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RADIOCARBON DATING AND QUMRAN

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Abstract. Samples from Qumran dated by Radiocarbon are potentially contaminated with preservatives or other contaminants. This includes some of the Dead Sea Scrolls, which were treated with castor oil in the 1950s. This castor oil is not removed by the standard AAA pre-treatment used for ^{14}C samples. We developed a pre-cleaning step, to be applied before the standard ^{14}C procedure, which has shown to remove such contaminants effectively.

Introduction

The Radiocarbon (^{14}C) dating method was developed during the years around 1950 [1]. Since that time, several "revolutions" have improved the method considerably. Among the most significant ones are improvements in measurement precision, the introduction of AMS, and calibration of the ^{14}C timescale.

AMS (Accelerator Mass Spectrometry) enables small (milligram size) sample analysis [2]. This is a factor of 1000 less than the original, so-called conventional method. AMS therefore enables ^{14}C dating of precious and intrinsically small samples—artwork, Neanderthal bone, delicate artifacts, pollen, and the Dead Sea scrolls.

Calibration now enables absolute dating back to more than 10.000 years ago [3]. In turn, this spawned "revolutions" in many fields of application, among which archaeology. It is important to note that Radiocarbon provides a "yardstick of time", enabling the measurement of past time by scientific means, independent of cultural assessments.

The method enables chronological comparison of different areas at excavation sites and also between sites and regions. This is essential for proper interpretation of archaeological or stratigraphical layers and association with data from other fields [4].

While the method is basically simple, it is complex in detail and errors in matters concerning both fieldwork and technical laboratory aspects. Therefore, quality control is necessary to build up reliable ^{14}C chronologies. This involves regular laboratory intercomparisons, duplicate measurements of samples, issues such as conventional versus AMS, sample selection, association, contamination, and others [5], [6].

In this contribution, a short review of the principles of the ^{14}C method, the conventions and the most recent developments are given, including the 2004 calibration of the timescale. Quality control issues and sampling strategies will be discussed. This covers the state of the art of ^{14}C dating with an emphasis on matters relevant to Qumran.

1. The ^{14}C dating method

The element Carbon consists of 3 isotopes in nature: ^{12}C, ^{13}C and ^{14}C. These three isotopes are all forms of Carbon with different atomic masses (12, 13 and 14, respectively). The isotopes ^{12}C and ^{13}C are stable and have abundances of about 98.9 and 1.1%, respectively; the isotope ^{14}C is not stable but radioactive, and has an extremely small natural abundance of about 0.0000000001% or 10^{-12}.

The isotope ^{14}C is continuously produced in the earth's atmosphere by cosmic radiation. Radiocarbon decays with a half-life of 5730±40 years [7]. A stationary state of production, distribution between the main carbon reservoirs (atmosphere, ocean and biosphere) and decay results in a (more or less) constant ^{14}C concentration in atmospheric CO_2 [8].

The ^{14}C enters the biosphere via photosynthesis in the plants. Next, it finds its way in all living organisms via the food chain. Upon death, there is no longer equilibrium, and the amount of ^{14}C decreases because of radioactive decay. This is schematically shown in figure 29. The half life is defined as the time needed for half of the radioactive ^{14}C atoms to decay. Thus, by measuring the amount of ^{14}C remaining in the sample its time of death can be derived. This is the simple basic principle of the ^{14}C dating method.
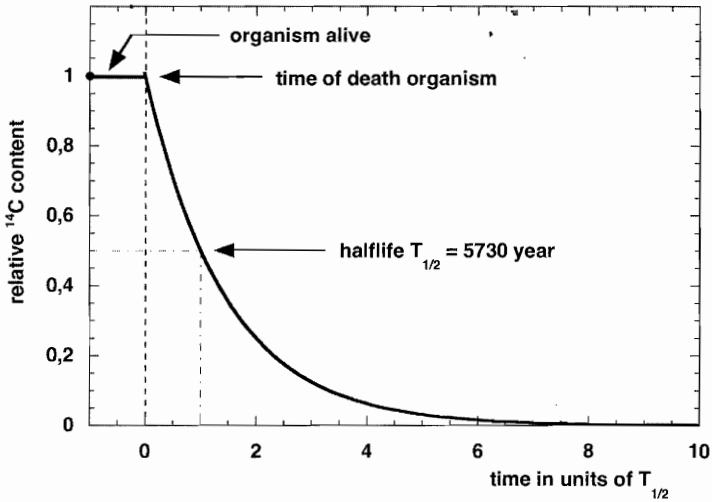
Figure 29. The radioactive decay curve for ^{14}C

In practice, samples back to 50.000 years ago (about 9 half lives) can be dated.

Although this principle is straightforward, in practice there are many complicating factors.

First, the half-life needs to be accurately known. This is a problem because in the early days of ^{14}C dating, the so-called Libby value of 5568 years has been used for the half life [1].

Second, it appears that the ^{14}C concentration of atmospheric CO_2 has not always been the same in the past. In tree rings, natural variations of the atmospheric $^{14}CO_2$ abundance were discovered on a time scale of one decade to a few centuries [9]. Later it was discovered that these variations can be attributed to variations in solar activity [10], which in turn influence the production of ^{14}C in the atmosphere. Also changes of the geomagnetic field strength influence the production of ^{14}C in the atmosphere [11]. This is understood because both solar activity and geomagnetic field strength determine the amount of cosmic radiation impinging on the earth, and thus the ^{14}C production rate in the atmosphere [12].

Third, there are mass dependent effects. This is called isotope fraction-ation. Biological, physical and chemical processes are usually mass dependent, which means they change the isotope concentration [13]. Translated in terms of ^{14}C, this changes the ^{14}C date.

Fourth, the accurate and precise measurement of ^{14}C is not straightfor-ward. The AMS method is based on a particle accelerator, needed to separate the very small amount of ^{14}C from other isotopes, present in abundances larger by many orders of magnitude [14],[15].

Fifth, only the ^{14}C that was part of the organism when it died should be measured. Any foreign carbon that has entered the sample since that time is contamination and must be removed. A mixture of physi-cal and chemical means does this pre-treatment. The pre-treatment also isolates a stable chemical fraction of a sample for dating—for example, cellulose for wood, or collagen for bone [16].

The solution to the complicating factors 1-3 mentioned above, is to define or standardize the ^{14}C measurements.

By definition, the ^{14}C timescale is expressed in BP = Before Present, where "Present" refers to the "standard year" 1950 AD [17]. Radio-carbon measurements are always measured with respect to a standard (=Oxalic Acid with a radioactivity of 0.226 Bq/gC) that corresponds to that year.

By convention, the original half-life (5568 years) used in the early days of the ^{14}C dating method [1] is used for this defined timescale.

Also by convention, the definition includes correction for mass dependent effects (fractionation). This fractionation can be deter-mined by measuring the isotope ^{13}C content of the sample. The isotope ^{13}C is stable and thus not (as is ^{14}C) subject to decay. The fractionation is expressed as $\delta^{13}C$ in per mil deviation from the $^{13}C/^{12}C$ ratio from a standard [13]: $\delta^{13}C = [^{13}C/^{12}C]_{sample}/[^{13}C/^{12}C]_{standard} - 1$. The standard value for $\delta^{13}C = -25‰$.

In summary, the ^{14}C timescale is *defined* and has to be *calibrated* to establish the relationship between ^{14}C time and historical time. Note that calibration takes into account not only the "wrong half-life" but also the natural ^{14}C variations. Both effects cause the ^{14}C clock to run at a varying pace, different from real clocks: ^{14}C time does not equal historical time. Calibration connects both independent clocks.

2. Calibration

Calibration involves measuring samples by both the ¹⁴C method (in BP) and another method. Ideally this other method has to be independent from ¹⁴C, yielding absolute dates (in AD/BC), and the samples have to be from the terrestrial (or atmospheric) reservoir. Calibrated ¹⁴C dates are reported as calBC or calAD [18]. The unit calBP is used as well; this is defined as calendar years with respect to 1950 AD (calBP=1950-AD).

The most ideal samples for calibration are tree rings, because they can be dated absolutely by means of dendrochronology. Following the early work of Suess et al. [19], the ¹⁴C community has issued special issues of the journal *Radiocarbon* with calibration curves based on dendrochronology. The latest and presently recommended calibration curve is Intcal04 [3]. The dendrochronological record now extends back to 12.400 years ago [20]. This calibration curve is shown in figure 30. The insert shows a detailed view if the wiggles for the fourth millennium BCE. These data are measured with the best possible precision [21]. The calibration curve has been extended beyond the tree ring limit by using marine data. Using these marine data, the Intcal04 curve
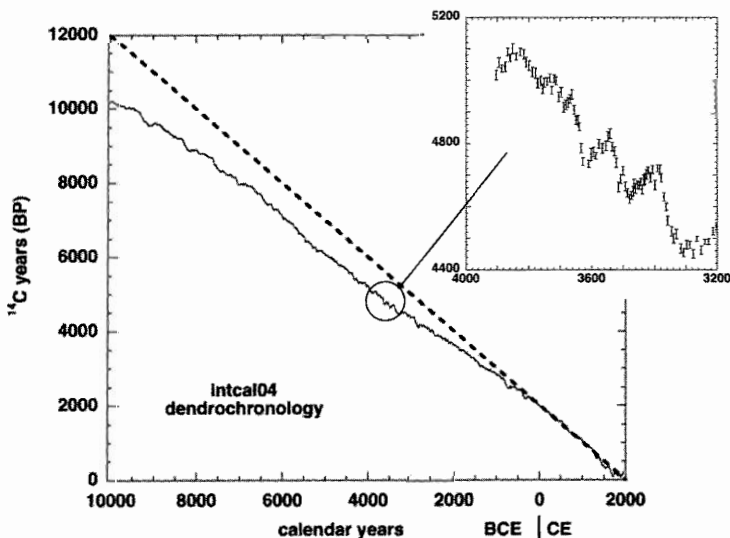
Figure 30. The ¹⁴C calibration curve Intcal04, based on dendrochronological datasets. The insert shows wiggles in detail.

has been constructed [3]. It is the presently recommended calibration curve back to 26.000 years ago (26.000 calBP).

Because of the irregular shape of the calibration curve, the translation of a ^{14}C age (in BP) into a calendar age is not straightforward. Special calibration software has been developed, producing calibrated age ranges with 1σ or 2σ confidence intervals [22],[23],[24]. These programs (updated with the Intcal04 datasets) can be downloaded from www.radiocarbon.org.

An example calibration is shown in figure 31. It is the calibration of one of the Dead Sea Scrolls: 1QpHab (Habakuk *Pesher* from cave 1), as measured by the Arizona laboratory (AA-13417) [25]. The figure shows the relevant part of the calibration curve Intcal04, with the uncertainties (1σ). This part of Intcal04 is constructed through the dendrochronological datasets with a temporal resolution of 5 calendar years [3].

Figure 31 shows two probability distributions. First, along the vertical axis, the probability distribution corresponding to the measurement 2054±22 BP is plotted. This is a so-called Gaussian, which represents the probability distribution of data around the mean value. The deviations from the average value (in this case, 2254 BP) are given in terms of the standard deviation σ. The meaning of this term is that the probability of observing values between 2254+σ and 2254-σ is
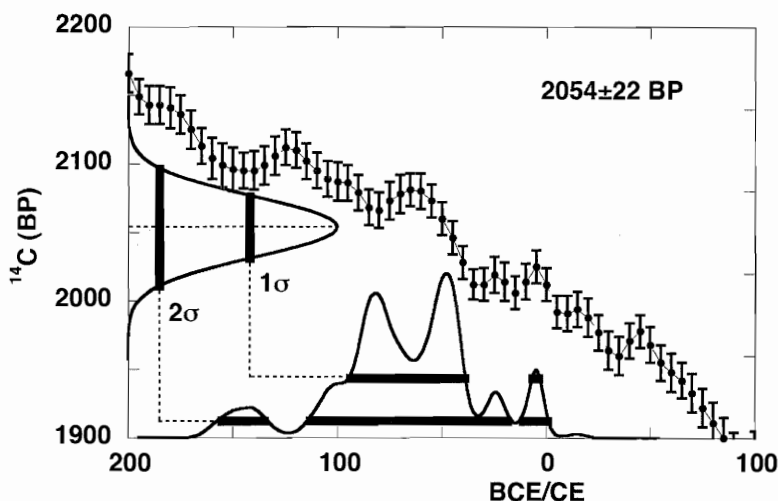

Figure 31. Calibration of the ^{14}C age 2054±22 BP, the published date for the scroll Habakuk (1QpHab)

68.3%, and between 2254+2σ and 2254-2σ is 95.4%. The 1σ and 2σ ranges for the Gaussian distribution are plotted as vertical bars in the figure.

Along the horizontal axis, the calibrated probability distribution is plotted. This distribution no longer has a Gaussian shape (it would be Gaussian only in the case that the calibration curve would be a straight line). As can be seen, the distribution has a complex shape due to the "wiggles" in the calibration curve. In theory, one ^{14}C date can correspond to several calendar ages. Computer programs are needed to calculate the errors in terms of confidence intervals. The program calculates the 1σ and 2σ confidence interval for the calibrated probability distribution, corresponding to 68.3 or 95.4% probability, respectively. These confidence levels are indicated as horizontal bars in the figure. This means that for these date ranges, the area under the probability curve is 68.3 or 95.4% of the total area, which corresponds to 100% probability.

For the ^{14}C date 2054±22 BP, the 1σ calibrated age range thus determined is 95-38 and 6-2 BCE; the 2σ calibrated age range is 157-133,114-16 BCE and 12 BCE-2 CE.

For completeness, we mention here that beyond 26.000 years ago, calibration datasets are available but they are not consistent.

Therefore, no calibration can be recommended for the time range 26-50.000 calBP. Hence the name "Notcal04" [26]. For a more updated discussion see [27].

3. The measuring of ^{14}C

The measuring process of the ^{14}C content of archaeological samples such as bone, charcoal, wood and so on, can be viewed from two perspectives: measuring technique and sample preparation. For ^{14}C, there are two methods for measuring ^{14}C: radiometry and mass spectrometry. The so-called conventional method is based on radiometry. This method requires large samples (around 1 gram of C) and is not further discussed here, as it is not relevant for Qumran. For detailed information we refer to [28] and [29]. The technique of AMS is based on mass spectrometry, for which method milligram size C is sufficient (e.g. [14],[2]).

Sample preparation follows similar procedures for both methods. The general rules are that contaminants have to be removed (physi-

cally and chemically) and that a reliable datable fraction needs to be isolated. Such contamination usually comes from the burial environment. Only the ^{14}C that was part of the organism when it died should be measured.

The commonly used chemical pre-treatment method for the samples is known as AAA (Acid-Alkali-Acid). The first Acid step is designed to remove soil carbonates and infiltrated humic or fulvic acids. Usually one uses HCl. The next step, Alkali, is performed with NaOH and removes soil humates. The final Acid step (again HCl) removes any CO_2 that is absorbed during the Alkali step.

The strength, temperature and duration of the Acid/Alkali treatments depend on the nature and quality of the sample material.

The AAA method is the standard, used for charcoal, charred material, wood, peat, and organic deposits. Details may differ depending on the sample material. A more or less complete overview of various recipes can be found in [8] and [16].

For fossil bone, the organic matrix collagen is isolated.

The sample pre-treatment chemistry provides quality parameters for the sample materials. A very important one is the organic carbon content (often denoted as C%) of the sample. For wood and peat, this must be in the range 45-55%; for charcoal, around 70%; for bone, 45-50 %.

When the organic carbon content is much lower, the material is degraded and the ^{14}C dates become less reliable.

Another quality parameter is the ^{13}C content of the sample. The $\delta^{13}C$ value is measured because it is needed for fractionation correction. But this $\delta^{13}C$ value also needs to be in a specific range for various materials. For (C3 plant type) charcoal, wood and peat this must be about –25‰; for bone, in the range –19 to –21‰. We note that for bone there are exceptions; the stable isotope content depends on the food intake of the organism—see, for example, [30].

In exceptional cases, the AAA pre-treatment method may not be completely sufficient to remove contaminants. For example, this is known to be the case for materials heavily impregnated with contaminants, or which are treated with conservation materials. It is possible to remove such contaminants by applying an extra pre-treatment step, using a so-called "soxhlet" extraction [31].

After proper pre-treatment and isolation of the datable fraction, the ^{14}C content of this fraction needs to be measured. The AMS requires solid graphite. This is produced by first combusting the datable mate-
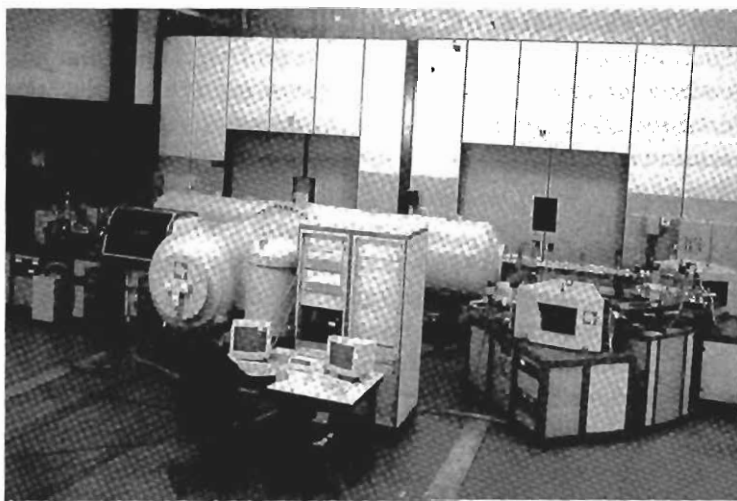
Figure 32. The Groningen AMS facility, dedicated for ^{14}C measurements

rial into pure CO_2. Next, this CO_2 is reduced to C powder (graphite); this graphite is pressed into sample holders (so-called targets). A carousel of 58 such targets can be loaded in the source of the AMS. The AMS facility of Groningen University is shown in figure 32.

In the ion source (on the left in figure 32), negatively charged C atoms are produced from the graphite. This beam of C^- ions is steered into the accelerator, which is the large T-shaped tank in the center of figure 32. A high voltage of 2.5 MV (Million Volt) accelerates the C particles to high energies. A set of magnets (on the right of figure 32) separates this high energy beam of C particles according to mass: 12, 13 and 14 for the isotopes ^{12}C, ^{13}C and ^{14}C, respectively. The ^{12}C and ^{13}C beams are measured by current meters, and from this the ratio $^{13}C/^{12}C$ is determined. This is used for the fractionation correction, necessary for the ^{14}C dates. A particle detector measures the ^{14}C counts, so that also the $^{14}C/^{12}C$ ratio can be determined. From all of this, the ^{14}C ages in BP are calculated. More technical details and status reports can be found in [32] and references therein.

4. Quality control issues

Radiocarbon (^{14}C) is the most common radiometric-dating tool applied in disciplines such as archaeology. Stringent quality control

(or "how good are ^{14}C dates") is required to build up reliable ^{14}C chronologies. Important aspects of quality control involve regular laboratory intercomparisons, multiple analyzes of selected samples, sample material selection, archaeological association, and sample size (i.e. conventional versus AMS as measuring technique) and contamination.

True point dates cannot be achieved with ^{14}C dating, as there will always be a standard deviation. Both equipment resolution and measurement stability, as well as the random nature of radioactive decay [8] causes the results of repeated measurements to spread around a 'true' value. The possible discrepancy between a measured value and the 'true' value is indicated by the standard deviation (σ). Multiple measurements will theoretically result in an average date that is both more accurate and precise than can be achieved with single measurements, provided that the ^{14}C laboratory does not have a systematic bias towards older or younger dates.

The quality of the BP date—i.e. the measured date, before calibration—forms always the basis for every radiocarbon age determination. It must be realized that a ^{14}C date *does* provide a very important universal physical measurement of time, independent of cultural-historical viewpoints and associative reasoning.

Sample selection is a critical component in the ^{14}C dating process. The layers from which archaeological or geological samples are taken during excavations have not always remained static and may have been affected by different kinds of post-depositional processes. Perturbation by plants, animals or human activities (e.g. digging) may cause migration or contamination of carbon in samples used for ^{14}C dating.

Another key question is the relationship between the age of the sample and the archaeological or historical question addressed: "how is the ^{14}C event related to the human event to be dated" [5]. A well-known problem in this respect is the so-called "old wood effect". Wood used (or re-used) to construct a building may have a ^{14}C date that differs from the human construction event by several centuries, depending on the age of the wood. It must be emphasized that the ^{14}C date of the wood (or charcoal) in such a case is not a measurement mistake. Rather the age of the wood sample is older than the age of the archaeological layer or building in which it was found.

The ^{14}C community has formulated general recommendations [33], which can be summarized as follows:

1. the sample needs to come from a closed archaeological context or secure stratigraphic layer
2. the sample must represent the event of archaeological interest
3. the sample needs to come from a context with artifacts pertaining to a specific cultural phase
4. the sample should not be contaminated
5. short lived samples are preferred for ^{14}C dating
6. more than one date per context or phase is recommended
7. the ^{14}C laboratory must adhere quality aspects as is common practice by the ^{14}C community (such as organic content and δ^{13}C of the sample)
8. a ^{14}C date can not be dissociated from the archaeological context; this means that statistics on sets of dates (like averaging) can only be applied to single archaeological contexts
9. the ^{14}C dates must be reported according to the convention—i.e. in BP, which is defined as measured relative to the oxalic acid standard, including correction for isotopic fractionation using δ^{13}C of the sample
10. the ^{14}C dates are to be calibrated using the most recent calibration curve (at present Intcal04), recommended by the ^{14}C community
11. calibrated dates are presented in calBC or calAD (or equivalents like calBP, BCE, CE)
12. upon publication, the archaeological context and the ^{14}C determination details need to be published
13. the ^{14}C laboratory must take part in the internationally organised intercomparison studies.

Another important matter related to sample selection is the respective choice of "conventional dating versus AMS". There can be a temptation to collect and submit all isolated seeds and tiny flecks of charcoal. The dating of such isolated samples by AMS should be discouraged, if larger samples (seed or charcoal clusters) are present in the same layer. If sufficient material is available, samples can be dated more cheaply and often more accurately by conventional means. The possibility of dating erratic post-depositional influences is considerable when isolated small fragments of charcoal or seeds are used, which are liable to movement by faunal or human digging activity. Such tiny samples have to be derived from a clearly defined context or association to justify dating. Lanting and van der Plicht [34] presented a detailed discussion about these issues, including examples. It is a "myth" that

AMS is better than conventional radiocarbon dating: standard deviations are usually not smaller.

Time-width effects represented by a sample have to be considered. Bulk samples of peat layers, for example, are centimetres thick for conventional ^{14}C analysis. Such a sample comprises many years of sedimentation or growth. Isolated seeds, macrofossils, and grains represent single-year samples and are typical AMS material, due to their small sample size, but the stratigraphic context must be clear, as noted above.

The correct calibration procedure of ^{14}C dates from multi-year or single-year samples needs to be carefully contemplated. Smoothed curves are recommended for multi-year samples, while single-year samples ought to be calibrated with the most detailed calibration curve available [8].

Intercomparison is a major part of quality assurance. By intercomparison is meant that different laboratories date the same samples. This may involve either samples of known age or blind samples. Thus a laboratory can "check" its performance—in particular, the sample (pre)treatment and ^{14}C measurement procedures. Intercomparison is a well-recognized issue in the ^{14}C community, and various exercises form a continuing process. The latest large-scale intercomparison is FIRI (Fourth International Radiocarbon Intercomparison) in which 84 laboratories participated worldwide. Several publications were generated by this program [35], and the final report is a special publication of the *Radiocarbon* journal [36].

This Fourth International Radiocarbon Intercomparison had aims of evaluating the comparability of routine analysis of both AMS and conventional laboratories, quantifying of the extent of and the sources for any variation, and investigating of the effects of sample size, precision and pre-treatment on the results.

The FIRI intercomparison results for the two Groningen laboratories (conventional and AMS) can be found in [6]. Other intercomparison measurements involving selected laboratories concern high precision measurements on dendrochronologically dated wood for calibration purposes [37], the development of working standards [38], and a presently ongoing Israel Iron Age project [39].

5. Qumran: ^{14}C dating

Thus far, there has been a minimal employment of ^{14}C dating of materials from the actual site of Qumran since the excavations in the 1950s. In the early days of Radiocarbon, the measurement errors were large, and there was no calibration into absolute ages. As it happens, one of the first ^{14}C dates in history was performed on a linen scroll wrapper, dated in 1949 by the pioneer Libby himself. The result was 1917±200, corresponding to 167 BC—233 AD or 33±200 AD [1]. This illustrates both the large measurement error, and the reporting relative to 1950, i.e. before the discovery of natural ^{14}C variations making calibration necessary. Also this was before the time of fractionation correction by ^{13}C measurements, and only large samples (grams of material) could be dated.

With the development of AMS, dating of small (milligram size) samples became possible. In the 1990s, fourteen Dead Sea texts were dated in Zürich [40], followed by another set dated in Tucson [25]. The dates suggest a possible range from the third century BC to the first century AD for texts from caves near Qumran, with a strong concentration of probable dates in the second or first century BC.

This set of ^{14}C dates obviously form a very important date list for our cultural heritage. Nevertheless, there are discussions concerning the dates as well. As an example, we mention a critique by comparing the ^{14}C dates with palaeography [41]. This critique, however, is based on a wrong understanding of concepts of measurement errors and calibration procedures, as is explained in a rebuttal by van der Plicht [42]. We mention this here as an illustration of discussions and misunderstandings between scholars representing humanities and sciences, going on to the present day. It illustrates the need for a multidisciplinary approach of research concerning Qumran and the Dead Sea Scrolls.

There is also a discussion concerning the original set of ^{14}C dates for the Dead Sea Scrolls in the scientific community. Rasmussen et al. [43] have shown that the use of castor oil by the original team of scroll readers may have contaminated some of the ^{14}C dated scrolls; contamination that could not be removed by the standard AAA pre-treatment procedures used prior to ^{14}C dating.

Also this "castor oil problem" pointed out by Rasmussen et al. [43] was criticized [44] and in turn rebutted [45].

It is necessary to state that the ¹⁴C dating method is a trustful method. It is a scientific measurement of past time, independent of other dating methods like palaeography, pottery assemblages or (pre/proto) historic data. When two independent dating methods produce different results, then at least one of them must be wrong. It is of course possible for a ¹⁴C date to be wrong, or better: not yield the expected result. There can be many reasons for this. One of the most common reasons is: contamination with foreign material (but see also the list in the paragraph on quality control).

The castor oil question is an example of this. The ¹⁴C content of the samples was undoubtedly measured correctly by the two laboratories involved, following standard procedures. In the event a sample was contaminated with castor oil, the date would be too young because the standard sample pre-treatment could not remove this. We note that in the ¹⁴C dating community, this is a very exceptional situation. Tens of thousands of dates are produced annually by the laboratories, continuously checking themselves through programs like intercomparisons, and castor-oil like problems only happen when materials are treated with preservatives—like the Dead Sea Scrolls and samples from museum collections. These are exceptional cases, and usually require additional chemical treatment to remove the humanly applied foreign carbon.

For the Qumran samples to be dated by ¹⁴C, a collaboration was started between the Universities of Southern Denmark and Groningen. In Odense (laboratory code KLR), the extra chemical pre-treatment (soxhlet and others) and contamination tests were applied to sample materials. In Groningen (laboratory code GrA), these samples were consequently treated by the standard AAA method and dated by AMS.

A battery of ¹⁴C dates of wood, linen and parchment excavated during the 1950s at Khirbet Qumran and in the caves at Qumran is obtained. We distinguish dates of (charred) wood or seeds, linen and textile, and scrolls/parchment. We will emphasize here mainly the castor oil tests of scrolls and parchments, and review here only a few results on other materials dated. A full report on contamination tests and decontamination experiments will be published shortly [46].

5.1. (Charred) wood and seeds

Radiocarbon dates for wood samples obtained thus far are summarized in Table 1. Dates were obtained for date stones (KLR-2610a2 and

2612); the latter one was charred. A sample of wood (KLR-2611) was contaminated with paraffin preservative, which was removed by pre-cleaning with soxhlet extraction, prior to standard AAA treatment.

A special find at Qumran, known as Jar-35 has been investigated thoroughly by various archaeometric means. Both TL and 14C date it. A full report will be published [47]; only the ^{14}C dates are shown here. Three samples of charcoal from inside the jar were dated. They all produce the same date within error; the weighted average for the dates is 2035±25 BP, which calibrates into 50-1 BC (1-sigma).

Table 1. ^{14}C dates for samples of (charred) wood and seeds.

Sample	excavation	KLR	GrA	^{14}C date (BP)	δ^{13}C (‰)	%C	calibrated age
date stone	KhQ-519	2610a2	17393	1955±40	-23.29	63.9	5-85 AD
wood	T-18	2611	17394	1970±40	-23.13	52.1	20 BC-75 AD
charred date	KhQ-519	2612	17395	1955±40	-23.20	65.6	5-85 AD
JAR 35		6624	33950	2060±30	-24.52	62.0	
JAR 35		6624	34165	1965±35	-25.71	60.9	
JAR 35		6624	34170	2075±35	-24.10	61.6	
JAR 35			averaged	2035±25			50-1 BC

The ^{14}C dates themselves cannot be used as an indicator of the reliability of the dates. But the carbon content (%C) and stable isotope values (δ^{13}C) can, because these values lie in certain ranges independent of age. The can also be used as an indicator of contamination.

For example, a wood sample QUM-515 (not shown in table 1) KLR-3327 (GrA-17412) is considered suspicious in terms of ^{14}C dating. The δ^{13}C value for this sample which is very deviating: δ^{13}C=-10.62‰. For reasons not discussed here, we think that this sample is probably contaminated. However, a C4 plant which has a different photosynthesis pathway yielding δ^{13}C values in the observed range can not be excluded at this stage.

5.2. Linen/textiles

The δ^{13}C values for linen and cotton samples, which are manufactured from plant fibers, are expected to fall in the same range as wood

samples, i.e. around −25‰. Samples made from animal tissue, such as wool, have $\delta^{13}C$ values around −21‰.

For samples characterized as "textile" there remains uncertainty since it is not known if the sample consists of plant fibers (cotton) or is made from animal tissue (wool).

Our Radiocarbon date list includes a piece of textile fabric stored in the Palestine Exploration Fund collection: GrA-24262 and 25588 (KLR-5466). This is a duplicate date of linen from a sample known as sample AF-25. The average of these 2 dates is 1985±30 BP, which calibrates into 40 BC-55 AD (1-sigma). Before dating, the sample was subjected to soxhlet pre-cleaning in Odense. In Groningen, the sample underwent standard AAA treatment and was dated by AMS. The results are shown in Table 2.

For a full discussion of archaeological implications of the linen date shown here we refer to [48].

Table 2. ^{14}C dates for samples of linen and textile.

Sample	material	KLR	GrA	^{14}C date (BP)	$\delta^{13}C$ (‰)	%C	calibrated age
AF-23	linen	5466	24262	1995±40	−24.10	40.8	
AF-23	linen	5466	25588	1975±35	−24.45	36.6	
			averaged	1985±30			5-55 AD

The $\delta^{13}C$ and C% sample quality data for these samples are within normal range.

5.3. Bones

A few samples of fossil human bone from the Qumran cemetery were submitted to Groningen for dating. For bone, the datable fraction is collagen. The bones were very fragile, and for that reason they dissolved immediately at the start of the chemical treatment. No collagen could be produced from Qumran bone material thus far.

Bones and textiles from the graves (as well as other materials from the desert) are very fragile, which is a good reason to apply preservatives for conservation purposes. Obviously this causes contamination for ^{14}C dating; it requires the materials to be exposed to additional pre-cleaning before the standard AAA treatment used for ^{14}C dating. This can be problematic for fragile materials because they can be destroyed

during the treatment before the desired datable fraction could be extracted.

We have performed extensive testing of samples in this respect. One series was conducted on samples treated only by the standard AAA procedure. In the other series, samples were pre-cleaned prior to AAA and ^{14}C dating. A detailed datelist will be published shortly [46]. Only a few results are shown here (tables 1 and 2).

Based on our results, we recommend that samples from Khirbet Qumran and the surrounding caves residing in museums should be analyzed and cleaned prior to AAA pre-treatment and ^{14}C dating.

Our findings also apply more in general to ^{14}C samples from museum objects, and are not limited to Qumran.

5.4. Scrolls and parchment

It is feasible that castor oil and similar components could lead to a reaction with the proteins of the parchment. If this indeed takes place, modern carbon atoms originating from the oil would be fixated to the parchment, and thus constitute a serious obstacle to any attempt at de-contaminating samples of castor oil polluted parchment prior to ^{14}C dating.

It is known that the original team of editors of the Dead Sea scrolls, both to clean the texts and to make the readings more clear, used castor oil extensively.

As far as castor oil is concerned, it is essential to determine whether the standard AAA pre-treatment procedure is capable of removing all traces of this specific contaminant from manuscript fragments.

Contamination of a sample with an oil derived from a modern natural plant (such as castor), if not removed by the pre-treatment, would give a younger age than the true age. Fossil oils (petroleum products from the oil industry) would give an older age than the true age. The effect is about 100 ^{14}C years for a contaminant 1% in weight.

We conducted experiments by contaminating pieces of French medieval parchment with oil, both modern and fossil. The results are shown in Table 3.

The untreated samples yield ^{14}C ages corresponding to the age of the parchment. The effect of oil contamination is obvious.

From these results we calculated how much of the oil was removed by the AAA treatment. The conclusion from this experiment is that the ^{14}C age offset is 2-3 centuries, for samples fully saturated with oil.

Also pure oils were dated. Old (fossil) oil is infinitely old on the ^{14}C timescale; indeed the ^{14}C concentration could not be distinguished from the background, which corresponds to a ^{14}C age of about 45.000 BP (GrA-14051). Modern oil indeed has a ^{14}C activity of 111.5%, which means it dates from after 1950.

For more details and calculations, we refer to [43].

Table 3. ^{14}C dates for scrolls and parchment testing the effects of castor oil

KLR	GrA	treatment	weight natural (mg)	weight with oil (mg)	weight after AAA	^{14}C date (BP)	δ^{13}C (‰)	%C
1894	13929	untreated	27.0	27.0	22.4	750±40	−22.43	46.7
1895	13930	old oil	24.7	31.5	22.8	2030±40	−23.10	49.8
1896	13931	modern oil	27.9	36.5	25.9	540±40	−23.48	49.6
2315	14044	old oil	31.7	38.2	27.3	1670±45	−23.04	46.1
2316	14043	new oil	24.9	32.7	23.3	475±45	−23.53	45.8
2317	14042	untreated	23.9	23.9	19.3	770±45	−22.61	43.7
2318	14038	old oil	24.0	30.3	17.9	1670±45	−22.84	44.4
2323	14051	pure old oil	–	–	–	>45000	−27.00	–
2324	14052	pure modern oil	–	–	–	111.5±0.6%	−28.80	–

After these initial experiments, we investigated various methods to remove contaminants (in particular castor oil) prior to the standard AAA pre-treatment.

Experiments for decontamination of the scroll materials by cleaning using this *soxhlet* extraction method, or by other techniques such as ultrasound cleaning and supercritical CO_2 cleaning, have proven to be successful [49]. The *soxhlet* method was chosen to be the best decontamination method; the others had a lower success rate, because of the fragile nature of the samples.

We have succeeded in devising a pre-cleaning strategy using soxhlet extraction that allowed complete removal of castor oil and linolic oil from both medieval parchment (KLR-6850 to 6854) and for samples of un-inscribed Dead Sea scrolls (KLR 7080 and 7081). These measurements, together with other pre-cleaning test results are shown in Table 4 [49].

Table 4. ¹⁴C dates for scrolls and parchment after soxhlet cleaning of the contamination with oil

KLR	GrA	contamination	¹⁴C date (BP)	$\delta^{13}C$ (‰)	%C
6850	37802	none	795±30	−22.14	47.5
6851	37803	castor oil	795±30	−22.02	47.6
6852	37897	linoleic oil	785±30	−22.21	47.9
6853	37898	castor oil	795±30	−22.03	47.6
6854	37899	linoleic oil	(failed)	−21.98	47.4
7080	39727	none	2120±70	−18.47	41.7
7081	39728	castor oil	2200±70	−18.11	39.5

The samples were cleaned using soxhlet with 1 hour in ethanol, 4 hours in hexane, and again 1 hour in ethanol.

The sample KLR-6854 was lost in the process due to a technical problem. The dates of the other four samples are (almost) identical, showing that the cleaning was completely effective.

Two samples of un-inscribed Dead Sea Scroll were tested; one was left untreated (KLR-7080), whereas the other was contaminated with castor oil (KLR-7081).

The samples were quite small, which explains the relatively large uncertainty (70 BP).

The results from Table 4 can be seen as "the ultimate test" for the castor oil (de)contamination experiment. The decontamination method we developed proved to be effective in removing castor oil from Dead Sea Scroll parchments, and is mechanically subtle enough not to damage the fragile material during the cleaning process.

We are in the process of selecting Dead Sea Scrolls, previously dated by ¹⁴C in either Tucson or Zürich, which would be candidates for re-dating. This concerns, among others, 4Q258 Community Rule (d), 4Q266 Damascus Document (a), 4Q171 Pesher Psalms (a), 4Q521 Messianic Apocalypse (see Plate XI), Xhev/Se 8a Kefar Bebayou/Kefar Baru, and 1QH Thanksgiving Hymns (a).

We propose to re-date these Dead Sea Scrolls, after pre-cleaning with the soxhlet procedure we developed for this purpose.

6. Conclusions ·

Since its conception around 1950, Radiocarbon (^{14}C) is developed into a well-established and reliable dating method. Calibration of the ^{14}C timescale enables absolute dating and therefore provides a scientific measure of past time.

The AMS method enables the dating of small (milligram size) samples, opening new horizons since the 1980s.

The application of the ^{14}C dating method can be limited by the temporal resolution, in particular in (proto)historic periods. It depends on the exact shape of the calibration curve during the relevant time frame, and may vary from a few decades to centuries.

In the context of Qumran, ^{14}C samples are fragile and therefore treated by preservatives or oil. This is a contamination that is difficult to remove from the sampled materials using chemical treatment protocols, which are standard for the ^{14}C method. This includes samples of the Dead Sea Scrolls, dated by ^{14}C almost two decades ago. Some of these scrolls were potentially contaminated by castor oil, which had been applied during the 1950s. Since this castor oil is not removed effectively by the standard chemical pre-treatment, some ^{14}C dates are affected and possibly too young.

We have tested pre-cleaning techniques, of which the so-called soxhlet extraction was selected for use. This pre-cleaning should be applied before the standard ^{14}C procedures are used. By performing a variety of experiments, we have shown that parchments, heavily contaminated with oil, could be cleaned effectively.

Therefore, we can now re-date by ^{14}C those Dead Sea Scrolls, which were contaminated reliably.

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