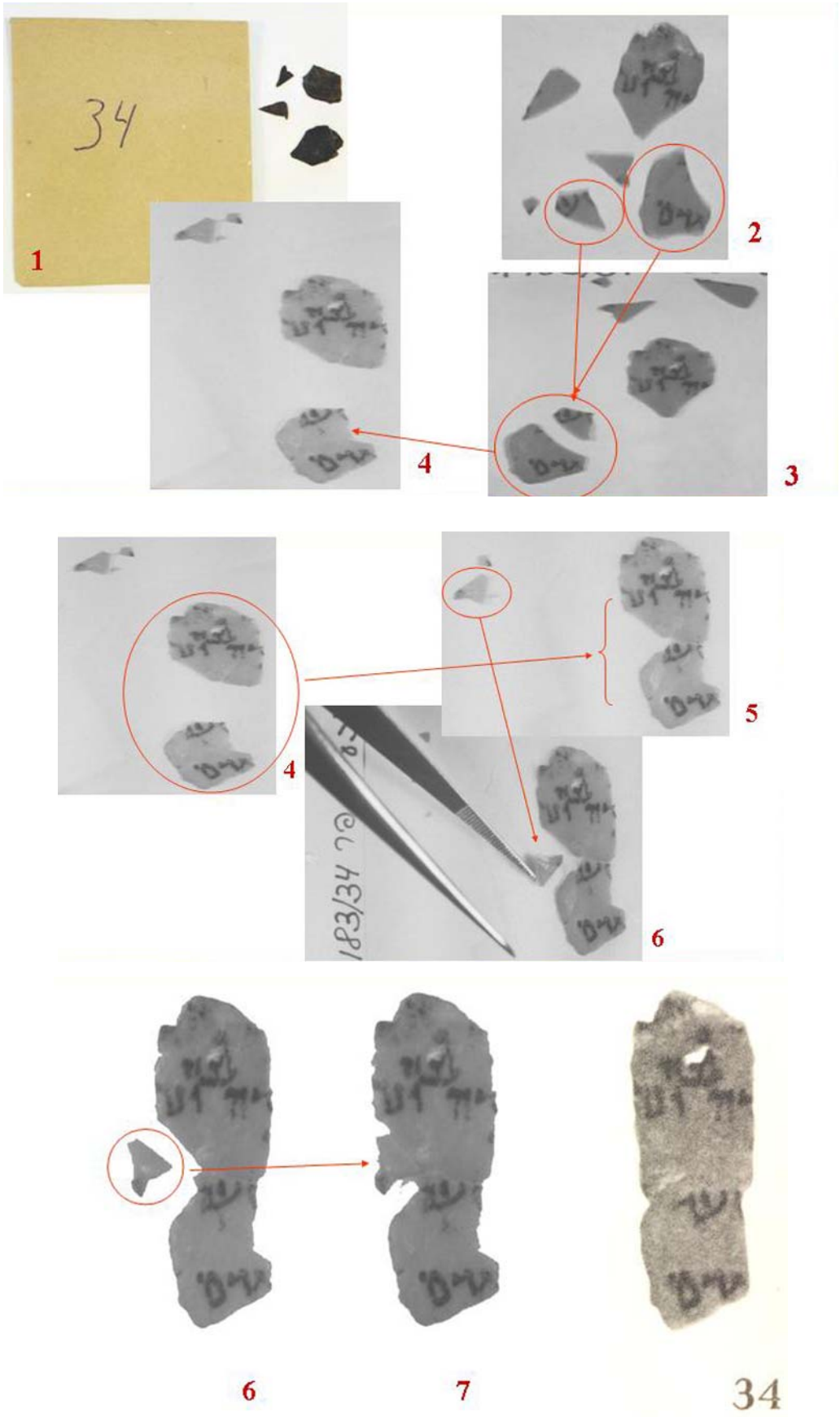
Figure1. Numbered envelopes containing fragments of the Thanksgiving manuscript.

Next, where possible, the old brittle “acid” paper was removed mechanically with a surgical scalpel. Obstinate patches were slightly moistened with 2% MC glue in water solution and then removed, again with the scalpel. Since the scroll is very gelatinized too much moisture might cause damage.

As we have no documentation about the previous conservation procedures of the scroll, the success in using MC glue with distilled water suggests that previously the glue that was used was PVA.

Some of the fragments went through a relaxation phase by slight moistening with Goretex, filter and silicon paper. Thus, their physical condition improved considerably and their mechanical strength increased. Unfortunately, the process of gelatinization is irreversible; therefore, we were unable to restore the original color of the parchment. Hopefully though, we have managed to slow it down.

Since it was impossible to recover the original appearance of the fragments, they still remained illegible. This is when science and scientists stepped in to aid. In the mid 1990's, Dr. Greg Berman, a scientist from NASA came to our lab with a camera with an infrared lens which he developed especially for the decipherment of illegible scroll texts. The camera is attached to a computer, thus when placing the illegible, as if carbonized fragments under the lens, the completely invisible texts come to life.



Figures. 2. Stages of reconstruction of the various pieces of fragment 34.

The additional advantage of working with such a unit is that once on the screen and in the computer, both scholars and conservators can manipulate the fragments, the first, to decipher and the latter to match and join the various fragments.

When the treatment of the small fragments began and we opened their envelopes and we observed that many of the fragments had deteriorated further more and had broken and crumbled.

Despair turned to joy when the idea of combining scholarly work with technology dawned on us. The combination of Prof. Stegemann's reconstruction, together with Berman's infrared photos of the fragments enabled us to rejoin the broken fragments and then to incorporate them in their place within the larger four restored fragments.

The treated and preserved fragments are now exhibited alternately in the Shrine of the Book among all of the other manuscripts restored by the Dead Sea Scrolls laboratory of Israel Antiquities Authority.

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DIGITAL NEAR INFRARED AND THE CONSERVATION OF THE DEAD SEA SCROLLS: THE GENESIS APHOCRYPHON

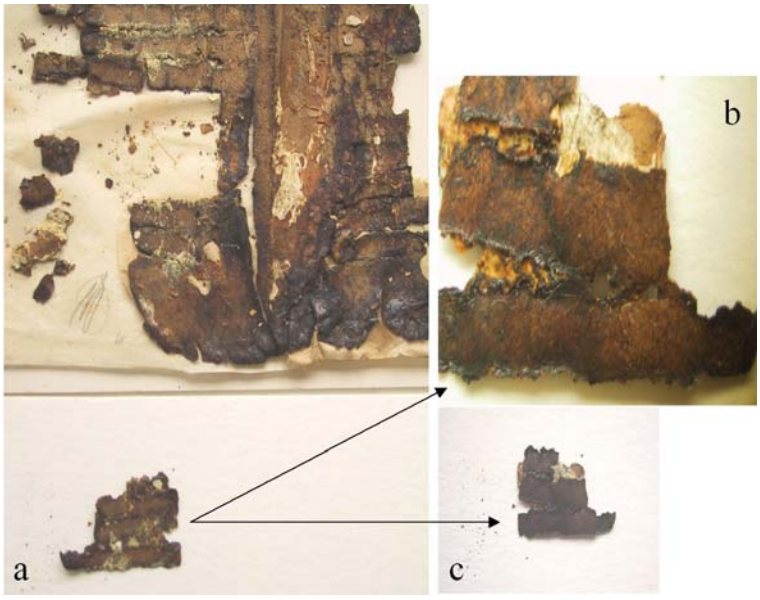
Michael Maggen

Paper Conservation Laboratory, The Israel Museum, Jerusalem, Israel
E-mail: michaelm@imj.org.il

When fragments of the scroll of Genesis Apocryphon were first observed by Yadin and his conservator Mr. Biberkraut, they noted that these fragments were in a very bad condition with comparison to the other scrolls. Genesis Apocryphon was found in a broken jar, which could be one of the causes to its advance deterioration state.

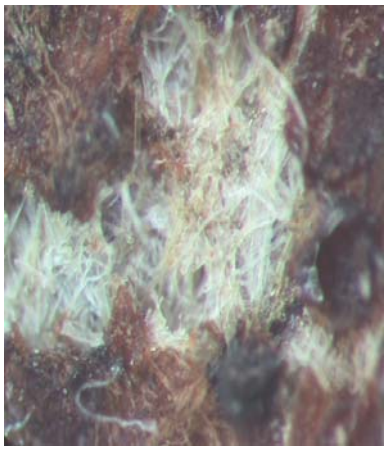
Digital photograph of the Genesis Apocryphon before restoration

Apart of the big losses of skin material the remains show high rate of gelatinization and darkening of the skin, mechanical deformation lost of flexibility and disintegration of skin layers. There were some fragment that shifted from their original location, and other small fragments that were found one on top of the other. Part of the surface was covered with a thin secondary skin substance, which masked the scroll text below. This layer could be the remains of the facing skin, which possibly could be stuck during the long time the scroll was still in a roll form disintegrating inside the unsealed jar. There were few conservation interventions in past to stabilized the rate of deterioration with these fragment. Apparently Mr. Biberkraut suggested at first to exclude any treatment due to the fragile condition of the skin. However observations of these fragments shows that they went through few conservation treatments. Part of the previous conservation practice concentrated with addition of few supporting layers; partly adhere strongly to the backing of the scroll. These extra layers were also in an advance deterioration state, primarily acidity and past microorganism activity namely foxing. The adoption of digital infrared video camera was found very efficient in documenting and mapping the fragment condition. The text, which could not be read by naked eye, could be seen very clearly under 750nm filter. Shadows of masked text could be traced and, in a few areas when the masked layers were revealed, the exposed remaining text could be deciphered. The old conservation supports were removed and replaced with a new flexible as lighter support system that put less pressure on the fragment. The fragment was finely inserted into two layers of synthetic mash that support the fragment from bottom and top.

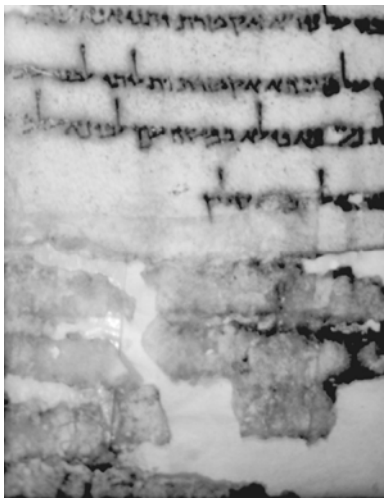


Parchment deterioration. (a) Disintegration and fragmentation; (b) Detail and (c) Detail - front & back

Ink deterioration



Analysis of the fibrous material



Fragment details viewed through infrared illumination (wavelength range: 650-1600 nm)

Digital photograph of the Genesis Apocryphon after restoration

CHARACTERIZATION OF ANCIENT PAINTING PIGMENTS USING SYNCHROTRON RADIATION

Nati Salvadó[1], Salvador Butí[1], Trinitat Pradell[2], Mark J. Tobin[3] and Emmanuel Pantos[3]

[1] Departament d'Enginyeria Química, Universitat Politècnica de Catalunya EPSEVG, Vilanova i la Geltrú, Barcelona, Spain

[2] Departament Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Edifici ESAB, Campus del Baix Llobregat, Castelldefels, Barcelona, Spain

[3] Daresbury Laboratory, Kecwick Lane, Warrington, UK

E-mail: e.pantos@dl.ac.uk

Abstract

One of the most challenging problems in characterizing pigments in ancient paintings is the presence of alteration products. These reaction compounds may be the result of the reaction of the pigments with the binding media, of the reaction with substances contained in the air or with impurities present in the paintings from the raw materials, or from the process of synthesis or purification followed in the pigment production. The detection of these compounds provides information of highest interest not only about the synthesis processes themselves, but also about the state of conservation of the pigments and painting and thus may provide clues for appropriate restoration and conservation. Finally, the type and amount of impurities present in the painting may give some indication on their geographical origin. Impurities and reaction compounds appear in small proportion and their determination with conventional analytical techniques is often difficult or even impossible bearing in mind the small size/weight of the samples. The high analytical sensitivity and high spatial resolution of synchrotron radiation based techniques, in particular, SR-XRD and SR-FTIR, allow the identification of the complex mixtures.

Introduction

The analysis of paintings is a challenging problem due to the small samples available, the complexity of the mixtures (organic and inorganic compounds), the great number of compounds present, and, the presence of impurities, reaction and aged compounds. Adequate sampling, sample preparation methods and, recently the use of synchrotron radiation has allowed the successful identification of ancient paintings materials. In particular, identification of aged compounds, impurities and reaction compounds is one of the difficulties with which we are faced. Impurities are present in the pigment either appearing as traces in natural pigments or as the result of the method of synthesis followed in synthetic pigments. In both cases their identification gives indication of the origin of the pigment. Another problem is the presence of aged compounds in the painting and, in particular, the organic part (binders and glues) of the painting where the effects of aging are more clearly evident. The study of the degradation and aging of the organic binders is fundamental in order to successfully identify the organic part of ancient paintings. Finally, the formation of reaction compounds resulting from the mixture of organic binders and pigments in particular, during the drying process and to a less extent afterwards produce new compounds which complicates the analysis.

The use of synchrotron radiation (SR) associated with the techniques of X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR), provides a number of advantages with respect to conventional radiation sources. SR allows focusing on areas of only a few microns, as a consequence of the high brightness and high collimation of the beam resulting in spectra with very good signal-noise ratio (Dumas and Tobin 2003, Williams 1995). In particular synchrotron radiation micro-XRD and micro-FTIR allows the successful identification of these compounds giving information about the origin, technology of production and stability and conservation of ancient paintings (Salvadó *et al.* 2002, 2004, 2005). We here present some examples of successful identification of such compounds.

Some examples are presented to show the capabilities of SR-micro XRD and SR-FTIR, in particular in the identification of impurities evidencing particular pigment synthetic processes; identification of mineral pigments; identification of reaction compounds during the drying process and also the identification of pigments/compounds present in extremely low amounts.

Materials and Techniques

SR-XRD measurements were taken at station 9.6 of the Synchrotron Radiation Source (SRS) at Daresbury Laboratory. This equipment has a very small (100 μm) beam footprint defined by the adjustable aperture of a collimator. The use of a CCD detector allowed two dimensional XRD patterns to be recorded at λ=0.87Å in transmission geometry over small fragments and thin sections too. A microscope alignment system allowed the location of the beam on the desired part of the sample. A translation stage attached to the phi-axis of the goniometer permitted the collection of two-dimensional compound maps of the thin sections.

SR-FTIR measurements were taken at the 11.1 infrared infrared microspectroscopy beamline of the SRS. The NEXUS FTIR Spectrophotometer is equipped with a Nicolet Continuum microscope, MCT detector, measuring range 4000-650 cm^{-1}. Spectra were obtained in transmission. Samples were pressed on a diamond cell. For each sample 128 scans were recorded with a resolution of 4 cm^{-1}.

We present here examples obtained from the study of the wall paintings (fresco technique) found in a rural Roman villa in Espelt situated in Catalonia (ancient Hispania). This site is in the middle of an agricultural area near a secondary road that made products for its own use but also export. The place was inhabited without interruption with more or less continuous activity from the first or second century BC until the 5th century AD. The paintings analysed are from the 2nd century AD, according to the archaeological data (Enrich 2004). We also present examples from the altarpiece of the Conestable from the chapel of Saint Àgata in Barcelona by the painter Jaume Huguet, one of the most important of the Catalan Gothic painters in the 15th century (Salvadó 2001, Salvadó *et al.* 2001). In the 15th century despite the beginning of a clear decadence, Barcelona was a political and commercial centre with great influence in all of the western Mediterranean and therefore was also open to influences.

The first example is the blue pigment found in the Roman wall painting from Villa de l'Espelt identified as a synthetic pigment known as Egyptian blue, where the presence of some impurities identified by SR-micro-XRD, is indirect evidence of the process followed in its synthesis. The second example corresponds to the identification of a natural pigment of extremely small particle size (ochre) from the same archaeological site. The third example corresponds to the reaction products obtained during a drying process, in particular, the influence of a magnesium containing compound (dolomite) in the carbonatation process of a Roman fresco from Villa de l'Espelt and the fourth example to reaction between the organic egg used as binder and the white lead used as pigment by Jaume Huguet. The fifth example

shows the capability of SR-XRD in the determination of compounds present in extremely low proportions, by the identification of the mixture of pigments that Jaume Huguet used (15th century AD) to produce a flesh colour.

Results

Figure 1 shows an XRD pattern obtained from the blue paint found in the Roman wall painting from Villa de l'Espelt. The blue pigment used was a copper calcium tetrasilicate ($CaCuSi_4O_{10}$) also known as Egyptian blue. This pigment is the first synthetic pigment produced by man about 2300 BC (Mirti *et al.* 1995, Baraldi *et al.* 2001, Riederer 1997). The XRD pattern shows the presence of calcite and quartz. Calcium hydroxide and quartz mixed with the pigment were applied to the wall and during drying a reaction of the calcium hydroxide with the carbon dioxide from the atmosphere resulted in the formation of calcite, and the pigment was fixed to the wall. The XRD patterns show the presence of small amounts of cristobalite. Cristobalite is a polymorph of quartz that forms at temperatures above 1000ºC. Cristobalite was formed during the sintering of the Egyptian Blue (Mirti *et al.* 1995, Baraldi *et al.* 2001, Riederer 1997) and is an indicator of the temperature reached.

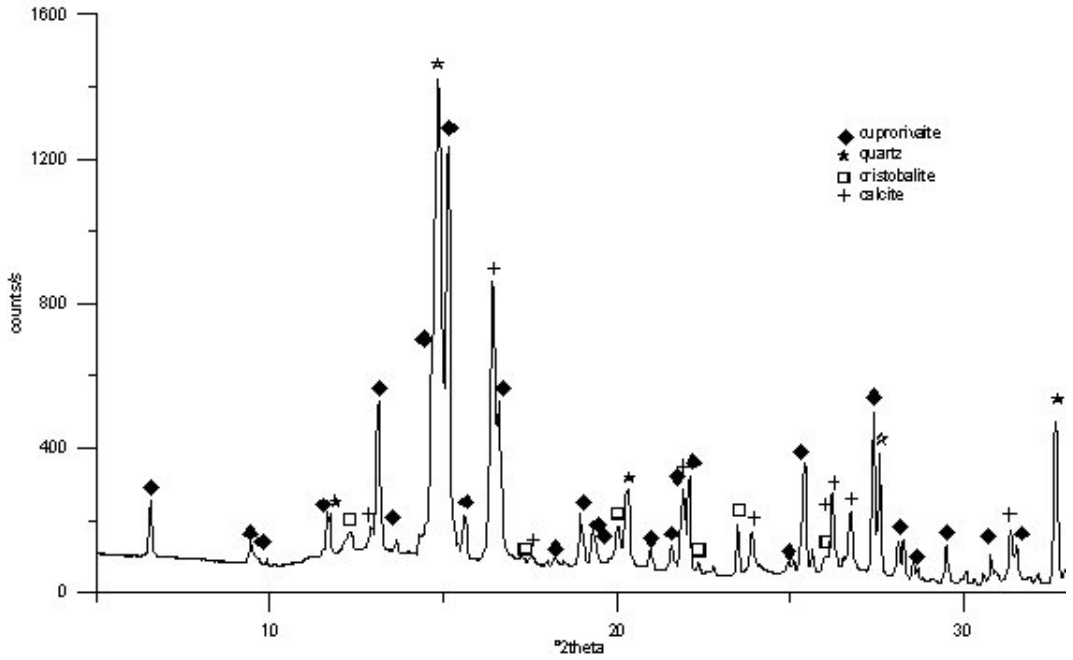


Figure 1. SR-XRD data obtained from the blue paint from the Roman Villa de l'Espelt. The blue pigment is cuprorivaite, a synthetic copper calcium silicate, known also as Egyptian Blue.

The SR-XRD pattern related to the ochre (Figure 2) indicates the presence of goethite which must be related to the use of iron rich sediment (Hradil *et al.* 2003). Goethite rich sediments were used as yellows to dilute or modify the green hues in roman frescos (Béarat and Pradell 1997).

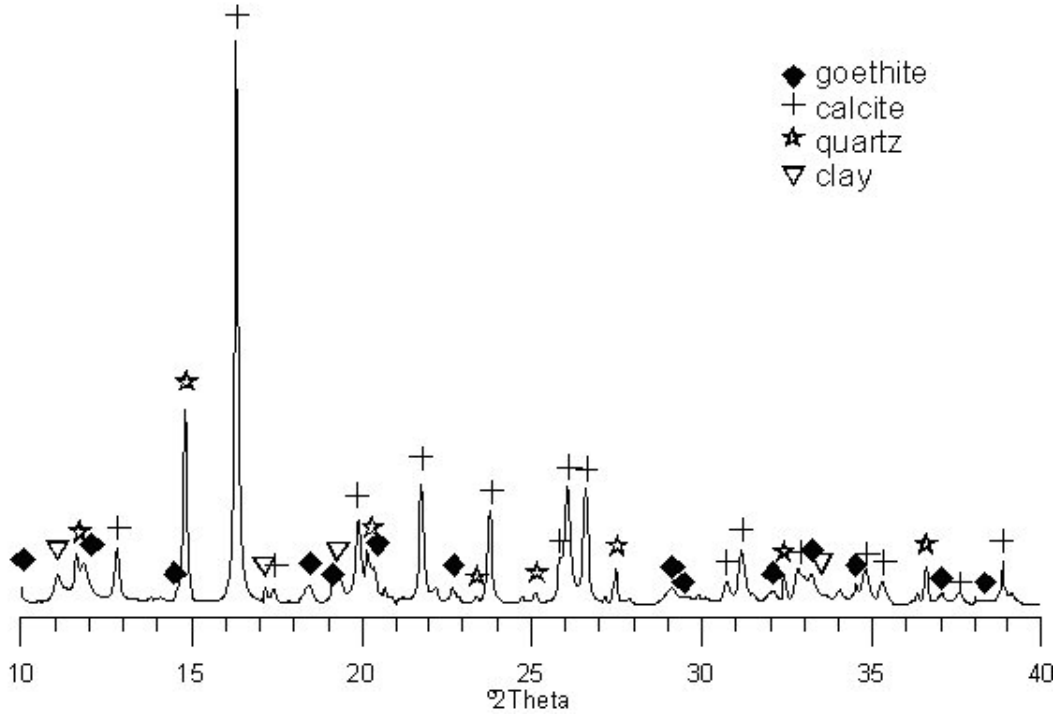


Figure 2. SR-XRD data obtained from the ochre paint from the Roman Villa de l'Espelt. The pigment corresponds to iron rich sediment, containing goethite of natural origin.

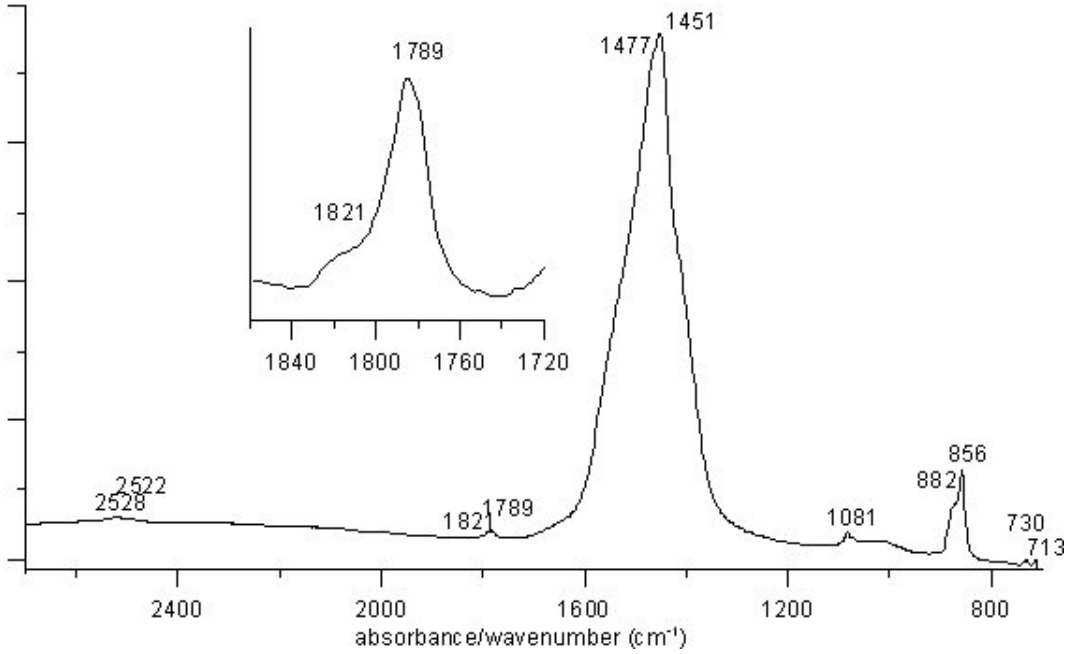


Figure 3. SR-FTIR obtained from the white paint from the Roman Villa de l'Espelt. Dolomite bands 2528, 1821, 1451, 1081, 882 & 730 cm^{-1}, and aragonite bands 2522, 1790, 1478, 856 & 713 cm^{-1}.

Figure 3 shows a SR-FTIR spectrum corresponding to the white pigment used in the Roman wall painting. The spectrum shows the presence of dolomite $CaMg(CO_3)_2$ and aragonite $CaCO_3$ (Jones and Jackson 1993). Dolomite is the natural white pigment used by the painter but Aragonite is a polymorph of calcite that forms under high pressures. However, the presence of Aragonite must not be related to this fact, it is known that under some special circumstances the precipitation of Aragonite instead of Calcite may also occur during the carbonatation process. In particular the presence of magnesium, which in our case is contained in the pigment, dolomite, may favour the precipitation of aragonite instead of calcite. However, aragonite should transform in time to the stable form calcite. The presence of aragonite may also vary the character of rock, in our case the properties of the fresco. The stability fields of calcite and aragonite are of great interest among sedimentologists, so it may be of interest in the study of the genesis and stability of these two polymorphs.

Figure 4 shows a diffraction pattern made on a thin section of a flesh colour painting from the scene of the Crucifixion from the Conestable altarpiece. In the figure we can see the presence of a white lead synthetic pigment, $PbCO_3$ and $2PbCO_3 \cdot Pb(OH)_2$, and the presence of some cinnabar (HgS) which gives a red tint to the painting giving the final flesh-like colouring. Cinnabar is present in very small amounts. It is also possible to determine the presence of very small amounts of calcium oxalates (weddellite). The presence of calcium oxalates must be related to aging of the binding media, in this case a protein of egg yolk. This was also identified by means of SR-FTIR. It is also worth noting that the chemical analysis obtained by an EDS (energy dispersive spectroscopy) analyzer attached to the SEM (scanning electron microscope) showed the presence of phosphorous, indicating that the protein was egg yolk.

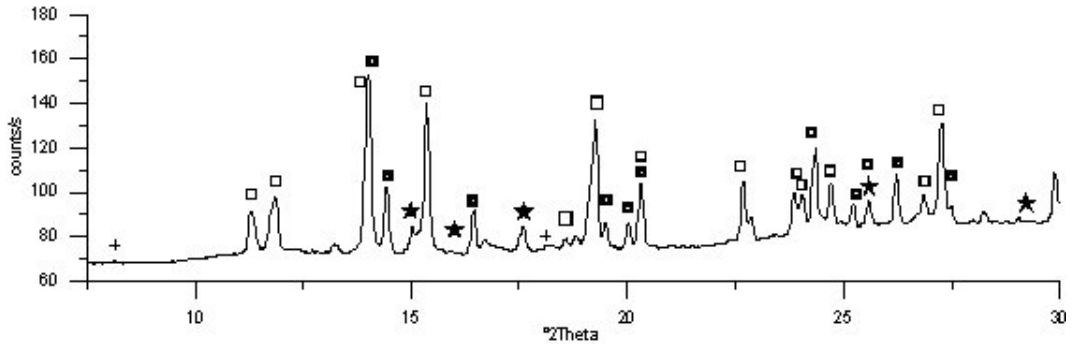


Figure 4. SR-XRD obtained from a cross thin section of a flesh colour from the scene of the Crucifixion from the altarpiece El Conestable, painted by Jaume Huguet.

Figure 5 corresponds to a SR-FTIR spectrum of the same painting as in figure 4 where the bands corresponding to $PbCO_3/2PbCO_3 \cdot Pb(OH)_2$ (677, 838, 1051, and ~1400 cm^{-1}/ 683, 780, 851, 1046, ~1410 cm^{-1}) are clearly seen (Clark *et al.* 1995, Gettens *et al.* 1986, Brooker *et al.* 1983). A band at 1516 cm^{-1} is attributed to the formation of carboxylate anions. We attribute these anions to a reaction compound formed by the reaction between the lead white and the fatty acids from the egg.

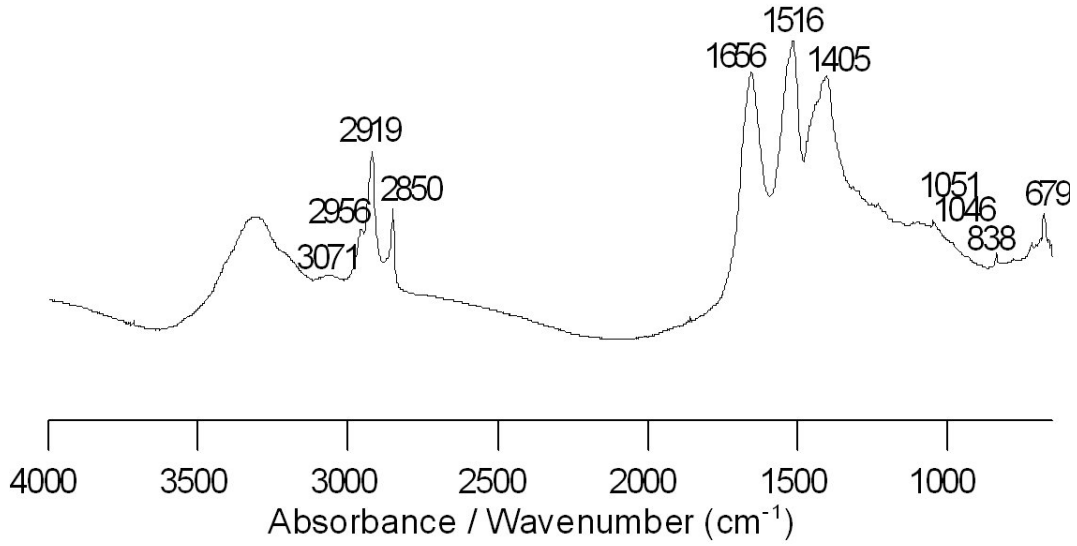


Figure 5. SR-FTIR spectrum corresponding to the same painting as figure 4 where the bands related to the lead basic carbonate are clearly seen. The extra band appearing at 1516 cm^{-1} must be related to carboxylate anions, most probably belonging to a reaction compound formed by the reaction between the lead white and the fatty acid of the egg yolk.

Conclusions

The combined use of synchrotron radiation micro-XRD and micro-FTIR allowed a full identification of pigments, organic binders, reaction compounds, impurities and aging effects of ancient paintings. Both Roman frescos and gothic altarpieces were studied and a selection of examples that clearly show the capabilities of the techniques are presented. In particular the identification of impurities gave valuable information about the particular pigment synthetic processes. The identification of reaction compounds during the drying process and result of aging are also of great importance to the stability and conservation of the paintings. Finally, the high resolution of the techniques allowed the identification of compounds present in extremely low quantities.

Acknowledgments

This work has been developed and funded by the Memorandum of Understanding Agreement between the Patrimoni UB-UPC (Universitat de Barcelona and Universitat Politècnica de Catalunya) and CCLRC-Daresbury Laboratory. We wish also to thank the "Museu de la pell d'Igualada i Comarcal de l'Anòia" and ArqueoCat for their assistance and permission to access the wall paintings from the Roman villa from Espelt. We would like to acknowledge Mr J. Pradell, restorer, for his advice and help in sampling and Mr J.M. Xarrié, Head of the Serveis de Restauració, de Bens Mobles (Generalitat de Catalunya), for the access given to sampling the altarpiece studied.

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A NOVEL APPROACH FOR CONSERVATION TREATMENT

František Peterka[1] and Petr Lukeš[2]

[1] Advanced Technology Group Prague, Czech Republic

[2] Institute of Plasma Physics, Academy of Sciences of the Czech Republic**,** Prague

E-mail: fpet@vol.cz

Photocatalytic surfaces based on titanium, with self-cleaning properties, which utilize light energy for the protection of architectural objects (including those of culture heritage) from the growth of biofilms, moss and leaches are in the process of being developed. Their application may even have other special advantages such as providing enhanced protection from vandalism.

A careful evaluation of this new conservation treatment is momentarily under trial within the working group “Conservation” of COST Action G8. It needs to be emphasized that for the verification of the coating performance and therefore its acceptance, the development of reliable standard testing methods is important.

Conservation of the Charles Bridge in Prague.

EDUCATIONAL SUITE AND DATABASE ON QUMRAN, THE DEAD SEA SCROLLS AND THE HISTORY OF THE SECOND TEMPLE PERIOD

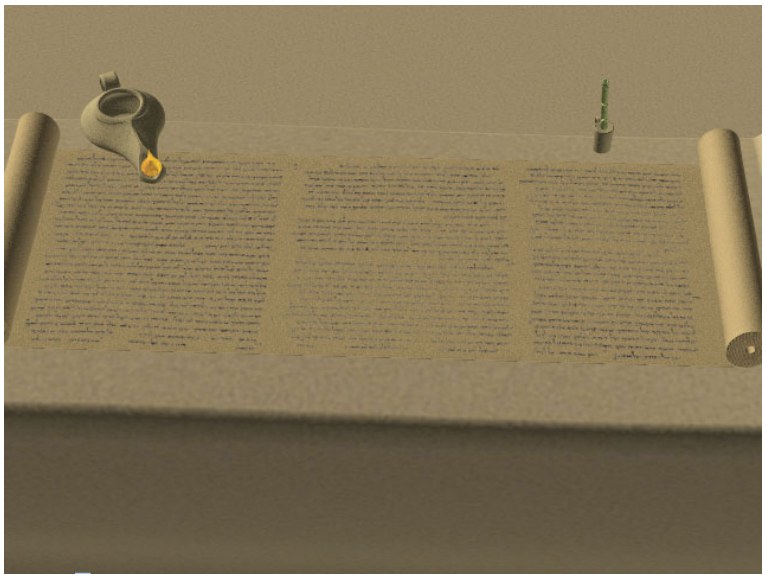
Stephen J. Pfann and Stephen Pfann, Jr.

University of the Holy Land, Jerusalem, Israel
E-mail: pfann@netvision.net.il

Introduction

The Dead Sea Scrolls, discovered more than fifty years ago, are certainly one of the most significant manuscript discoveries of all time. The scrolls, the people(s) who produced them and their associated sites of Khirbet Qumran and Ein Feshkha provide a fascinating locus of study for individuals of all ages from a wide range of disciplines. In order to bring the richness of this area of research out of the Holy Land and into the international classroom, office, and home, the University of the Holy Land has developed an educational, multimedia application focused on the history and peoples of Qumran and the Dead Sea Scrolls. This educational suite draws on a number of sources to reach a broad audience. It is intended to be able to teach and interest the inquisitive minds of high school level students, but at the same time to provide rich and in-depth information that will satisfy even the most experienced and learned scholar. The application provides engrossing, graphic user-interfaces that feature such aids as maps of Qumran and its surrounding area, fly-throughs of various locations, various three-dimensional enhancements and illustrations, and many more media to aid (and entertain) the user in his or her study. One of the main forms of interactive education is the archaeological virtual reality tour. Featuring both footage from the sites themselves, and their three-dimensional reconstructions, this interface allows users to explore Qumran and various other Essene communities. By navigating through the site, the user is able to access information via hotspots located throughout the map. This information includes a general description of the location and its significance for the community as well as the excavation

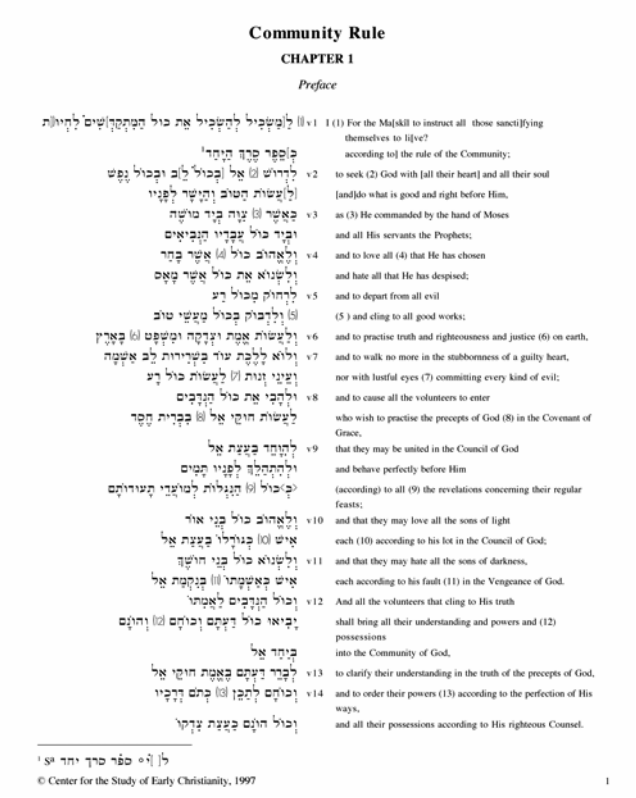
notes of each location within the site. These, in turn, link to additional information and aids such as photographs of the site, articles, and information regarding the material finds of the site including the pottery. The various transitions at Qumran are illustrated through the pottery, as well as through the manuscripts, which have been dated on the basis of both paleography and Carbon 14 testing. These dating sources are incorporated into a reconstruction of the Essene Community's historic timeline. This historic timeline illuminates the Essene Community's development, as well as providing a broader view of the history of the period, and serves as an aid to help the researcher navigate through this history. The user can utilize the timeline to link to various literary sources that speak of the Essene community including the Dead Sea Scrolls themselves and the writings of ancient historians such as Josephus, Philo and Pliny.



Qumran Multimedia Educational Suite. Credit: The University of the Holy Land

The project features access to all of Qumran's ancient literature in the newly formatted "Essene Library". The user may choose in which format he or she wishes to view the documents depending upon his or her level of expertise. If he or she wishes to simply read the translation of the text in his or her native language, he or she may choose the "Novice" level setting. To see both the vocalized Hebrew text of the Essene New Testament and its translation, he or she may choose the "Member" level setting. The "Scribe" level provides scholars with the ability to critically examine the Hebrew text alongside high-resolution photographs of the scrolls themselves. The user has access to such aids as an advanced search engine, extended bibliography, references and, perhaps of greatest use, to the Dead Sea Scrolls concordance. This concordance has been in development by the University for well

over a decade and is nearing its completion now. This concordance is the only one to be proofread and approved by the Dead Sea Scroll Editors themselves.



Community Rule

CHAPTER 1

Preface

לַ[מַּשְׂכִּיל לְהַשְׂכִּיל אֶת כול הַמִּתְהַלְּכִ]ים לְהִתְהַלֵּךְ	v1	1 (1) For the Ma[skil to instruct all those sancti]fying themselves to li[ve?
כְּ[סֵפֶר תּוֹרַת הַיָּחַד]		according to] the rule of the Community;
לִדְרוֹשׁ [2] אֶל וּבְכול לֵב וּבְכול נֶפֶשׁ	v2	to seek (2) God with [all their heart] and all their soul
[וְ]לַעֲשׂות הַטּוב וְהַיָּשָׁר לְפָנָיו		[and]do what is good and right before Him,
כַּאֲשֶׁר [3] צִוָּה בְיַד מושֶׁה	v3	as (3) He commanded by the hand of Moses
וּבְיַד כול עַבְדֵי הַנְּבִיאִים		and all His servants the Prophets;
וְלֶאֱהוב כול [4] אֲשֶׁר בָּחַר	v4	and to love all (4) that He has chosen
וְלִשְׂנוא אֶת כול אֲשֶׁר מָאָס		and hate all that He has despised;
לְהִרָּחוק מִכול רַע	v5	and to depart from all evil
וְלִדְבוק בְּכול מַעֲשֵׂי טוב [5]		(5) and cling to all good works;
וְלַעֲשׂות אֱמֶת וְצֶדֶק וּמִשְׁפָּט [6] בָּאָרֶץ	v6	and to practise truth and righteousness and justice (6) on earth,
וְלוא לָלֶכֶת עוד בִּשְׁרִירוּת לֵב אַשְׁמָה	v7	and to walk no more in the stubbornness of a guilty heart,
וְעֵינֵי זְנות [7] לַעֲשׂות כול רָע		nor with lustful eyes (7) committing every kind of evil;
וּלְהָבִיא אֶת כול הַנִּדָּבִים	v8	and to cause all the volunteers to enter
לַעֲשׂות חוקֵי אֵל [8] בִּבְרִית חֶסֶד		who wish to practise the precepts of God (8) in the Covenant of Grace,
לְהִיָּחַד בַּעֲצַת אֵל	v9	that they may be united in the Council of God
וְלִתְהַלֵּךְ לְפָנָיו תָּמִים		and behave perfectly before Him
כְּ[כול [9] הַנִּגְלות לְמוֹעֲדֵי תְעודָתָם		(according) to all (9) the revelations concerning their regular feasts;
וְלֶאֱהוב כול בְּנֵי אור	v10	and that they may love all the sons of light
אִישׁ [10] כְּגורָלו בַּעֲצַת אֵל		each (10) according to his lot in the Council of God;
וְלִשְׂנוא כול בְּנֵי חושֶׁךְ	v11	and that they may hate all the sons of darkness,
אִישׁ כְּאַשְׁמָתו [11] בְּנִקְמות אֵל		each according to his fault (11) in the Vengeance of God.
וְכול הַנִּדָּבִים לַאֲמִתּו	v12	And all the volunteers that cling to His truth
יָבִיאו כול דַּעְתָּם וְכוחָם [12] וְהונָם		shall bring all their understanding and powers and (12) possessions
בְּיִחַד אֵל		into the Community of God,
לְבָרֵר דַּעְתָּם בַּאֲמֶת חוקֵי אֵל	v13	to clarify their understanding in the truth of the precepts of God,
וְכוחָם לְהֵתֵּן [13] כְּתֹם דְּרָכָיו	v14	and to order their powers (13) according to the perfection of His ways,
וְכול הונָם כְּעֵצַת צִדְקו		and all their possessions according to His righteous Counsel.

[1] 1Q S ספר סרך יחד

Member level access to the Community Rule. Credit: The University of the Holy Land

Interaction with virtual Essenes. Credit: The university of the Holy Land

A number of educational games are incorporated into the program in order to aid the student in the task of learning. One such game calls upon the player to live as an Essene in the "Virtual Reality Qumran," thus bringing to life and into use, the lessons learnt about these people. The player must learn what he or she can and cannot do, and where he or she can and cannot go in the site, based on his or her own state of ritual purity. He or she must also interact with the Essenes themselves to succeed in fulfilling his or her goals and objectives in the game. Other games similarly require the user to interact with diverse inhabitants of the site from other periods. Ultimately this will help the user in the reconstruction and illustration of the life and worldviews of the different communities who occupied the site in its various phases.

Rationale

In order to better understand how to best reconstruct an ancient culture or society, three

main sources of information are sought by the historian: (1) primary literary sources written by the members of the group; (2) outside or secondary literary sources, contemporary with the group, which convey information about it; and (3) material remains which help to reflect the material world and thus the culture in which the group lived and, in particular, the unique character of the group itself.

It is rare that an ancient society can boast of the continued existence of all three of these sources. Happily, for the Essene movement all three of these sources exist in abundance.

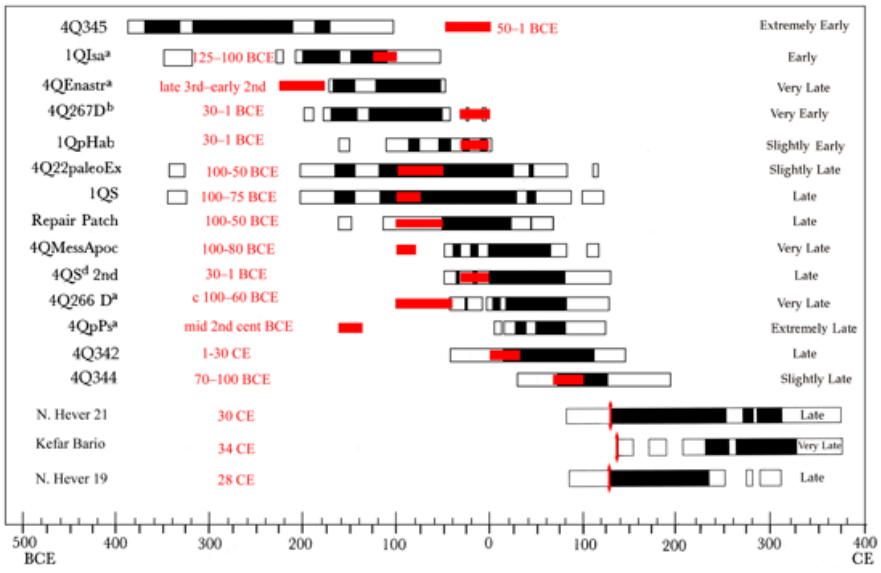
1. The residual remains of a once substantial library of thousands of manuscripts has left the modern historian with more than 800 manuscripts actually used, and at least in part produced, by the community. Besides these, some later copies of Essene books have survived in the Cairo Genizah. The sectarian documents among the Dead Sea Scrolls include rule books, liturgies and Biblical commentaries that provide important first-hand details for the historian.

Sectarian Rule Books. Credit: John Trevor

2. Ancient writers (Josephus, Pliny, Hippolytus, and Philo) were more or less contemporaries of the Essenes as well as of certain historical events, which directly involved them. In addition to these, there are references to the Essenes in other sources, such as the historical geography of Pliny the Elder.
3. The material remains, both architecture and artifacts, which have been derived from at least two Essene settlements—Khirbet Qumran and Ein Feshkha—are substantial. These provide us with an important witness concerning the life and religious practice of this group.

Material remains.
Credit: The University of the Holy Land

This project proposes to reconstruct as thoroughly as possible the daily life, as well as developments in the group's thought, self-definition and social composition based upon the three types of sources available. This is carried out by, first, setting the three sources side-by-side, using historical indicators of each to interlink them. These indicators include: (1) Paleographic, Carbon-14 dating, and other internal indicators for dating manuscripts; (2) the date of the composition of the secondary source or the sources upon which they rely; and (3) the stratigraphic sequence of levels at the archaeological sites linked to pottery, coins and other datable objects.



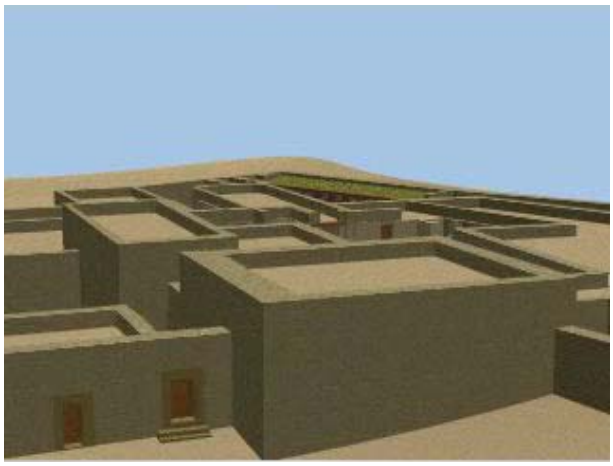
Radio Carbon dating. Credit: The University of the Holy Land

From the author's initial research it seems that the intentional changes and revisions in later copies of the key community documents reflect changes in the group's circumstances, thought and self-definition. When these changes are considered alongside the periodic changes in architecture, floor plan and material remains found at the community's settlements, a new and more complete picture emerges of the history of the Qumran community. Contemporary Jewish thought, religious practice and society are an important source for understanding the surrounding context of the Essene world.

The Database

Features of the Database

- Primary sources: The main sectarian Dead Sea Scrolls in vocalized Hebrew with English translations, together with other Jewish literary works not authored by the Essene community but preserved among the Dead Sea Scrolls
- A concordance to the texts of Dead Sea Scrolls
- Secondary sources: The historical accounts of Josephus, Philo, and Pliny
- The Hebrew Bible
- Background articles on various aspects of Essene life and literature
- Select photographs of the Dead Sea Scrolls and Cairo Genizah manuscripts
- Interlinked maps of the Holy Land in the last centuries BCE and first century CE
- 3-D models according to historical period of the community buildings at Kh. Qumran and the Temple
- Integrated historical timeline
- Images of the artifacts of the Qumran community
- A glossary of important Essene terms
- Suggestions for further reading and study
- The ability to print out select parts of the database, including the maps
- Five compatible interfaces which aid the user in accessing texts, photographs, articles and information



3D model of Qumran. Credit: The University of the Holy Land

Structure of the Database

- The Dead Sea Scroll Texts

At the heart of the Educational Suite are the Dead Sea Scrolls, presented in two major groups.

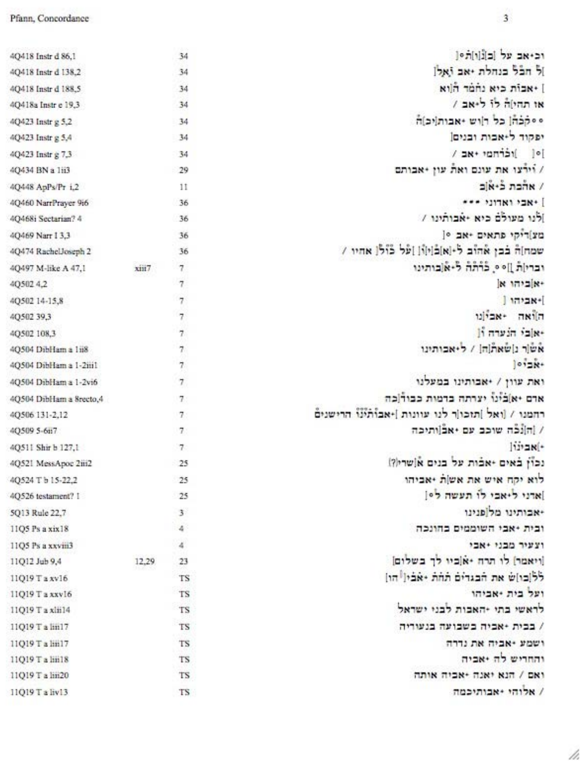
1. The major sectarian documents of the Dead Sea Scrolls, reconstructed from all the surviving manuscripts. The texts are preceded by a brief introduction to the Essenes and their literature. Gaps in the previously known text have been restored based upon unpublished and recently published manuscripts. The texts have been vocalized (vowel pointing added) by a member of the International Team of Editors of the Dead Sea Scrolls so that the individual who has a basic knowledge of modern or Biblical Hebrew can read these texts with ease. The English translation is written in language that conveys a Biblical flavor, helping the reader to more readily see the relevance of these texts to his or her own Biblical studies.

Dead Sea scroll text. Credit: John Trevor and The University of the Holy Land

2. The major Jewish, non-sectarian literary works among the Dead Sea Scrolls presented in their original Hebrew or Aramaic, together with an English translation. For the compositions already known from the Apocrypha and Pseudepigrapha (e.g., Enoch or Tobit), the cross references to the standard publications are given.
3. In addition, selected Rabbinic, New Testament and extra-biblical sources in English are provided.

- Concordance

The concordance is comprehensive for the documents presented in the Educational Suite. It includes the standard line reference (i.e., cave no., manuscript name, frg., col., line) for the non-sectarian texts, or the chapter and verse number for the sectarian texts; earlier reference numbers (e.g., as found in the Preliminary [Card] Concordance); cross references to known compositions (e.g., Jubilees, Tobit, etc.); both vocalized and unvocalized dictionary forms of the word; basic grammatical form of the word; Strong’s concordance number for the word (modified, and for use as a sorting tool); a quotation of the text according to colon/sense unit, with the word marked within the quote); and an English translation of the colon/sense unit.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4Q504 DibHam a 1ii8		7	אש]ר נ]שאת]ה / ל+אבותינו
4Q504 DibHam a 1-2iii1		7	+אבי◦]
4Q504 DibHam a 1-2vi6		7	ואת עוון / +אבותינו במעלנו
4Q504 DibHam a 8recto,4		7	אדם +א]בינו יצרתה בדמות כבוד]כה
4Q506 131-2,12		7	רחמנו /]ואל]תזכו]ר לנו עוונות]+אבותינו הרישנים
4Q509 5-6ii7		7	/]ה]נבה שוכב עם +אב]ותיכה
4Q511 Shir b 127,1		7	+]אבינו]
4Q521 MessApoc 2iii2		25	נכון באים +אבות על בנים א]שרי(?[
4Q524 T b 15-22,2		25	לוא יקח איש את אש]ת +אביהו
4Q526 testament? 1		25	]ארני ל+אבי לו תעשה ל◦]
5Q13 Rule 22,7		3	+אבותינו מל]פנינו
11Q5 Ps a xix18		4	ובית +אבי השוממים בחונכה
11Q5 Ps a xxviii3		4	וצעיר מבני +אבי
11Q12 Jub 9,4	12,29	23	]ויאמר] לו תרח +א]ביו לך בשלום]
11Q19 T a xv16		TS	לל]בו]ש את הבגדים תחת +אבי]הו[
11Q19 T a xxv16		TS	ועל בית +אביהו
11Q19 T a xlii14		TS	לראשי בתי +האבות לבני ישראל
11Q19 T a liii17		TS	/ בבית +אביה בשבועה בנעוריה
11Q19 T a liii17		TS	ושמע +אביה את נדרה
11Q19 T a liii18		TS	והחריש לה +אביה
11Q19 T a liii20		TS	ואם / הנא יאנה +אביה אותה
11Q19 T a liv13		TS	/ אלוהי +אבותיכמה

The annotated concordance to the Dead Sea scrolls. Credit: The University of the Holy Land.

- The Witness of the Ancient Historians

The pertinent passages from the ancient histories of Philo and Josephus; from the historical

geography of Pliny the Elder and from Hippolytus of Rome, are included in Greek, and accompanied by an English translation. Together these represent a substantial corpus of material describing the life, the beliefs and the practices of the Essenes.

Josephus Flavius.

- Articles

General articles are provided which will help the newcomer to the Scrolls begin his or her study. Topics to be treated include paleography, codicology, Jewish groups of the Second Temple period, Messianic Banquet, Midrash, Essene Community Structure, Purity, Calendars, etc.

Select Photographic Images of the Dead Sea Scrolls and Cairo Genizah

- Manuscripts

Representative photos of Dead Sea Scrolls held in the Israel Museum's Shrine of the Book and of related manuscripts from the Cairo Genizah collection are featured in the Educational Suite. In addition, video footage of the process of Scroll restoration provides a unique glimpse into the modern condition of the Scrolls.

- Maps

Interlinked maps of the Holy Land, with known Essene settlements demarcated, are provided.

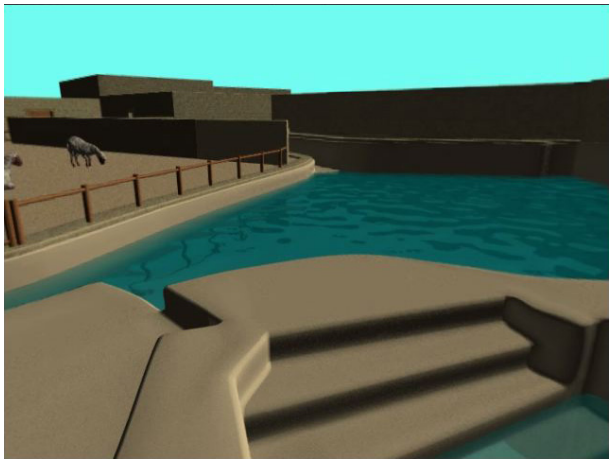
- 3-D Models and Virtual Tours

Two 3-D models, allowing the user to 'walk through' via computer imaging, are included.

1. The sites of Qumran and Ein Feshkha, reconstructed in detail according to the various periods of their occupation and including artifacts in the places where they

were found. The walls, doors, floors, ritual immersion pools, and contents of the library at Qumran change according to period.

2. A reconstruction of the Essene 'third Temple' as described in the Temple Scroll.



Virtual Tours of the Sites.
Credit: The University of the Holy Land

Both of the 3-D models are of special importance in drawing the younger viewers into the world of the Qumran community. A virtual tour of Qumran and its caves is provided. The student is able to "walk" the area of the Essene settlements of Qumran and Ein Feshkha, to enter the scroll caves (caves 1 through 11), and to visit the spring of Ein Feshkha.

- Integrated Historical Time Line

The time line reconstructs the history of the sect against the larger history of Second Temple Period Judaism and the Roman Empire. It also links the history of the sect to the descriptions provided by the secular historians and links the archaeological levels of the site with the compositions from each specific period.

- Images of the Artifacts of the Qumran Community

A rich visual library including photographic and slide images of the site of Qumran, the artifacts, the caves, the Scrolls, and other relevant items is presented together with video footage of Jerusalem and the Dead Sea region.

Archive jar. Credit: Shrine of the Book.

- Glossary of Essene Terminology

The Essene community utilized a number of terms (e.g. Yahad, Maskil, etc.) that had specific meanings within their community structure. The glossary provides the user with the nuances of these terms within the sectarian documents.

- Suggestions for Further Reading and Study

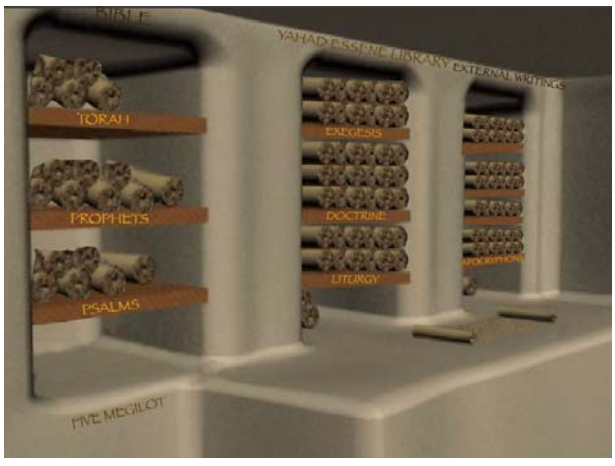
A bibliography of articles and books on the Dead Sea Scrolls is provided for users wishing to do additional research beyond the scope of the Educational Suite.

The Interfaces

- The Textual Interface

The viewer enters the literature of the Essenes through a 3-D reconstruction of the library from Qumran. In it he or she will find a bookcase of scrolls, presented according to the various phases in the site's history and organized according to genre. The cubbyholes of the bookcase include:

1. Data for understanding the genre and contents of all the scrolls in the library.
2. The statistics as to how many copies of a given document were found in each period and in toto.
3. Links with articles covering specific documents found within the library.
4. Charts comparing the overlap of fragments from different manuscripts of the same composition.



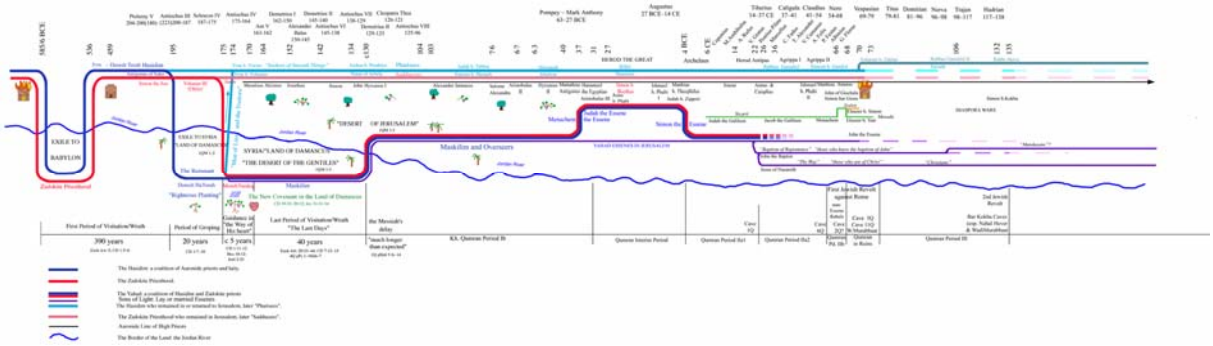
Library interface Credit: The University of the Holy Land

- Historical Time Line Interface

By means of an interactive time line extending from about 200 BCE to 100 CE, the user can place the Essenes, their literature, and the use of the community site at Qumran within the framework of the major political periods of secular history. The time line integrates three

major components historically:

1. The Scrolls, with the various copies of the individual works dated paleographically, thus charting the relative histories of the compositions
2. The stratigraphy of the various elements found at the sites of Qumran and Ein Feshkha
3. The accounts of the ancient writers placed in chronological order. By selecting a particular section of the time line, the user is presented with all the data associated with that period: scrolls, archaeology of the site, material remains, histories, and helpful background articles.



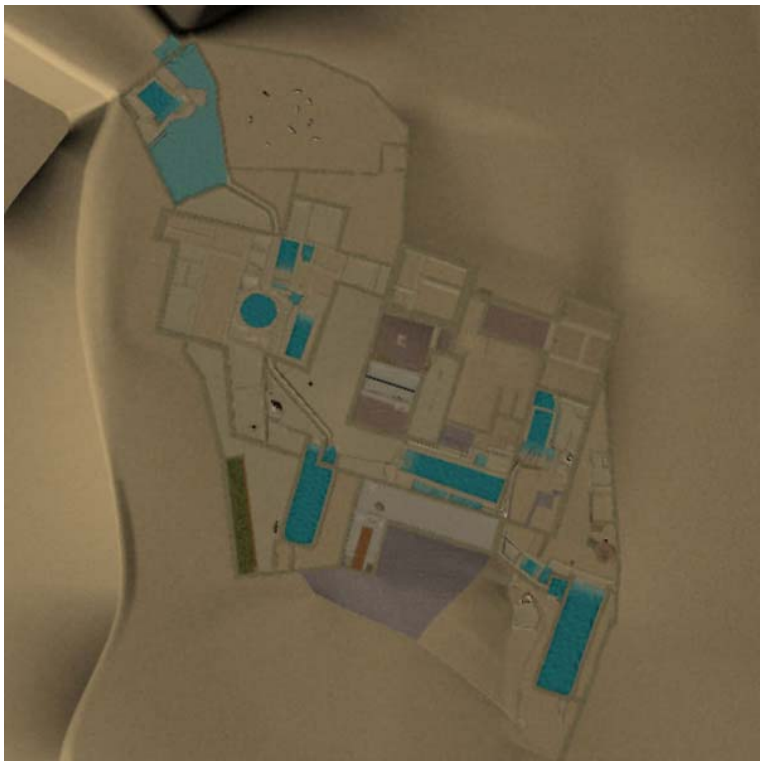
Historical timeline. Credit: The University of the Holy Land.

- Map Interface

From a 3-D, fly-over map of the Holy Land, the user can move to a map of Judea with known or suspected Essene sites demarcated, and then to a series of maps of the site of Qumran during the various phases of its existence. By interacting with the hot spots marked on a given map, the user can explore the use of the community site in the phase represented, view the archaeological remains of that period, and access the literature associated with that phase. The maps include:

1. The Judean desert with likely Essene camps demarcated.
2. The Qumran region and caves (double-click on caves for pictures and lists of contents)
3. Qumran and Ein Feshkha top plans, linked to database and pictures of finds, other maps, pictures of various areas, 3-D reconstruction and information cards
4. Enlargements of integrated areas of Qumran and Ein Feshkha (linked to the same data as in no. 3)

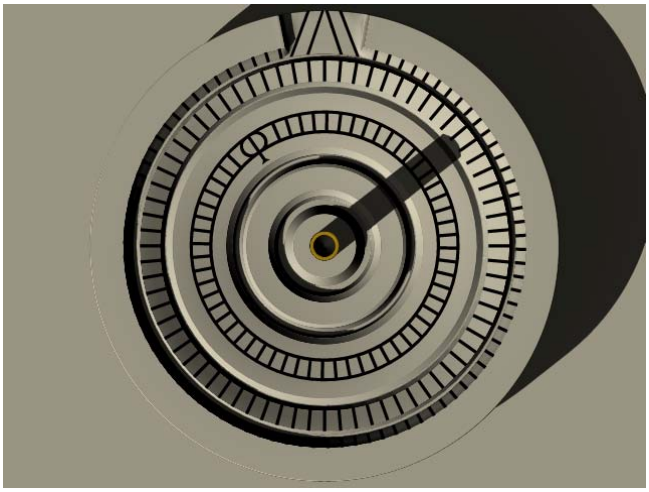
The 3-D models allow for a ‘walk-through’ of the site and change according to modifications performed at the various stages in the evolution of the Essene community’s history.



Map interface. Credit: The University of the Holy Land

- Sacred Time: Sundial and Calendar

The calendar interface introduces the user to the Qumran community through its liturgical year, based upon the calendars found in the Qumran caves and the sundial found at the site. The liturgical year is represented graphically by a circular calendar of fifty-two weeks. By double-clicking on a particular week, that full week at Qumran will appear on the screen. The week-at-a-glance is shown with special days such as feasts, if any, indicated, as well as the readings from the liturgical documents of that week. The reconstruction of the daily schedule is based on the descriptions in the sectarian scrolls, the archaeology of the site, and the accounts of the ancient writers.



Sundial. Credit: The University of the Holy Land

- Natural Setting

Qumran and its people(s) represent an important part of the larger natural environment of the Dead Sea region. Their interactions with the environment can be seen in both their agricultural works as well as the locations they chose to call home. To understand their lifestyle, it is necessary to understand the **natural** environment in which they lived. To this end, the database provides abundant information about the flora and fauna of Qumran, the oasis of Ein Feshkha, and various other areas in the Judean Desert. Detailed scientific descriptions, illustrated with color photographs, tie the various plants and animals into the broader view of the regional ecosystem, and amplify the interaction between man and nature in this wilderness. This picture is further enhanced through an examination of the material remains from the sites, such as the organic food remains.

Wild date palm. Credit: The University of the Holy Land

FUNGI AND CULTURAL HERITAGE

Itzhack Polacheck

Department of Clinical Microbiology and Infectious Diseases, Hebrew University – Hadassah Medical School, Jerusalem, Israel
E-mail: polacek@md.huji.ac.il

Fungi are a major agent in the destruction of cultural heritage by their ability to degrade biopolymers, including collagen (parchment, like the Dead Sea Scrolls), cellulose (paper and wood), chitin (insect collections and shells) and keratin (hair and horn). The hyphae and resulting mycelia invade articles of historical importance and cause them to decay. Any organic material or manufactured product can provide a source of carbon and energy to the invading fungus. Cellulose - the most abundant biological material on earth - is a prime source of energy for many fungi. Therefore, cellulose-based materials, including paper, wood and cotton products, are at risk. Proteinaceous materials - the 2nd most abundant substance - such as leather products (parchment and scrolls) are also particularly susceptible to direct attack by molds.

Generally, fungal attack is favored by high humidity or abundant moisture and warm temperature. The decomposition of biopolymers occurs through the induction and secretion of unique exo- and endo- hydrolyzing enzymes for each biopolymer. Exo and endo cellulases first cleave the cellulose polymer into shorter linear chains of oligomers. These oligomers are converted to cellobiose, and cellobiose by cellobiase to glucose by cellobiase. There are three types of mold damage: surface damage, discoloration, and structural destruction. Some of these activities can be easily detected while others are subtler.

An example of this damage is seen in the Aleppo Codex (Figure 1), where the culprit, thought at first to be fire, was an *Aspergillus* (Figure 2). The Aleppo Codex, the earliest known manuscript of the Hebrew Pentateuch, was written on parchment in Tiberias in the 10th Century. After a period in Jerusalem and Egypt it was kept for 600 years in a synagogue in Aleppo. In 1947 the synagogue was set on fire. The deterioration and fragmentation in the

outer lower corner could be attributed to the effect of the fire. However, appearance of the deterioration in a photo from 1910 and the pattern of aubergine discoloration and brittleness of the outer lower corner are more characteristic of damage caused by fungi. This suggested that fungi, and not fire, caused the damage. Proof of fungal invasion was obtained by microscopy (Figure 3). The manuscript was exposed to ethylene oxide to prevent further damage.

Figure 1. A page from the Aleppo Codex showing typical discoloration and deterioration in its outer lower corner

In other cases, paper manuscripts and works of art are attacked by *Trichoderma, Penicillium* and *Chaetomium* (Figure 2). Most of the practical disinfection methods require the use of hazardous chemicals. Current decontamination processes include thymol (orthophenyl-phenate), formaldehyde, ethylene oxide, carbon dioxide and gamma irradiation. All these are hazardous to health and/or the environment, the equipment is expensive and durations of treatment are relatively long.

We have suggested an alternative non-hazardous disinfection method based on natural crushed garlic. Its effectiveness can be seen in the following simple experiment. Two contaminated items - a paper blotter (cellulose), which has been left damp for 2 weeks and

became contaminated by various fungi (Figure 4a), and an old moldy book – were utilized. After being exposed for 24 hours to a 20% volume of crushed garlic, the paper blotter did not show any contamination (Figure 4b). The moldy book was sealed in a polyethylene envelope containing 20% volume of fresh crushed garlic. No fungal activity was observed in different parts of the book (paper leather and cloth) after exposure for 24 h. These results show that fresh crushed garlic effectively eliminates viable fungi, and suggest that new methods of prevention and treatment based on non-hazardous natural products can be developed.

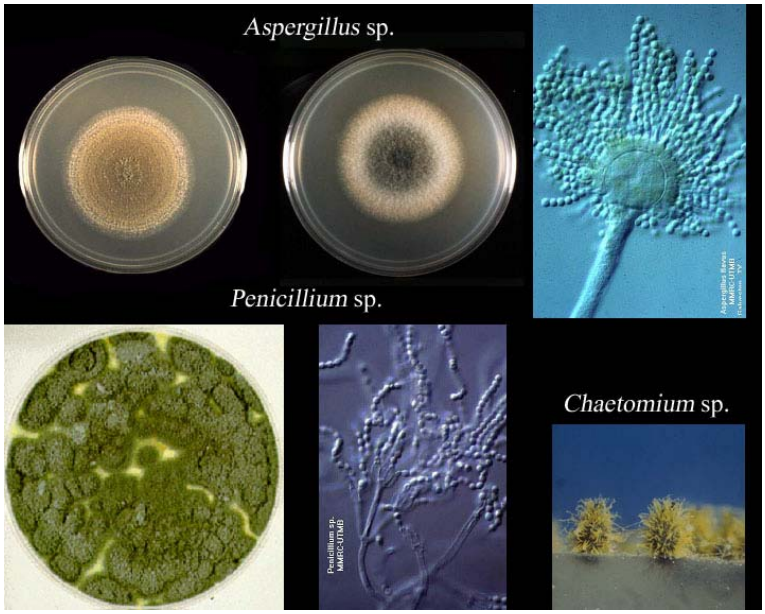


Figure 2. Different fungi that attack paper manuscripts and works of art

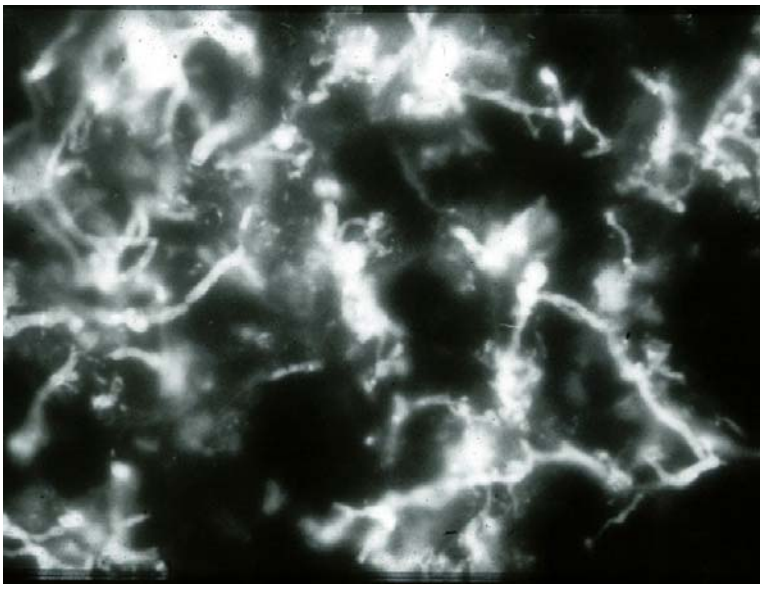


Figure 3. Fluorescence photomicrograph of fungus-like filaments from the damaged areas of the Aleppo Codex. Preparations mounted in the fluorescent fungal stain *Cellufluor* (Polysciences), KOH and glycerol (600x).

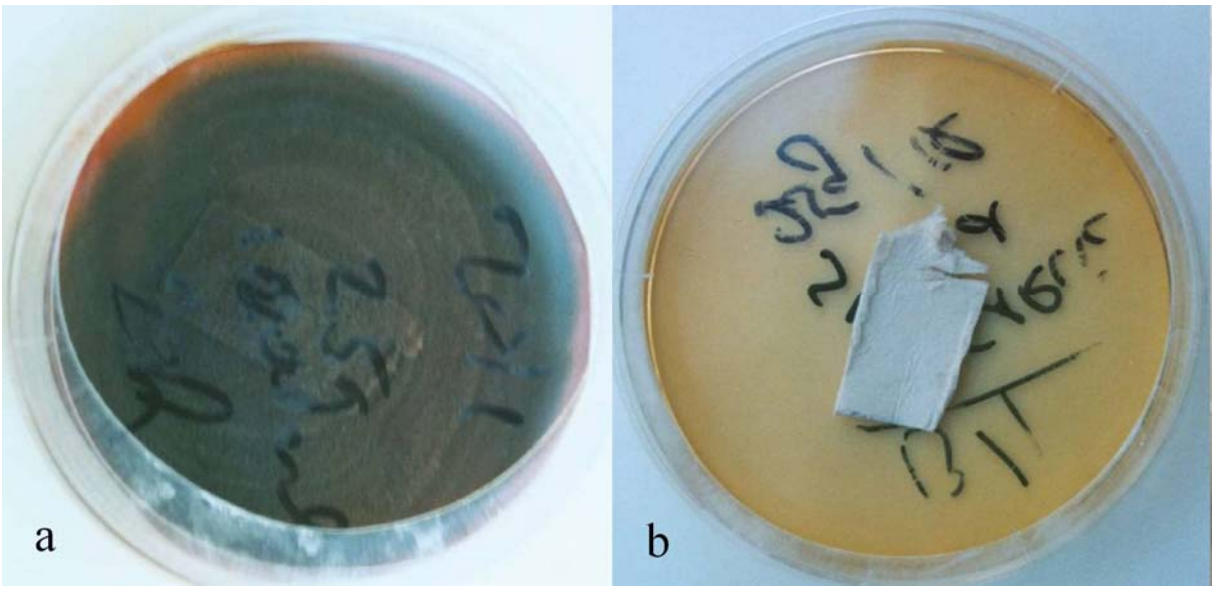


Figure 4. New method of prevention and treatment based on non-hazardous natural product

a) Contaminated blotting paper - control

b) Contaminated blotting paper exposed to crushed garlic 20%

MICROSCOPY AND PARCHMENT DEGRADATION: A COMPARATIVE STUDY

Ira Rabin[1] and Steffen Franzka[2]

[1]Israel Antiquities Authority, Jerusalem, Israel
[2]Universität Duisburg-Essen, Essen, Germany
E-mail: rabin@fhi-berlin.mpg.de

Abstract

The aim of our study is to assess the state of parchment preservation by means of microscopy. To this end, we investigated samples of new, artificially aged, and naturally aged parchment by scanning electron microscopy (SEM), atomic force microscopy (AFM), confocal microscopy, and light microscopy. Structural differences between the parchment surface and its bulk revealed by SEM and AFM topographies suggest that damaged surface acts as a protective shield to the bulk. Moreover, we found that compactness and regularity of the collagen fiber network can serve as simple and reliable criteria to assess the damage of parchment specimens. Particularly, confocal microscopy can be used to image the superstructure characteristic of the bulk and to distinguish it from the one found in the outermost surface layer.

Introduction

Degradation of parchment has been the object of studies for many years. Parchment starts degrading from the very moment the manufacture process is over. Therefore, an operational definition for the state of parchment preservation would be desirable. Monitoring changes in parchment mechanical properties could form the basis for such a definition. Indeed, studies on parchment deterioration and its effect on the mechanical properties are known (Fuchs *et al.*

2001, Odlyha *et al.* 2003). On the other hand, chemical analysis could supply information about the state of the collagen molecule (Weiner *et al.* 1980, Larsen *et al.* 2002a, 2002b). Furthermore, it is well known that a specific fibrillar form of arrangement enhances the strength of collagen molecules in tissues. With the help of X-ray diffraction measurements, the periodicity of collagen molecules in the fibrils of intact parchment has been established (Wess and Orgel 2000, Kennedy and Wess 2003).

We have approached the issue of degradation through the study of parchment super structure by means of microscopy. To this aim, we investigated samples of new, artificially aged, and naturally aged parchment by scanning electron microscopy (SEM), atomic force microscopy (AFM), confocal microscopy, and light microscopy. None of these techniques requires any special preparation of parchment samples. Thus, we were able to avoid overlapping effects due to sample preparation. The second aim of our study was to compare the information delivered by each technique. Since mechanical properties mainly correlate with the state of the bulk, we were particularly interested in comparing the surface layer, which is usually subjected to most environmental influences, to the bulk. Last, but not least, we wanted to address the question of which technique could detect the earliest possible stage of degradation.

Experimental

In this study we have used modern parchment obtained from goatskin as a reference. Artificial ageing has been carried out for 10 day at 50C under irradiation with UV light at 255nm. Naturally aged samples comprised samples of goat parchment from 17^{th} to 19^{th} century and Qumran (1^{st} century AC). No special preparation was used prior to microscopic imaging.

Scanning electron microscopy was performed with Phillips SEM 505 equipped with a detector for back-scattered electrons. The samples were mounted in a high-pressure chamber.
Atomic force microscopy was performed with either Veeco MM Nanoscope IIIA or Veeco CP Research devices. Due to the limited dynamic of AFM's, only the flesh side of parchment samples could be inspected. To investigate the bulk structure, we removed the uppermost layer of some samples by microtome.

Confocal microscopy was performed with Zeiss LSM 410 instrument. We used light at 488 nm to excite the sample, and detected the fluorescence in the red part of the visible spectrum (> 600 nm).

Results and discussion

The fibrous structure of fresh parchment is well resolved in SEM images of the surface (Figures 1a and 1c). On the grain side, the rounded portions correspond to hair follicles. The structure is dense and the fibers are long. Figures 1b and 1d present images of the grain and flesh side of an artificially aged parchment sample. Here the sample surface seems to be covered by a smooth, semitransparent layer. The intact collagen structure is clearly seen through cracks in this layer. This layer appeared after the process of artificial ageing. It can be also seen in AFM images of the same sample (Figures 1e and 1f). The height differences on the grain side are beyond the dynamic range of the AFM, which constrained the use of AFM to the flesh side. The fine structure shown by the surface topography of the fresh parchment is absent in the topography of the artificially aged parchment. Here the surface seems molten or covered by an unstructured material. This layer has been also observed by light microscopy and named “glassy layer”. It seems to be the very first manifestation of structural change due to parchment degradation: the transformation of collagen into gelatin.

The formation of the glassy layers is also found in naturally aged parchment as clearly demonstrated by the scanning electron micrograph of a parchment sample from 17th century (Figure 2a). In contrast, a much older and severely damaged Qumran sample exhibits only the rests of this glassy layer. In addition, here we observe a loosening of the fibers network as compared to the intact one found in undamaged parchment (Figures 1a and 1c).

The bulk microstructure of the same samples was studied with the help of atomic force microscopy. In Figure 2c we find intact fiber structure of the parchment sample from the 17th century after the glassy layer has been removed with the microtome. Moreover, both the characteristic periodicity of collagen fibrils and the onset of fibers fragmentation are seen at the same time. In comparison, the advanced stage of degradation of the Qumran sample is manifested by the absence of long fibers. The short fragments, however, exhibit the characteristic periodicity and seem to be intact (Figure 2d).

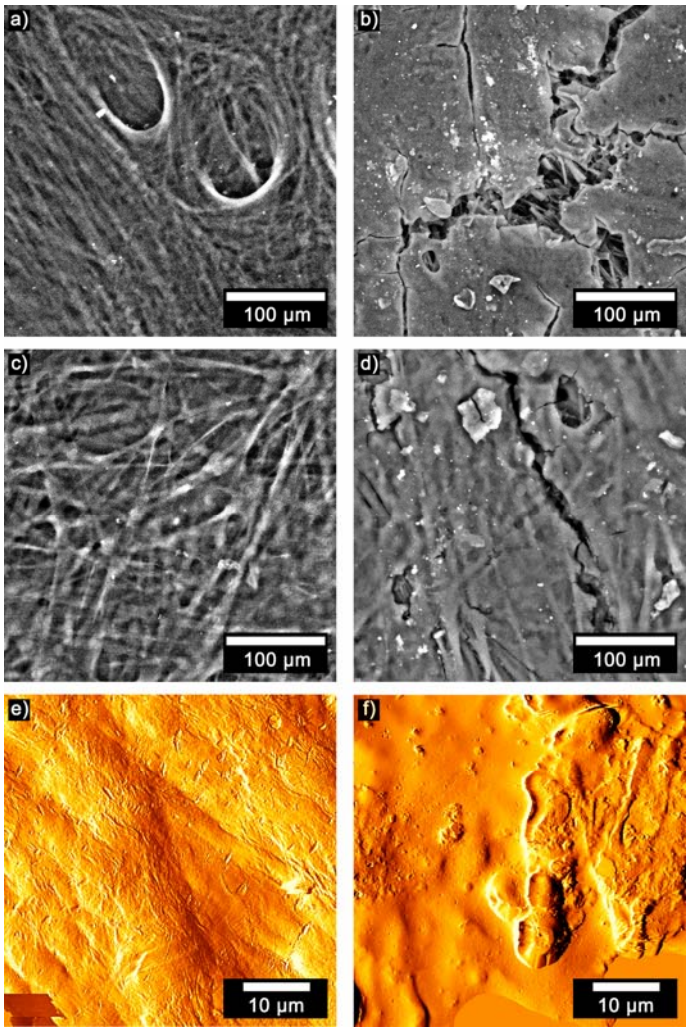


Figure 1. SEM (a-d) and AFM (e, f) images of goat parchment: fresh and artificially aged samples are on the left and right side, respectively. (a) SEM image of grain side (fresh), (b) SEM image of grain side (artificially aged), (c) SEM image of flesh side (fresh) (d) SEM image of flesh side (artificially aged), (e) AFM in contact mode, shaded image of topography, fresh parchment: flesh side, (f) AFM in contact mode, shaded image of topography, artificially aged: flesh side

Based on the evidence shown in Figure 3, we believe that damage first occurs on the parchment surface and leads to the formation of a “glassy layer” or gelatin film. This film has a protective function toward the bulk of parchment, i.e. it protects the underlying collagen structure from further deterioration. In Figure 3a we present a detail of the image shown in Figure 1e, i.e. the AFM topography of the flesh side of a fresh parchment sample. Here, one sees the typical structure of single fibrils in a healthy parchment. It is impossible to detect such a structure on the surface of an artificially or naturally aged parchment. The intact structure is, however, found when the upper surface layer is removed. This is shown in Figure 3b, in the detail of the topography of an artificially aged sample whose upper layer has been cut off with the help of a microtome. The periodicity of collagen molecules is found to be in the range of 60-62 nm. It is slightly lower than the values (64-65 nm) determined for the fresh parchment from Figure 3a. The decrease of the periodicity number might indicate that ageing process was accompanied by some dehydration (Wess and Orgel 2000). The bulk of the naturally aged samples from the 17th century and Qumran displays a periodicity of the same

order of magnitude (60-64 nm and 60-65nm, respectively), which fact points to the presence of the intact fibrils.

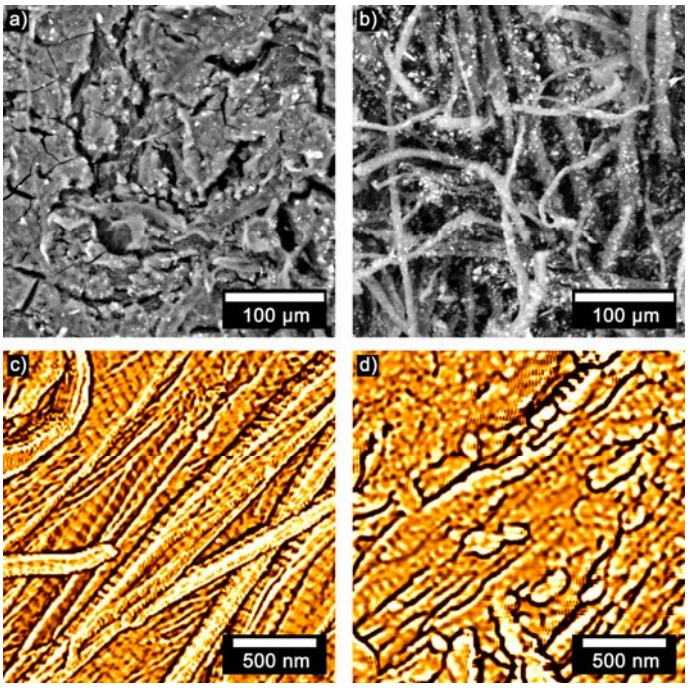


Figure 2. SEM and AFM images of naturally aged parchment samples. (a) SEM image of the surface of the 17th century sample, (b) SEM image of the surface of the Qumran sample, (c) AFM topography of a sub surface slice of the 17th century sample, (d) AFM topography of a fiber from the Qumran sample

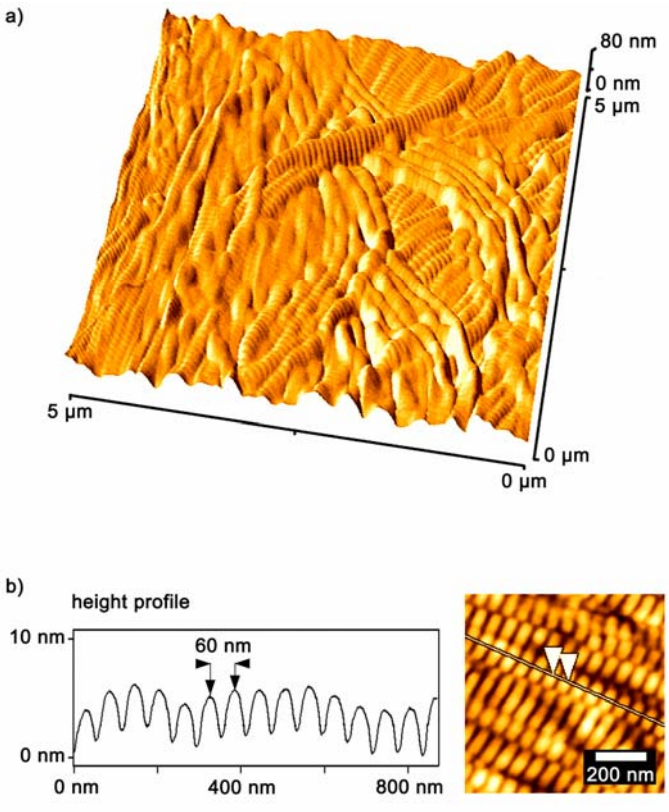


Figure 3. AFM images. (a) Contact mode, 3D topography: fresh parchment, flesh side (detail from Figure 1e), (b) Tapping mode, line profile and topography: artificially aged sample, sub surface slice.

The fact that parchment degradation processes must be studied separately for the surfaces and the bulk led us to use confocal microscopy, a technique that allows to transverse the sample vertically. Application of confocal microscopy to the study of parchment is based on the auto-fluorescence of proteins. With this technique we are able to image the samples at different focal planes from the top (surface) to the depth of some hundreds of microns 'taking individual shots' at micrometer distances. Figures 4a and 4b show surface fluorescence images of fresh and artificially aged parchment, respectively. The formation of the "glassy layer" due to ageing and an intact fiber network underneath the surface are perfectly discernable in these pictures. The study of the series of vertical "slices" reveals that parchment state can be addressed in terms of its compactness. Artificial ageing doesn't affect the compactness of the network. Fresh and well-preserved parchment exhibits a fiber network that is confined within one plane. In Figures 4c, d and e we compare the profiles of the confocal series of artificially and naturally aged samples, respectively. We observe the broadening of the compact structure in the sample from the 17th century as compared to that of the artificially aged one. This broadening indicates that the deterioration process is not limited to the surface anymore but has penetrated the bulk. In the case of a severely deteriorated Qumran sample (Figure 4e), the fluorescence profile shows loose fibers that practically stick out in all directions. In this case the regular planar network structure has been lost due to the deterioration of the whole parchment (although some short range order is still present, as shown by the fibrils structure). One sees that a correct assessment of deterioration can be achieved with the help of confocal microscopy, a non-destructive technique that is much less demanding experimentally than the complex and time-consuming atomic force microscopy.

Summary

Artificial ageing produces visible changes in parchment such as color and flexibility. However, a SEM and AFM study of the surface and bulk of the artificially aged samples indicate that the damage is confined to the narrow surface region. The oxidized (or rather, gelatinized) surface acts as a protective shield for the parchment bulk preventing further deterioration of collagen. SEM and AFM comparison of naturally aged samples at various degrees of deterioration corroborates the hypothesis that damaged surface does not necessarily reflect the degradation state of the bulk. In fact, intact portions of ordered collagen fibrils

could be detected in samples with extremely advanced deterioration. A better measure of parchment preservation state is given by the compactness of its fiber network. This can be assessed effectively and non-destructively by means of confocal microscopy.

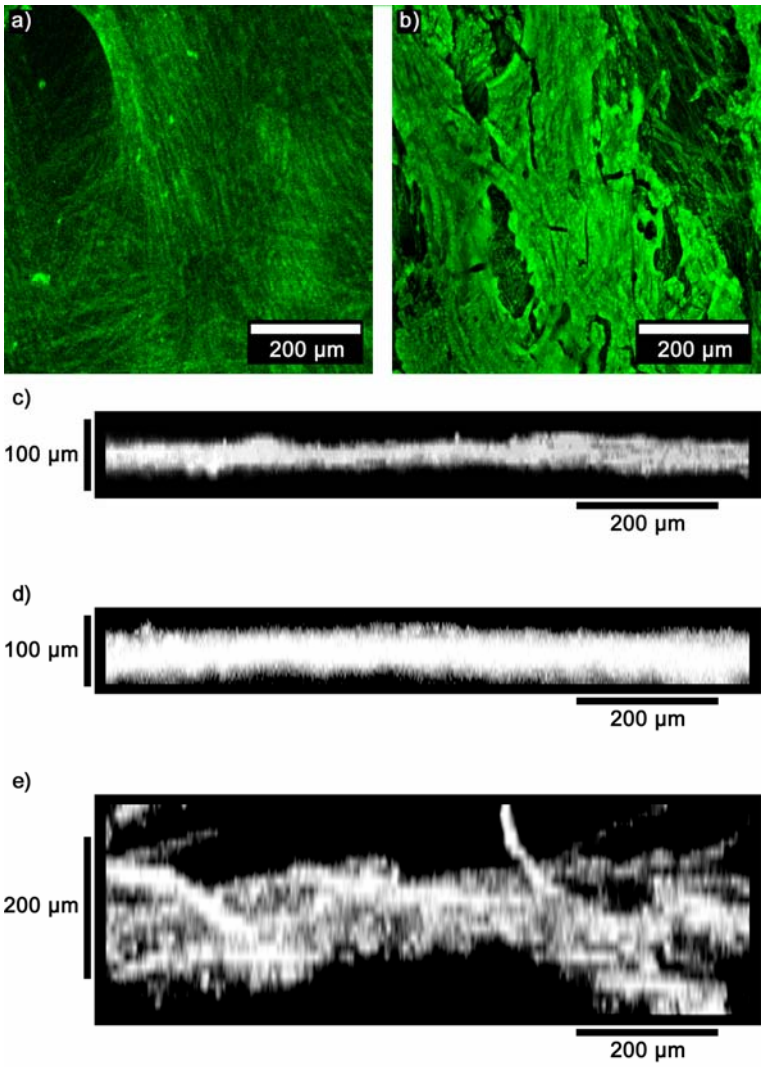


Figure 4. Confocal microscopy. (a) Fluorescence image of the fresh parchment: grain side, (b) Fluorescence image of the artificially aged sample: grain side, (c) Cross section profile of the confocal series: artificially aged sample, (d) Cross section profile of the confocal series: 17th century sample, (e) Cross section profile of the confocal series: Qumran sample

Acknowledgements

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discussions. We also thank T. Szeintuch and I. Kessler for their invaluable comments on parchment restoration.

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THE SHRINE OF THE BOOK – HOW TO VISIT AND WHAT TO TELL

Adolfo Roitman

Shrine of the Book, The Israel Museum, Jerusalem, Israel
E-mail: shrine@imj.org.il

Abstract

The Shrine of the Book, situated near Givat Ram and Israel's government institutions, was inaugurated on April 20th 1965 for the purpose of preserving and exhibiting the world famous Dead Sea Scrolls and outstanding ancient biblical manuscripts. The building, designed by American-Jewish architects A. Bartos and F. Kiesler, is considered a milestone of modern architecture. Its uniqueness lies in the fact that it is an "ideological" structure, a kind of sanctuary that seeks to convey a spiritual message. The stark contrast between its white dome, which symbolizes the lids of the jars in which some of the scrolls were found, and the black wall opposite the building alludes to the tension between the spiritual world of the "Sons of Light" (as the sectarians referred to themselves) and that of the "Sons of Darkness" (the enemies of the sect) expressed in the scrolls. The Dead Sea manuscripts fall into three major categories: biblical, apocryphal, and sectarian. The biblical manuscripts comprise some two hundred copies of biblical books, representing the earliest evidence for the biblical text in the world. The discovery of the Dead Sea Scrolls represents a turning point in the study of the history of the Jewish people in ancient times, for never before has a literary treasure of such magnitude come to light. Thanks to these remarkable finds, our knowledge of Jewish society in the Land of Israel during the Hellenistic and Roman periods as well as the origins of rabbinical Judaism and early Christianity has been greatly enriched. At present, two major exhibitions are on display at the Shrine of the Book. One is called “A Day at Qumran”, which is devoted to the daily life of the Qumranites (the Essenes?) from sunrise to sunset. The other one, called “A Wandering Bible: The Story of the Aleppo Codex”, is purported to tell the story of this exceptional biblical manuscript from medieval times (Tiberias, 10th cent.) through our times. The Aleppo Codex is the earliest known Hebrew manuscript comprising

the full text of the Bible. It is also the most authoritative, accurate, and sacred source document, both for the biblical text and for its vocalization, cantillation and Massorah (literally, "transmission" of the Bible, the oral and written tradition by which the Holy Scriptures have been preserved and passed on from generation to generation).

Introduction

The “Shrine of the Book” is known in Israel and abroad as the only location to display one of the most important archeological finds of the 20th century: the Dead Sea Scrolls. In addition to the Dead Sea Scrolls, additional items on display are the “Keter Aram-Tzuba” codex and finds from the “Cave of Letters” from the time of Bar-Kochba.

The structure itself is a benchmark in world architectural annals in its uniqueness. This paper will refer to the historical, artistic and cultural aspects found in the structure, in the displays and in the ways they are presented to the visiting audience.

Historical Background

In the 18th-19th centuries, during the time of enlightenment and the emancipation of the Jews of Europe, the ideal of the “New Jew” was born, a Jew who was not connected to the rabbinical culture and a two thousand-year-old tradition. Sources of inspiration and designs were sought for this ideal. These were found in the world preceding the rabbinical world – during the Second Temple period and the Hellenistic/Roman period –, which previously was not central to national life. People began to take interest in the Jewish writers from these periods (such as the writings of Philo of Alexandria and the Apocrypha) and in Jewish streams differing from the rabbinical stream. At the end of the 19th century, with the beginning of Zionism, interest in the Bible increased due to the desire to find a connection with Eretz Yisrael. The search for roots and the connection with the land greatly increased interest in archeology. Frenchmen, Germans and Englishmen who were digging in the Holy Land with the aim of supporting the stories of the Bible, did so principally in the areas of Jerusalem and Jericho. The Jews who arrived in the country widened the areas of research. Sukenik dug in Beit Alpha, and archeology became a tool in the hands of the Zionist movement to connect the new Jew to his land and his past.

Part of the idea of the new Jew in his land also connected to the return-to-nature movement and to the creation of an artistic infrastructure in the land. “Bezalel” was established and thought was given to architecture as a means for communicating ideas. With the establishment of the university in Jerusalem, the basic idea of the university as a temple, as well as considering it on a monumental scale, was established as a direct continuation of the days of the Second temple, while overlooking a gap of two thousand years.

The Hidden Scrolls

At the end of 1946 and the beginning of 1947, seven ancient scrolls were discovered (according to their version) by Bedouins near the Qumran ruin, about 40 kilometers east of Jerusalem, on the edge of the Dead Sea. These scrolls were the most ancient biblical writings ever found. Until then, only writings from the 10th century and later were known, and generally in translation. Amongst the scrolls, written in Hebrew, were two copies of Isaiah (A and B) – a complete sequence of the 66 chapters of the Book of Isaiah. Four scrolls were bought by the head of the Syrian Church in Jerusalem (Samuel), and were smuggled out of Israel in 1948 to be sold. Sukenik bought three scrolls (two of them were bought on November 29th 1947, a date that seems most symbolic). In the end, about 800 scrolls were discovered in ten caves in what was Jordanian territory, and included many copies of writings from the Tanach.

In the years 1947-51 the scroll of Isaiah, the Book of Habakook and the Book of Yachad were displayed in different places in the USA. A curatorial-artistic-cultural connection was formed as the viewer grasped the Christian or proto-Christian connection of the Scrolls, and their Jewish importance was recovered.

Establishment of the “Shrine of the Book”

In 1954, Samuel published an announcement in an American newspaper about the sale of four scrolls. Yigal Yadin threw himself into the mission of obtaining them, and getting governmental support that, together with other donors, enabled their acquisition. The Prime Minister, Moshe Sharett, announced their presence in the country in 1955. A discussion was initiated on the possibilities for displaying them. The then-Minister of Education, Ben-Zion

Dinur, suggested the name “The Shrine of the Book” and a foundation was established for its creation. The declared aim of the foundation was “to faithfully use the Dead Sea Scrolls and to file and gather writings, documents and other remnants connected with the Tanach and fragments of closely related literature; to establish a special hall in the National and University Library in Jerusalem to be used as a repository and a museum to preserve and display these writings and all other material connected with the Tanach.

In the beginning, it was thought to display everything in the previously established National Library, but on July 29, 1957, a conference on Jewish Sciences was held, coinciding with the opening of the first building on the Givat Ram campus, and the scrolls were displayed in a small and crowded room. A search for money began and a place dedicated to the display of the scrolls was planned. The donor S. Gustman agreed to finance the project.

In 1957 it was decided to grant the design of the structure to Armond Bartos (an American architect with experience in designing university buildings, a gallery and a synagogue, and Gustman’s son-in-law) and Frederick Kiesler (an Austrian-American of gypsy descent who had an international reputation in the areas of sculpture and design of facades and in the theory of architecture). Kiesler came up with the idea of “the infinite building”, and in the concrete context of a place to display the scrolls, the theme of a double parabolic dome. This dome was the source of argument in negotiations surrounding the planning of the National Library structure on Givat Ram, since the Bauhaus style of the campus appeared to contradict it.

It was suggested that the dome would be above ground level and the rest of the structure would be underground, as a separate building, which would be connected to the library by an underground tunnel, and by a system of steps to the monastery of the Valley of the Cross.

Opposition was raised against the garish exhibitionism that was attributed to the planned structure, which stood in apparent opposition to the functional architectural spirit then in fashion, and to the concept of Jewish humility (according to the President Yitzchak Ben-Tzvi).

In 1959, it was finally decided to cancel the construction on the university grounds, and the planning was transferred to Museum Hill. Building continued over the years 1961-64, and a number of changes were made to the original plan: a small library and exhibition hall, researchers’ rooms and the black wall adjacent to the structure (which will be discussed below) were added. The Shrine of the Book was inaugurated in 1965 in a dignified ceremony, and different reviews were immediately published on the building and its suitability for the purpose for which it was built. There were those who were against the splendor and

exhibitionism it represented and its contradiction with the reigning functional approach in architecture, and others who praised the uniqueness and originality of the building.

The “Shrine of the Book” was not built solely as a functional structure (one for the preservation and display of the scrolls), but as an ideological building. The designers thought of building a “temple” which would be characterized by its architectural components, and would tie in with the idea of the renewed state renewing its connections with its past. Kiesler claimed that the architecture should be a tool for passing on messages and to enable the viewer to undergo a spiritual experience. The designers used architectural tools, such as rich materials, changes of intensity of the amount and type of light, a continual flow between the outer and inner spaces, the sculptural character of the structure, and use of different geometrical shapes in order to deliver the spiritual and universal messages which make a visit to the structure a “religious” experience. The secret of the success of the “Shrine of the Book” lies in the unusual combination of the architectural design with the symbolism, which the visitor experiences during the course of the visit.

The Shrine of the Book at the Israel Museum, Jerusalem

Main hall of the Shrine of the Book

A Tour of the Shrine of the Book

Visitors have two options to reach the entrance of the Shrine: from the central boulevard, which ascends and crosses the “Acropolis” of the museum to an open square. This approach mirrors the concept of the museum as a cultural temple, and is reminiscent of the religious ceremonial processions, which create a transition from the secular to the holy.

One can come from the grove, a place from which one can view and observe the structure and/or contemplate (meditation), and prepare for entering the site. The square is paved in polished cylindrical stone, and the perpendicular element in it is set between two geometrical shapes, monumental and special - a round white dome, covered in porcelain, which appears to be floating in a pool of water with fountains, and a quadrilateral basalt wall, black and shiny. This wall was added because of the esthetic need to emphasize the structure so that it is not be lost in the background view; however, meanings were attributed to it, tying it to the aim of the Shrine. There is a figurative opposition of colors, of straight lines versus curved ones, the massivity of the structure versus the lightness of the water, and there is a place also for a flame on the black stone structure.

The contrasts emphasize the grasp of the dualistic reality of Dead Sea cults that spoke of a war between the Sons of Light (the white dome) and the Sons of Darkness (the black wall), Michael and Belil. The designers also intended to mark the resurrection of the People of Israel in their country (the white dome rising up) against the background of past suffering (the black wall). The dome itself is reminiscent of the tops of the vessels in which the scrolls were preserved for two thousand years. The water and the fountains symbolize the elements dealing with purification, which were central to the philosophy of the special Judaism of the Dead Sea cults. The pool has four corners suggesting the horns of the altar, and lighting towards the dome. The visitor descends on steps protected by a railing made from quadrilateral pillars of differing heights. According to Yadin, this is similar to the descent into the Qumran mikves, and is similar to a purification ritual (before entering the “sanctity” of the Shrine). The entrance to the Shrine is similar to a monumental entrance to a temple or an ancient luxurious burial chamber.

The first space in the structure is intended as an introduction and orientation to the spaces that continue on from it. The space is dim, and the little light enters through the windows under the roof. At certain times, the light passes through colored panes and is reminiscent of the light in cathedrals from the middle Ages. The gradual passage from the external “secular” to the internal “holy” is made via a bronze gate leading to a dark tunnel, lit only by light from the showcases in its rounded walls. This space is reminiscent of the caves in which the scrolls were discovered. Its ceiling is low and there are no straight lines. On the walls are displayed finds demonstrating the day-to-day life of the people of the Judean Desert sect. From the dark tunnel, the visitor ascends to a light and open space, under the dome seen from outside. Here the scrolls are displayed. The Scroll of Isaiah is displayed in the centre, in a round showcase on a raised base, to which one must ascend a number of steps. Around the hall the other

scrolls are displayed. The vertical element which sets the Scroll of Isaiah in the centre and toward the top emphasizes the importance associated with this scroll. The structure of the showcase is reminiscent of the structure of a vessel and also perhaps of the crown atop a Torah scroll. Above, the lighting is similar to the pantheon lighting at the apex of the dome. Originally, there was meant to be an opening to connect the interior with the outside, between the earth and the heavens. A spiral line guides the visitor along the round walls of the hall and up and down and symbolizes the infinite perfection.

From this hall, one descends to a dark underground hall, similar to a church crypt. In aspiring to match form to content, the building material changes from polished marble to rough-cut, wild brown rock. The space is reminiscent of a cave hewn from the rock, and on display are finds from the "Cave of Letters" in Nachal Hever, from the time of the Bar-Kochba revolt. The visitor again ascends to the central round hall, and exits via and narrow opening to the outside of the structure, to light and to the secular atmosphere. In front of him lies a modern view of Jerusalem, of modern buildings and the Knesset. A connection is made between the past and the present.

Location of the Structure

The "Shrine of the Book" is located in the vicinity of institutions that symbolize the political and cultural independence of the State of Israel – the Knesset, government offices, the Supreme Court, the Bank of Israel, the Israel Museum and the Hebrew University. It has nearly governmental standing and has become a central factor in the design and strengthening of the cultural/national identity of the state.

The COST Action G8 group at the entrance of the Shrine of the Book

TEXTILES AND GARMENTS FROM QUMRAN - CHALCOLITHIC AND ROMAN PERIODS

Orit Shamir

Curator of Organic Materials, Israel Antiquities Authority, Jerusalem, Israel
E-mail: orit@israntique.org.il

Abstract

In 1955 Crowfoot published 77 textiles from Qumran Cave 1. In addition to those, a few hundred uncleaned textiles from other caves have been lying in nylon bags for fifty years. Belis (2003) examined them before conservation. As a historian, she emphasized such issues as the material relationship between the manuscripts and the textiles rather than technical details. Only in August 2003 these textiles as well as some two hundred pieces from various caves were conserved by Raisa Vinitsky from the IAA and restored in the Israel National Collections. Some of the wool Roman textiles have decorations of bands - representing tunics - and some have gammas - representing mantles. Others were used as scroll wrappers, sacks and probably as bandages.

State of Textile Research in Israel

The first pioneering efforts in the study of ancient textiles of the Land of Israel were made in the fifties by Grace Crowfoot and her daughter Elizabeth Crowfoot, who examined the textiles from Qumran Cave 1 (1955) and from Murabba'at (Crowfoot & Crowfoot 1961) and later by L. Bellinger at Nessana (1962). In 1963 Y. Yadin published the textiles from the Cave of the Letters and in 1974 the Wadi ed-Daliyeh textiles were published (Crowfoot 1974).

Later on, research was conducted mainly by A. Sheffer with the assistance of others (1988, 1991a, 1991b, 1994a, 1994b, 1988).

T. Schick made a huge progress in the research of textiles from Neolithic and Chalcolithic periods: Nahal Hemar (Schick 1988); Cave of the Warrior (Schick 1998); Caves in the Northern Judean Desert (Schick 2002); Lower Wadi el-Makkukh (Shamir & Schick, in press).

Later on, A. Baginski and this author conducted the research (1994, 1995, 1998, 1999, 2001, 2002, 2003).

Thousands of the textiles discovered in Israel were described in the author's PhD dissertation entitled “Textiles in the Land of Israel from the Roman Period till the Early Islamic Period" (carried out under the supervision of Prof. Gideon Foerster, Institute of Archaeology - The Hebrew University of Jerusalem, and Dr. John Peter-Wild, Department of Art, History and Archaeology - University of Manchester).

Yet, there is still a lot of research to do about carbon dating, fibers, dyes, wear and tear. Due to the limits, this article will not deal with other organic materials from Qumran such as wood, basketry, cordage, fruits, seeds and leather that are stored in the national collections of the IAA.

Qumran Textiles - Publication and Conservation

Crowfoot catalogued 77 textiles from Cave 1 and about an additional 130 fragments from Caves 8Q, 11Q, Christmas Cave and from unknown provenance was published briefly by Bélis in 2003.

This author catalogued the textiles. Two hundred twenty eight are dated to the Roman period: 176 are made of linen, 52 are made of wool, and 5 are made of goat-hair. Fifty-three linen textiles are dated to the Chalcolithic, c. 4 millennium BCE, and a few to the mediaeval periods. A few are probably modern.

Qumran Materials for Spinning and Weaving

Linen and wool were the most common textiles in the Land of Israel. Linen is known from the Neolithic period (c. 6500 BCE) at Nahal Hemar. Linen objects from this place were

not produced by weaving but rather by other techniques such as looping and knotted netting (Schick 1988).

The linen textiles from the Chalcolithic period were discovered in many caves in the Judea Desert such as the Warrior Cave (Schick 1998).

The state of preservation of the Chalcolithic textiles from Qumran is relatively good: most of them are not worn (they were not used a lot), not even damaged by insects. It seems that the original clothes are not used much.

All the textiles are made of undyed, unbleached linen. Their present color ranges from off white through cream, beige to brown.

The threads are S spun, sometimes plied in a final S twist for better cohesion. In some textiles the threads are very fine and delicate - in others they are crude. A few have threads of varied thickness in the same cloth. The predominant weaves are various tabby weaves (Figure 1). This serves to confirm that the textile crafts were already very advanced and accomplished in the 5^{th}–4^{th} millennium BCE.

It is worth to mention that among the fragments are narrow, cut band-like specimens, probably used for tying or bandages.

Figure 1. Linen textile, Chalcolithic period, tabby weave, No. 577053 [B-7759-150614152320]. Photo by Clara Amit, IAA. By courtesy of the Israel Antiquities Authority

Flax was one of the important raw materials for clothing in the Roman Empire and was found at many sites in the Land of Israel: Qumran, `En Gedi (Sheffer 1994), Cave of Letters (Yadin 1966), `En Rahel (Shamir 1999) and Masada (Sheffer & Granger-Taylor 1994).

Linen is mentioned quite often in the written sources of the Mishnah and Talmud period, Roman and Byzantine periods. It became a major economic factor in the Land of Israel from the second half of the second century CE. The price edicts of Diocletian (third century CE, Ch. 26) describe the flax of Beth She'an as the most expensive in the whole world.

Wool textiles from Qumran (Figure 2) are usually undyed and undecorated.

Figure 2. Wool textile decorated with red band, Roman period, and part of a tunic, No. 577004 [B-7765-150614154132]. Photos by Clara Amit, IAA. By courtesy of the Israel Antiquities Authority.

The earliest wool textiles in the Land of Israel were found in Jericho dating to the Middle Bronze Age, c. 2000 BCE (Shamir, pers. obs., University College of London). Wool was also the most common material for textiles from the Roman Period till the end of the Islamic Period, the eighth century CE.

Jewish law forbids the weaving of woolen threads together with linen, or vice versa (*Sha'atnez*, Deuteronomy 22:11; Leviticus 19:19). These mixed materials were neither found at Qumran nor at any of the Jewish sites. *Sha'atnez* textiles have been found in Israel at non-Jewish sites such as 'En Tamar of the Nabatean people and many more were found in Syria and Egypt.

Goat hair was also found at Qumran (Figure 3). It is coarse and non-elastic, with a natural color range of cream to dark brown. Goat hair is known in the Land of Israel from the Late Bronze Age at Timna (Shamir & Baginski 1993) but apparently was in use prior to this period. It was common in the Roman period and later. It was usually used for ropes, tents, rugs, sails and carrying cushions, sacks and saddlebags.

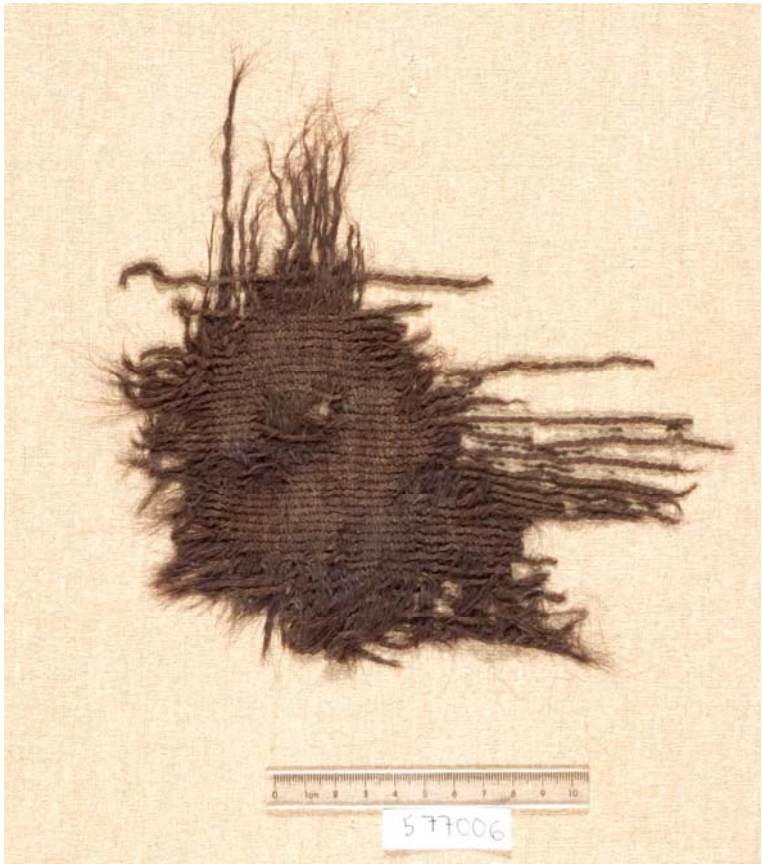

Figure 3. Goat hair textile, Roman period, No. 577006 [B-35392-26090334513]. Photos by Clara Amit, IAA. By courtesy of the Israel Antiquities Authority

Dyeing Materials and Techniques

Dyeing was very expensive because it was a complicated. The materials for dyeing textiles were taken mostly from vegetable or animal sources. Plant sources of textile dyes were the most plentiful and widely used. Different parts of the plants were used for various dye sources. In some plants, the flowers are utilized for extracting the dye material. In other it could be the leaves, or just the roots.

The most common dyes in Israel for blue were indigo (*Indigofera tinctoria*) of Asian origin or Woad (*Isatis tinctoria*) of local origin, for red – Madder (*Rubia tincorum*), kermes (oak-kermes insect dye - *Kermes vermilio*) (Koren 1993, 1994, 1995, 1999; Precker 1992: 126-127). Madder mixed with indigo usually gives a purple color used for imitating the royal purple (*Murex brandaris*). In Israel this was only discovered in one textile from Masada.

One textile from Qumran, probably served as scroll wrapper, is made of linen decorated with blue bands with patch (Figure 4). One edge of the cloth is cut, folded and whipped with a two-ply blue thread.

Figure 4. Linen textile, scroll wrapper, decorated with blue bands, No. 578620 [B-28014-21071111051]. Photo by Clara Amit, IAA. By courtesy of the Israel Antiquities Authority

A few other scroll wrappers from Qumran made of linen decorated with blue bands and stripes creating rectangles represent the ground plan of some religious building. This design corresponds with the plan of the temple as described in the Temple Scroll (Yadin 1983:198-200, Magness 2002: 198).

Blue dye was used at Qumran only with connection to the scrolls contra to other sites in Israel where it was used for decorating garments.

Garments in Light of the Finds

The fashion of displaying social status and wealth through clothing differed in time and space, but always gave clear message. In the Roman era the message was in the color (and thus the quality) of the material, the size of the garment (the larger, the more important the

bearer), and the type, quality and color of any decoration (Gillis 2000:24). Fragments of tunics and a mantle were found at Qumran.

Tunics

The garment that was the most common during the Roman and Byzantine periods, also in the Jewish community, was the tunic made of wool or linen. Both women and men wore it. The tunic was decorated with bands (Figure 2) descending from the shoulders on the back and front (*clavi* in Latin, *imrah* in Hebrew) (Yadin 1963: 204-205).

Mantles

Outergarments over tunics include items such as mantles worn by both men and women (*talit* in the Talmudic sources, *himation* in Greek and *palium* in Latin for a specific type of mantle). The mantle consisted of a one-piece rectangular sheet decorated at the corners with H-or gamma-shaped pattern. One textile decorated with gamma-shaped pattern was found at Qumran (Figure 5).

Figure 5. Wool textile, Roman period, mantle decorated with gamma-shaped pattern, No. 577000 [B-6906-120513093011]. Photo by Clara Amit, IAA. By courtesy of the Israel Antiquities Authority.

Hairnets

Women used hairnets to cover their hair. Sometimes the color suited the color of the hair and they appear to have been intended to blend in, with the wearer's hair. The linen hairnet from Qumran was found with hair attached to it (Figure 6).

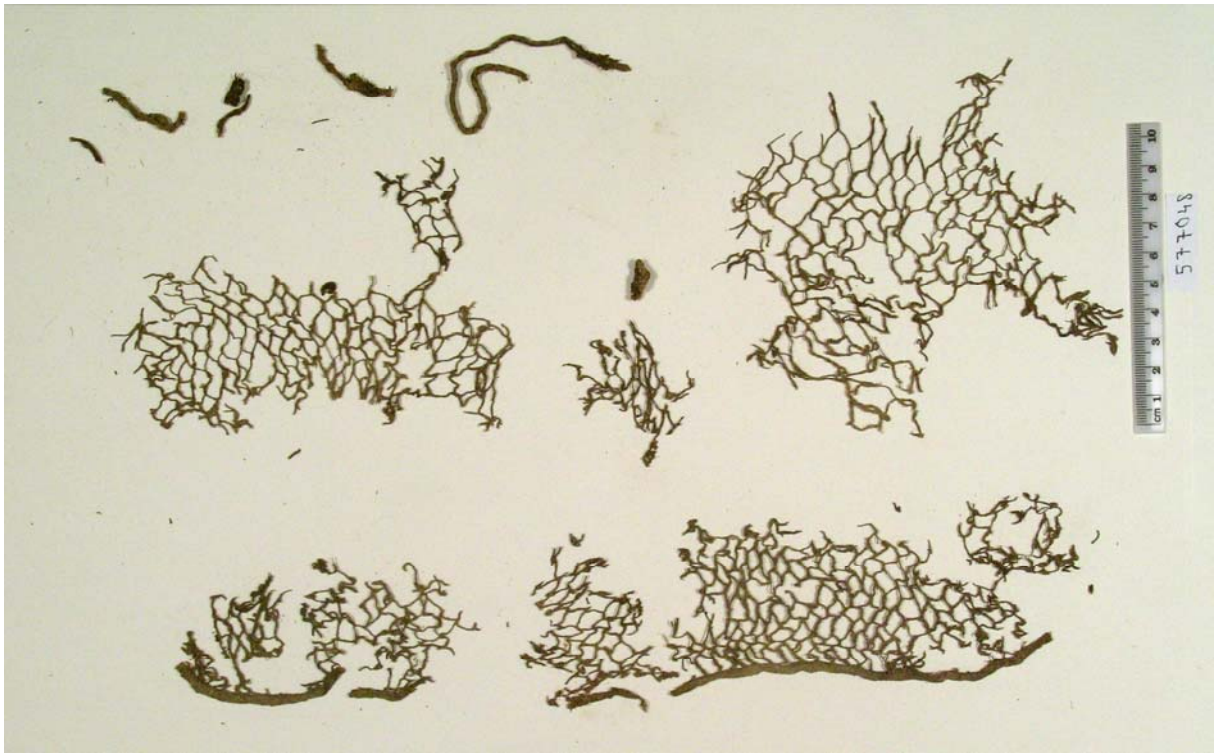

Figure 6. Linen hairnet, No. 577048 [B-6900-12051309292]. Photo by Clara Amit, IAA. By courtesy of the Israel Antiquities Authority

Secondary Uses

Textiles were too expensive to be thrown away. When a garment could not be patched any longer, it was cut into pieces and either remade into another garment or used for patches. Due to the cost of new clothes, there was a flourishing Roman second-hand clothes industry, the centonarii, who collected rags, centones, which were converted into blankets, and, most important, cheap clothing for the poor and the lower ranks – low status clothing for low status people.

Jar covers

Textiles from Qumran other than garments included scroll wrappers (Fig. 4), jar covers (Figure 7) and bandages. The corners of jar covers were twisted or tied round with linen

string or strong linen thread. The square was placed over the mouth of a full jar, and tied either round the neck or sometimes to the handles.

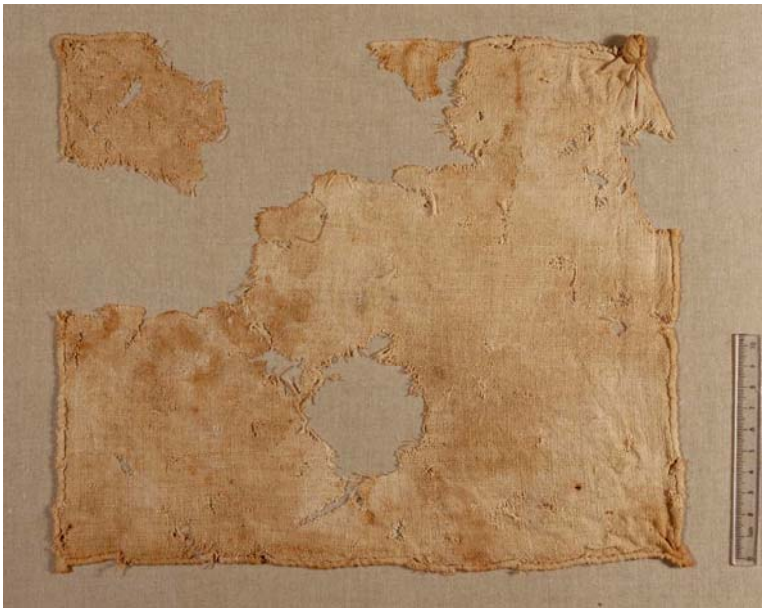

Figure 7. Linen Jar cover, No. 351288 [B-42421-21121540135]. Photo by Clara Amit, IAA. By courtesy of the Israel Antiquities Authority.

Bandages

Many thin strips were found at Qumran. They could be used as bandages for binding injuries. In the Cave of Letters some of the textiles bore stains that did not wash out during the cleansing by the conservators (Yadin 1963: 264). They might also have been used for tying. At Murabba'at strips of linen had also been wrapped like bandages, some with ties, and in some cases appeared as if stained with blood (Crowfoot & Crowfoot 1961: 52). They were usually of reused cloth.

Summary

The number of linen textiles from the Roman period at Qumran (70%) is in contra to other sites. C. 2000 textiles from the Roman period discovered in Israel were examined and 35% are linen, the other materials are wool, goat hair and camel hair.

Magness (2002: 193-204) emphasized that Essene sectarian people wore only undyed linen garments considered to be pure. This is indicative of the anti-Hellenizing attitude of the

sectarian. Since the width of the *clavi* indicated the wearer's rank in society, the sectarians' adoption of all-white clothing suggests a rejection of this society.

Due to time limits we didn't touch on the topics of gender, production techniques, origin, differences among the sites from the same period and the economic situation of the inhabitants of a site, which can be determined by studying quantity of patches used on the textiles.

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