QUALITY CONTROLLED RADIOCARBON DATING OF BONES AND CHARCOAL FROM THE EARLY PRE-POTTERY NEOLITHIC B (PPNB) OF MOTZA (ISRAEL)

Meirav Yizhaq¹ • Genia Mintz² • Illit Cohen¹ • Hamudi Khalaily³ • Steve Weiner¹ • Elisabetta Boaretto^{2,4}

ABSTRACT. Radiocarbon dating of early Pre-Pottery Neolithic B (PPNB) deposits at the site of Motza, Israel, was achieved by first prescreening many charcoal and bone samples in order to identify those that are in the most suitable state of preservation for dating. For assessing bone preservation, we determined the collagen contents, and by infrared spectroscopy the collagen purity. The collagen samples of the best preserved bones were then further characterized by their C/N ratios and amino acid compositions. Prescreening of the charcoal samples involved monitoring the changes in infrared and Raman spectra during the acid-alkali-acid treatments. In some samples, we noted that the clay content increased with additional alkali treatments. These samples were rejected, as this could result in erroneous dates. No differences were observed in the ¹⁴C dates between charcoal and bone collagen samples. The dates range from 10,600–10,100 cal BP, which is consistent with dates for the early PPNB from other sites. This is of much interest in terms of better understanding where and when domestication of animals began in this period, and how agriculture spread throughout the Levant.

INTRODUCTION

The quality of a radiocarbon date includes the degree of confidence in the archaeological context from which the sample is recovered, the demonstrated purity of the material to be analyzed (van Klinken 1999; Alon et al. 2002), and the known accuracy and precision of the analytical method. All the parameters that define the quality of the date should be judged independently of the actual date obtained, so that this powerful technique can more often be used to discover unexpected phenomena, and less often for confirming or negating existing concepts. Here, we report the dates of the early Pre-Pottery Neolithic B (PPNB) layer at the site of Motza, about 5 km west of Jerusalem, Israel (Figure 1), using this approach.

The PPNB period (about 11,000–8200 cal BP) is the time when domesticated plants; herding of goats, sheep, and cattle; as well as tending of pigs spread across the Levant, to Cyprus and into the Zagros foothills (Bar-Yosef 2001). However, only a few sites dated to the early phase of this period are known in the Levant (Figure 2) (Goring-Morris and Belfer-Cohen 1998; Kuijt and Goring-Morris 2002; Kuijt 2003). For this reason, several investigators have doubted the presence of the early PPNB period in the southern Levant (Rollefson 1998; Kuijt 2003; Edwards et al. 2001). The dates obtained from some of the early PPNB sites in the Levant range from 9600–8800 BP uncalibrated. In calibrated years, this range corresponds to approximately 1200 yr (ranging from 11,000–9800 cal BP). Even though in most cases only a few dates were obtained from a site, and these were almost always from wood charcoal, some authors have used this data to propose that the early PPNB culture originated in the northern Levant and then spread south (Bar-Yosef 2001). As the whole period of time involved is about 1200 yr and falls in a part of the ¹⁴C calibration curve that has some plateaus, distinguishing between this and other possibilities requires high-resolution dating after the sample material and context have been proven to be suitable for dating.

The early PPNB deposit at Motza lies directly on the limestone bedrock and is on average about 2 m thick. It is overlain by several meters of sediments from younger periods (Late PPNB, PN, and Iron

¹Department of Structural Biology, Weizmann Institute of Science, Rehovot 76100, Israel.

²Radiocarbon Dating Laboratory, Environmental Science and Energy Research Department, Weizmann Institute of Science, Rehovot 76100, Israel.

³Israel Antiquities Authority, P.O. Box 586, Jerusalem, 91004, Israel.

⁴Corresponding author. Email: Elisabetta.Boaretto@weizmann.ac.il.

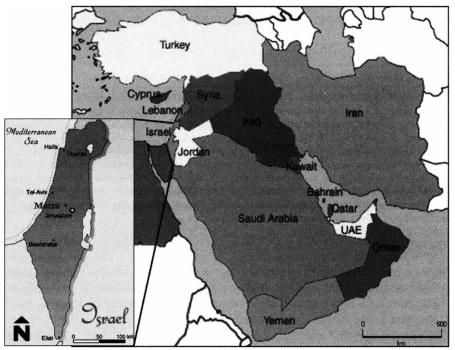


Figure 1 Motza is located 5 km west of Jerusalem, Israel

Age). The early PPNB period is recognized primarily by types of flint arrowheads (Helwan and Jericho points) (Gopher 1994). The sediments are composed mainly of clay, and the calcite content tends to decrease with increasing depth in the section. Most of the ¹⁴C samples were obtained from clay-rich layers in the basal part of the section. Several human skeletons were found in the early PPNB, mostly in relation to plaster floors. One collagen sample from a human bone was also dated.

Our approach was to be involved on a regular basis with the excavation itself, and in so doing to become acquainted with the stratigraphy and collect samples as they were exposed. Many samples of bone and charcoal were collected and then screened for state of preservation using several analytical methods. For bones, the collagen content and the mineral splitting factors were used for screening. The purified collagen was examined for C/N ratio, amino acid composition, and infrared spectrum (DeNiro and Weiner 1988a). For charcoal, we monitored the behavior of the samples during the acid-alkali-acid (AAA) treatments at each stage using both infrared and Raman spectroscopy (Alon et al. 2002), and then used this information to choose the samples for dating. We note that very little is currently known about fossil charcoal structure and diagenesis, a subject that is currently under investigation in our laboratory (Cohen-Ofri I, Weiner L, Boaretto E, Mintz E, Weiner S, unpublished data). After selection of the best samples for dating, graphite targets were prepared. As high-resolution dating was required, 3 targets from each sample were analyzed separately by accelerator mass spectrometry (AMS) at the NSF-Arizona AMS facility.

This study shows that all the dates of the lower part of the early PPNB layer at Motza fall within the 9300–9000 BP uncalibrated range. The dates of the bone collagen are similar to the charcoal dates, and there is no systematic difference between them.

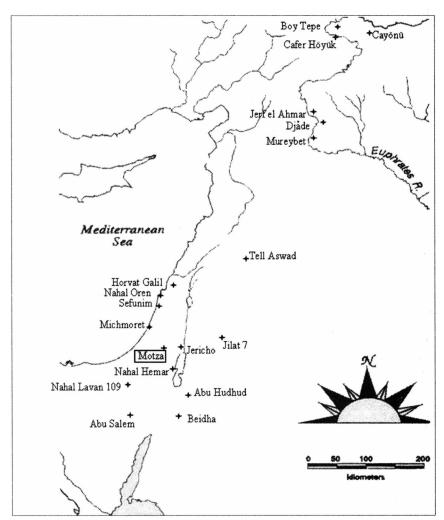


Figure 2 Approximate locations of early PPNB sites throughout the Levant

MATERIALS AND METHODS

Bone and charcoal samples were collected at the site of Motza during the excavation of 2003 (and not from preexisting sections) and were placed in aluminum foil. The samples were air-dried following collection. Samples from the lowest part of the early PPNB section were used.

Infrared Spectroscopy

Bone and charcoal samples were homogenized and powdered in an agate mortar and pestle. A few tens of micrograms were mixed with a few milligrams of anhydrous KBr (Aldrich), and the mixture was formed into a pellet. Infrared spectra were obtained at 4 cm⁻¹ resolution using a Fourier transform infrared (FTIR) spectrometer (MIDAC Corporation, Costa Mesa, California, USA). The infrared splitting factors (IRSF) were calculated from the bone spectra following the method of Weiner and Bar-Yosef (1990).

Bone Collagen Content and Quality

In order to define the state of preservation of the collagen, several methods were used. First, the weight percent (wt%) of collagen was determined by dissolving a weighed aliquot of the bone powder (about 200 mg) in 1N HCl (to remove the mineral phase) and immediately washing the insoluble fraction 3 times in deionized water (DW) by centrifugation (6000 rpm for 2 min) and resuspension of the pellet. The dried sample was weighed and a portion was used to obtain an infrared spectrum, to verify that this fraction is collagen and to assess its purity (Figure 3). Then, those samples with collagen were further tested for their C/N ratios using an elemental analyzer (CHN-O EA1108-1 elemental analyzer). Their amino acid compositions were also determined by hydrolyzing at 120 °C in 6N HCl for 22 hr in vacuo and then lyophilizing the sample. The hydrolyzates were analyzed using an automatic amino acid analyzer (Waters 2690 Separation ModuleTM).

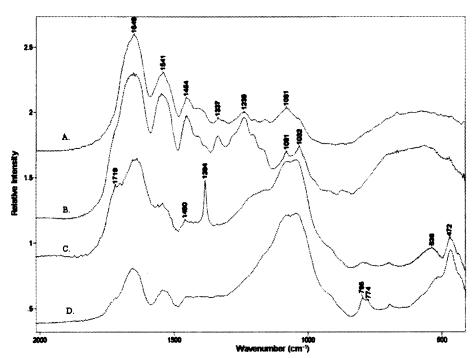


Figure 3 Representative infrared spectra of collagen: A) collagen extracted from modern bone; B) sample 16—well-preserved collagen; C) sample 27—poorly preserved collagen. The absorbance peak at 1384 cm⁻¹ is due to nitrate from the soil; D) sample 12—poorly preserved collagen together with quartz and clay.

Bone Collagen Extraction and Purification

The cleaning procedure for the collagen samples chosen for dating was based on the acid-alkaliacid (AAA) technique (de Vries and Barendsen 1954; Hattè et al. 2001). The bone (2–4 g) was ground to powder and homogenized. Ten to 20 mL of 1N HCl was added and after 30 min the sample was centrifuged for 3 min at 3000 rpm. The supernatant was removed and the pellet was washed with DW to pH 7. The pellet was resuspended in 7 mL of 0.1% NaOH for 15 min and centrifuged again for 7 min at 3000 rpm. The supernatant was then removed and the pellet was washed with DW to pH 7. The atmospheric CO_2 adsorbed during the alkali treatment was removed by adding 7 mL of 1N HCl for 30 min and washing the pellet until the supernatant reached pH 3. A few milliliters of solution were left over the pellet.

Gelatinization was achieved by heating the pellet in acid solution pH 3 to 70 °C for 20 hr (Law and Hedges 1989). The solution was then filtered through a polyethylene filter (Eezi-filterTM) and then by superfiltration (Vivaspin 20^{TM}) (Bronk Ramsey et al. 2004). The filtrate was lyophilized (Heto LyoLab 3000^{TM}) to produce pure dry collagen (Brown et al. 1988). The quality of the collagen was checked again using infrared spectroscopy.

Raman Spectroscopy of Charcoal

Monitoring the removal of humic acids from the charcoal samples by Raman spectroscopy is based on the fact that humic acids tend to fluoresce strongly (Yang and Wang 1997). Measurements were made using a Raman Imaging Microscope (Renishaw) through a $50 \times$ lens. The excitation at 632 nm was produced by a 25-mW He/Ne laser. Each homogenized sample was measured 10 times at different places, and the spectra were averaged. The spectral resolution was 4 cm⁻¹ and the range analyzed was 1200–2000 cm⁻¹. For details of the method, see Alon et al. (2002).

Charcoal Purification

The cleaning procedure was essentially based on the AAA procedure (de Vries and Barendsen 1954; Hattè et al. 2001), except that after each step, the pellets were dried at 60 °C, weighed, and a few milligrams were taken for infrared and Raman analyses. The alkaline step was repeated 3 times, and in the last step after adding the 1N HCl, the solution was placed on a hot plate and heated slowly to 80 °C for an hour, centrifuged, and the pellet was washed with DW to pH 7 and dried at 60 °C.

Target Preparation and AMS Analysis

The samples prepared for dating were combusted to CO_2 in quartz tubes containing about 200 mg of copper oxide (Merck) and heated to 900 °C for 200 min. The CO_2 was divided into 3 aliquots and each was reduced to graphite using cobalt (Fluka) (about 1 mg) as a catalyst and hydrogen, then heated to 700 °C for 20 hr. The graphite samples were analyzed for ¹⁴C content at the NSF-AMS Radiocarbon Laboratory in Tucson, Arizona, USA.

The ¹⁴C ages were calibrated to calendar years BP using the IntCal98 tree-ring calibration curve (Stuiver et al. 1998) and the software OxCal v 3.9 from Bronk Ramsey (2003).

RESULTS

Screening of Bone Samples

We analyzed 30 bones from the early PPNB layer at the site of Motza.

The infrared splitting factors (IRSF) and the weight percentages (wt%) of the insoluble collagen of bones from the site are listed in Table 1. Of the 30 bones analyzed, 21 had IRSF values in the range of fresh bone, i.e. 2.6 to 3.0 (Ziv 1991). IRSF as defined by Weiner and Bar-Yosef (1990) reflects a combination of relative sizes of the crystals as well as the extent to which the atoms in the lattice are ordered. The higher the value, the larger and more ordered are the crystals.

The weight percentage of insoluble collagen in the samples ranges between 0 to 5.9% (Table 1). Fresh bone has about 20 wt% collagen (Doty et al. 1976). Even though relatively little collagen is preserved, 15 out of 30 collagen samples have infrared spectra similar to collagen from modern

Sample	IRSF	% collagen
1	3.0	1.7
2	3.2	1.7
2 3	2.9	0
4	2.9	0
5 6	2.8	4.1
6	2.9	0.4
7 8	3.1	0.7
8	3.0	2.1
9	3.3	2.2
10	2.9	3.0
11	3.5	2.0
12	2.9	0
13	3.7	1.4
14	3.2	2.3
15	2.9	0.1
16	3.1	5.0
17	2.8	0
18	2.9	0.1
19	2.9	1.0
20	3.0	0.9
21	2.9	0.6
22	2.9	1.0
23	2.9	1.0
24	2.8	0.2
25	2.9	5.9
26	2.9	1.9
27	2.8	0.3
28	2.8	0.1
29	2.7	0.5
30	3.2	3.4

Table 1 IRSF values and weight percentages of the collagen in the bones analyzed.

bone (e.g. Figure 3), with a strong peak at 1454 cm^{-1} due to the amino acid proline, together with the amide I and amide II absorptions at about 1650 and 1540 cm⁻¹, respectively. Therefore, even though the weight percentage of the collagen is low, its quality is very good.

The selection of the samples for dating was based both on their collagen quality and stratigraphic locations, i.e. located in the deepest layers possible of the early PPNB stratum. The C/N ratios of these collagen samples all lie within the range of 2.7 to 2.8 (Table 2), which is the same as modern collagen. Their infrared spectra show no evidence of additional components, particularly humic acids that absorb strongly around 1100 cm^{-1} . Their amino acid compositions are also very similar to modern collagen, as can be seen in Table 3 for the major amino acid constituents. The collagen is therefore clearly well preserved and free of contaminants.

We also dated a bone from a human skeleton (sample 9) buried below a plaster floor. Although the IRSF is rather high, the quality of the collagen is good. The position of the skeleton in the stratigraphic sequence is deeper than the surface related to the death event. The age of the bone is therefore expected to be younger than the adjacent layers. This is the reason for not including it in the analyses of the age of the stratum itself.

Sample	Lab code	IRSF	% collagen	C/N ratio
21	RTT 4749	2.9	0.6	2.77
20	RTT 4750	3.0	0.9	2.80
18	RTT 4751	2.9	0.1	2.78
16	RTT 4752	3.1	5.0	2.76
9	RTT 4753 ^a	3.3	2.2	2.80

Table 2 IRSF values, collagen percentages, and C/N ratios of the bones chosen for dating.

^aHuman skeleton.

Table 3 The amino acid compositions of the 5 bones (listed by sample number) chosen for dating in mole percent compared to modern collagen. The modern bone collagen values are from Wyckoff (1972). Hydroxylysine was not determined.

Amino acids	4749 (mole %)	4750 (mole %)	4751 (mole %)	4752 (mole %)	4753 (mole %)	Modern collagen (mole %)
Asp	4.28	4.15	4.11	4.31	4.18	4.50
Ser	2.71	3.00	2.67	2.86	2.90	4.30
Glu	7.33	7.28	7.20	7.27	7.14	7.10
Gly	35.48	35.36	35.68	35.27	36.08	33.10
His	0.00	0.00	0.35	0.00	0.47	0.41
Arg	5.07	5.17	4.99	5.13	5.06	5.00
Thr	1.93	1.84	1.96	1.99	1.73	1.99
Ala	11.75	11.29	12.01	12.13	11.46	10.70
Pro	11.61	11.98	11.10	11.75	11.48	12.20
Tyr	0.00	0.00	0.09	0.00	0.06	0.39
Val	2.31	2.39	2.36	2.33	2.59	2.29
Met	0.47	0.20	0.55	0.37	0.42	0.84
Lys	2.58	2.67	2.58	2.80	2.83	2.69
Ileu	1.14	0.97	1.18	1.12	1.00	0.96
Leu	2.16	2.17	2.18	2.19	2.19	2.36
Phe	1.14	1.18	1.17	1.17	1.08	1.19
HyPro	10.03	10.36	9.82	9.33	9.31	9.42

Screening of Charcoal Samples

We monitored 9 charcoal samples during the acid-alkaline-acid (AAA) procedure using infrared and Raman spectroscopy. The infrared spectra show that in 6 out of the 9 samples examined, clay concentrations (strong peaks at 1033 cm⁻¹ together with peaks at 535 and 472 cm⁻¹) increase and the charcoal contents (peaks from 1718 to 1595 cm⁻¹) decrease after each consecutive wash (before HCl, HCl, NaOH) (Figure 4). In the other 3 samples, the charcoal component remains the dominant component throughout the whole treatment (Figure 5).

Removal of the humic acids after each wash with NaOH was monitored using Raman spectroscopy (Alon et al. 2002). The peak around 1600 cm^{-1} is the so-called G-peak and is characteristic of graphite. The peak around 1300 cm^{-1} is the D-peak and represents the disordered material outside the graphite layers (Tuinstra and Koenig 1970). The reproducibility of individual analyses is not good (e.g. Figure 6); therefore, the intensities of each frequency measurement of 10 spectra were aver-

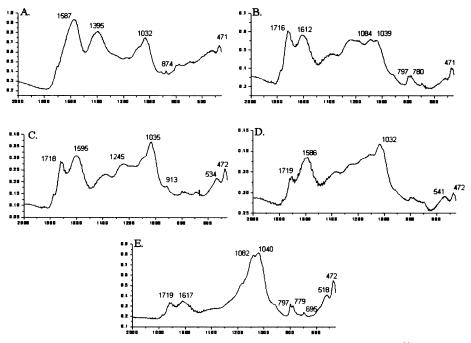


Figure 4 The infrared spectra of one representative charcoal sample (Mos 27), which was not ¹⁴C dated, after the different treatments: A) before HCl; B) after HCl; C) after the first wash with NaOH; D) after the second wash with NaOH; E) after the third wash with NaOH. Note the increasing intensity of the absorption peak around 1035 cm⁻¹, which originates from clay.

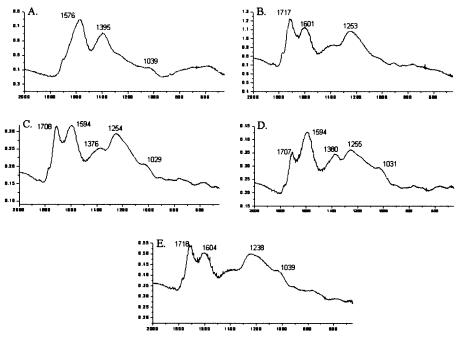


Figure 5 The infrared spectra of one representative sample (RTT 4865) after the different treatments: A) before HCl; B) after HCl; C) after the first wash with NaOH; D) after the second wash with NaOH; E) after the third wash with NaOH. Spectrum E is characteristic of pure fossil charcoal.

aged, resulting in an average intensity across the entire frequency range. This was repeated for each sample during the different treatments. A plot of the mean intensity of each spectrum at each washing stage (Figure 7) shows that intensity decreases until the third wash. This decrease in fluorescence implies that most of the humic acids were removed after the second wash, as noted by Alon et al. (2002). The rise in the fluorescence after the third wash may be related to the increasing clay concentrations observed by infrared spectroscopy.

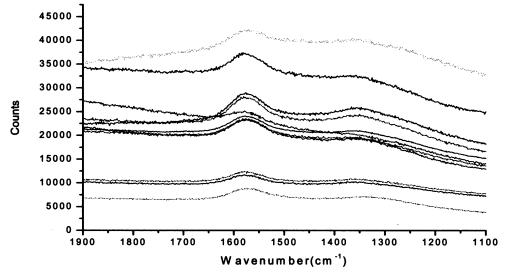


Figure 6 Ten Raman spectra of the same sample (RTT 4865) showing poor reproducibility

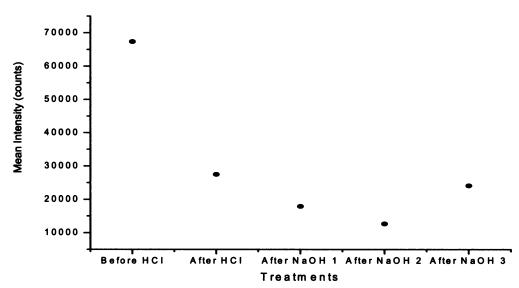


Figure 7 Average fluorescence intensity of charcoal sample RTT 4865 after the different treatments

The selection of the best charcoal samples for ¹⁴C dating was based on their infrared spectra, namely, the 3 samples containing the smallest amount of clay at the end of the series of treatments.

14C DATES

The uncalibrated ¹⁴C dates of the selected collagen and charcoal samples are listed in Table 4. The average of the ¹⁴C dates for each sample range from about 9000 to about 9300 BP. The range of the charcoal and bone dates overlap, with bones having a higher scatter (their average and standard deviation is 9185 ± 100 BP without sample RTT 4753 from the human skeleton) than the charcoal samples (their average and standard deviation is 9130 ± 30 BP), and there is no correlation with depth in the stratigraphy (Table 4). All dates fall within the range of the early PPNB (Gopher 1996; Kuijt and Goring-Morris 2002).

Sample	Material	Excavation square	Depth asl (m)		BP dates (r	epetitions) ^a		Average year BP ^b
RTT 4749	Bone	N19a	587.91	9130 ± 50	9155 ± 50	9100 ± 50		9130 ± 30
RTT 4750	Bone	N18d	587.97	9350 ± 50	9290 ± 50	9290 ± 50		9310 ± 30
RTT 4751	Bone	N18d	588.18	9080 ± 50	9090 ± 50	9100 ± 50		9100 ± 30
RTT 4752	Bone	N18a	588.35	9230 ± 50	9200 ± 50	9200 ± 50	9210 ± 50	9210 ± 25
RTT 4753	Bone	O19c	589.01	8990 ± 50	8990 ± 70	9000 ± 55		8995 ± 35
RTT 4865	Charcoal	N19a	588.88	9030 ± 55	9120 ± 65	9085 ± 55	9100 ± 75	9080 ± 30
RTT 4866	Charcoal	East wall	588.19	9215 ± 55	9190 ± 60	9035 ± 55		9150 ± 35
RTT 4867	Charcoal	East wall	588.24	9161 ± 125	9199 ± 79	9217 ± 59	9138 ± 114	9200 ± 40

Table 4	⁴ C dates of bon	es and	charcoal.

*Single measurement $\pm 1 \sigma$.

^bAverage dates are weighted averages $\pm 1 \sigma$ and are rounded to the nearest 5 yr.

DISCUSSION

We present here a comprehensive approach to high-resolution ¹⁴C dating that involves prescreening many bones and charcoal samples in order to select the best preserved samples for dating. This is followed by characterization of the purified samples and analysis of multiple targets for each sample. Five bone samples were chosen out of 30 bone samples screened, and 3 charcoal samples were chosen from 9 that were screened.

The state of preservation of the mineral fraction of the bones from Motza is exceptionally good, as the splitting factor of the mineral phase of most of the bones is within the range of modern bone. This is unusual because the bones in most of the sites surveyed previously have higher splitting factors (Weiner and Bar-Yosef 1990). Despite this, the quantity of collagen present in these bones is low. The quality of the extracted collagen, however, is good. In fact, the extracted collagen samples are comparable to modern collagen with respect to their infrared spectra, C/N ratios, and amino acid compositions. The reasons for the good preservation of the mineral phase and the collagen may both be related to the high clay content (more than 80 wt%; Yizhaq 2004) of the sediment at the base of the section, which minimizes exposure to water (Weiner and Bar-Yosef 1990). It is also possible that the preserved collagen is trapped within crystal aggregates (DeNiro and Weiner 1988b), and because the mineral phase is so well preserved, the aggregated crystals protect the collagen.

Charcoal samples were chosen according to the variations in their infrared and Raman spectra during purification. In contrast to bones, our knowledge about archeological charcoal structure and diagenesis is limited. Thus, at present the choice of the most suitable charcoal samples for dating is not based on state of preservation per se, but more on behavior of the sample during purification by the AAA method. The observation of increasing clay content during the alkali treatment for 6 charcoal samples has important implications for dating. Dating the clay instead of the charcoal could produce high-precision dates, but their accuracy may be very low. In other words, the dates will all be very similar but will not represent the age of the stratum of interest. Therefore, we avoided using these samples. Monitoring the reduction in fluorescence of the charcoal during the alkali washes (Alon et al. 2002) showed that most of the removable humic acid was extracted from the sample. Although the reduction in fluorescence was very significant (Figure 7), we note that it did not reach zero. We do not know the nature of the source of the residual fluorescence.

Dating both charcoal and bone from the same stratum enabled us to compare dates obtained using these 2 materials. Bone collagen is a short-lived material, whereas wood charcoal may be several hundred years old (Blong and Gillespie 1978; Mook and Waterbolk-Groningen 1985). In Motza, the bone collagen and charcoal dates are similar. Charcoal is often favored over bone as a material for dating, mainly because of the susceptibility of bone to contamination with younger carbon and the decay of collagen with time (Stafford et al. 1987; Jöris et al. 2003). Jöris et al. (2003) and Zilhão and d'Errico (1999) found that bone samples were systematically younger than charcoal samples in the same layer, often differing by several thousand years in the Paleolithic period. Charcoal, on the other hand, is often regarded as a "mobile" material, sensitive to stratigraphic disturbance. The old wood effect (Zilhão and d'Errico 1999; Zhiyu et al. 2000) may also make charcoal-based dates older and hence less reliable. Apparently all these potential problems were not relevant in this study. The similarity between bone and charcoal dates excludes the possibility of a significant old wood effect. It also excludes the possibility of the charcoal sample being systematically displaced in the stratigraphic sequence relative to the bone samples.

A partial list of ¹⁴C dates of early PPNB sites in the Levant is presented in Table 5. The ¹⁴C dates from Motza all fall within the range of the early PPNB (Gopher 1996; Kuijt and Goring-Morris 2002). After calibration, the range of the dates for the lowermost early PPNB stratum at Motza is 10,600–10,000 cal BP. Figure 8 shows the calibrated ages for the sites listed in Table 5 including Motza (Table 4). Most of the sites overlap in age with Motza within 1- σ error. As other early PPNB sites have not been as systematically and accurately dated as Motza, it is premature to conclude that the sites in the northern Levant are older than those in the southern Levant.

Site		¹⁴ C date (BP)	$\pm 1 \sigma$	Material	Lab nr	References
Mureybet IVA	NL	9600	150	Charcoal	MC-861	Cauvin 1979; Cauvin 1987
Mureybet IVA	NL	9130	150	Charcoal	MC-862	Cauvin 1979; Cauvin 1987
Mureybet IVA	NL	9030	150	Charcoal	MC-863	Cauvin 1979; Cauvin 1987
Mureybet IVB	NL	9280	150	Charcoal	MC-736	Cauvin 1979; Cauvin 1987
Mureybet IVB	NL	8910	150	Charcoal	MC-737	Cauvin 1979; Cauvin 1987
Tell Aswad IB	NL	9340	120	Charcoal	Gif-2370	Delibrias et al. 1982; Cauvin 1987
Tell Aswad IB	NL	9270	120	Charcoal	Gif-2371	Delibrias et al. 1982; Cauvin 1987
Tell Aswad	NL	9285	50	Charcoal	LY-11383	Lyon Lab Report 2003
Tell Aswad	NL	9220	70	Charcoal	LY-11384	Lyon Lab Report 2003
Horvat Galil	SL	8950	100	Charcoal	RT-1396	Carmi and Segal 1992; Gopher 1996
Horvat Galil	SL	9340	70	Charcoal	RT-1397	Carmi and Segal 1992; Gopher 1996
Sefunim	SL	9395	130	Charcoal	HV-3368	Bar-Yosef 1981
Munhata IVB	SL	9160	500	Soil	M-1793	Crane and Griffin 1970
Jericho	SL	9170	200	Charcoal	BM 115	Baker and Mackey 1963
Jericho	SL	9140	70	Charcoal	GRO-942	Bar-Yosef 1981
Nahal Hemar	SL	9210	300	Linen yarn	BM-2299	Bar-Yosef 1988
Nahal Hemar	SL	8850	90	Linen yarn	Pta 3625	Bar-Yosef 1988
Nahal Hemar	SL	8810	120	Fabric	OxA 1016	Bar-Yosef 1988
Beidha	SL	9128	103	Charcoal	P-1330	Stuckenrath and Lawn 1969

Table 5 Early PPNB ¹⁴C dates uncalibrated: NL = northern Levant; SL = southern Levant.

Atmospheric data from Reimer et al (2004);OxCal v3.10 Bronk Ramsey (2005); cub r:5 sd:12 prob usp[chron]

early PPNB end 9000±50BP	
early PPNB beg 9600±50BP	
Beidha P-1330 9128±103BP	
Nahal Hemar OxA-1016 8810±120BP	
Nahal Hemar Pta-3625 8850±90BP	
Nahal Hemar BM-2299R 9210±300BP	
Motza RTT-4753 8995±35BP	<u>A</u>
Motza RTT-4865 9080±30BP	
Motza RTT-4751 9100±30BP	<u>+</u>
Motza RTT-4749 9130±30BP	
Motza RTT-4866 9150±35BP	
Motza RTT-4867 9200±40BP	
Motza RTT-4752 9210±25BP	
Motza RTT-4750 9310±30BP	
Jericho GRO-942 9140±70BP	· · · · · · · · · · · · · · · · · · ·
Jericho BM-115 9170±200BP	
Munhata IVB M-1793 9160±500BP	
Sefunim HV-3368 9395±130BP	
Horvat Galil RT-1396 8950±100BP	
Horvat Galil RT-1397 9340±70BP	
Fell Aswad LY-11384 9220±70BP	
Tell Aswad LY-11383 9285±50BP	
Fell Aswad IB Gif-2371 9270±120BP	
Fell Aswad IB Gif-2370 9340±120BP	
Mureybet IVB MC-737 8910±150BP	
Mureybet IVB MC-736 9280±150BP	
Mureybet IVA MC-863 9030±150BP	
Mureybet IVA MC-862 9130±150BP	

Calibrated date

Figure 8 Probability distribution of 14 C ages for the early PPNB sites listed in Tables 4 and 5. In the plot, the dates are organized by sites (from north to south) and for each site the strata are the oldest to the youngest according to the 14 C date. The calibrated range for the assumed beginning and end of the early PPNB period are represented at the end of the plot.

CONCLUSION

This study shows that prescreening of many bone and charcoal samples is important in dating the early PPNB deposits of Motza. This methodology may well be applicable in other sites in order to resolve difficult chronological problems.

ACKNOWLEDGMENTS

We thank the Israel Antiquities Authority, and in particular, Dr A De Groot, A Irich-Rose, and Z Greenhut. We also thank Dr A Tishbi (Weizmann Institute) for assistance in the Raman and amino acid analysis, and Prof O Bar-Yosef (Harvard University) for helpful comments on the paper. We thank George Schwartzmann, Sarasota, Florida (USA) and the American School of Prehistoric Research (Peabody Museum, Harvard University) for financial support; the Kimmel Center for Archaeological Science at the Weizmann Institute; and the US National Science Foundation (Grant EAR01-15488).

REFERENCES

- Alon D, Mintz G, Cohen I, Weiner S, Boaretto E. 2002. The use of Raman spectroscopy to monitor the removal of humic substances from charcoal: quality control for ¹⁴C dating of charcoal. *Radiocarbon* 44(1): 1–11.
- Baker H, Mackey J. 1963. British Museum natural radiocarbon measurements IV. *Radiocarbon* 5:104–8.
- Bar-Yosef O. 1981. The "Pre Pottery Neolithic" period in the southern Levant. In: Cauvin J, Sanlaville P, editors. *Préhistoire du Levant*. Paris: Centre national de la recherche scientifique. p 551–70.
- Bar-Yosef O, Alon D. 1988. Excavations in the Nahal Hemar Cave. Atiqot 18:1-30.
- Bar-Yosef O. 2001. The world around Cyprus: from Epi-Paleolithic foragers to the collapse of the PPNB civilization. In: Swiny S, editor. *The Earliest Prehistory of Cyprus from Colonization to Exploitation*. Boston: American Schools of Oriental Research. p 129–64.
- Blong RJ, Gillespie R. 1978. Fluvially transported charcoal gives erroneous ¹⁴C ages for recent deposits. *Nature* 271:739–41.
- Bronk Ramsey C, Higham T, Bowles A, Hedges R. 2004. Improvements to the pretreatment of bone at Oxford. *Radiocarbon* 46(1):155–63.
- Brown TA, Nelson DE, Vogel JS, Southon JR. 1988. Improved collagen extraction by modified Longin method. *Radiocarbon* 30(2):171–7.
- Carmi I, Segal D. 1992. Rehovot radiocarbon measurements IV. Radiocarbon 34(1):115–32.
- Cauvin J. 1979. Les fouilles de Mureybet (1971–1974) et leur signification pour les origines de la sedentarisation au Proche-Orient. In: Freedman DN, editor. *Annual of American Schools of Oriental Research* 44: 19–48.
- Cauvin J. 1987. Chronologie relative et absolue dans le Neolithique du Levant Nord et d'Anatolie entre 10,000 et 8000 BP. In: Aurenche O, Evin J, Hours F, editors. Chronologies in the Near East: Relative Chro-

nologies and Absolute Chronology 16,000–4000 BP. Oxford: British Archaeological Reports International Series 379:325–42.

- Crane HR, Griffin JB. 1970. University of Michigan radiocarbon dates XIII. Radiocarbon 12(1):161-80.
- Delibrias G, Guillier MT, Labeyrie J. 1982. GIF natural radiocarbon measurements IX. *Radiocarbon* 24(3): 291-343.
- DeNiro MJ, Weiner S. 1988a. Chemical, enzymatic and spectroscopic characterization of "collagen" and other organic fractions from prehistoric bones. *Geochimica et Cosmochimica Acta* 52:2197–206.
- DeNiro MJ, Weiner S. 1988b. Organic matter within crystalline aggregates of hydroxyapatite: a new substrate for stable isotopic and possibly other biogeochemical analyses of bone. *Geochimica et Cosmochimica Acta* 52:2415–23.
- de Vries HL, Barendsen GW. 1954. Measurements of age by the carbon-14 technique. *Nature* 174:1138–41.
- Doty S, Robinson RA, Schofield B. 1976. Morphology of bone and histochemical staining characteristics of bone cells. In: Aurbach GD, editor. *Handbook of Physiology*. Washington, DC: American Physiology Society. p 3–23
- Edwards PC, Falconer SE, Fall PL, Berelov I, Davis C, Meadows J, Meegan C, Metzger MC, Sayej G 2001. Archaeology and environment of the Dead Sea plain: preliminary results of the first season of investigations by the joint La Trobe University/Arizona State University project. *Annual of the Department of Antiquities of Jordan* 45:135–57.
- Gopher A. 1994. Arrowheads of the Neolithic Levant: A Seriation Analysis. American Schools of Oriental Research Dissertation Series 10. Winona Lake, Indiana: Eisenbrauns. 325 p.
- Gopher A. 1996. What happened to the EPPNB? In: Kozlowski SK, Gebel HGK, editors. *Neolithic Chipped Stone Industries of the Fertile Crescent, and Their*

Contemporaries in Adjacent Regions. Berlin: Studies in Early Near Eastern Production, Subsistence, and Environment 3. p 443-52.

- Goring-Moris N, Belfer-Cohen A. 1998. The articulation of cultural processes and late Quaternary environmental changes in Cisjordan. *Paleorient* 23:71–93.
- Hattè C, Morvan J, Noury C, Paterne M. 2001. Is classical acid-alkali-acid treatment responsible for contamination? An alternative proposition. *Radiocarbon* 43(2A):177-82.
- Jöris O, Fernández E, Weninger B. 2003. Radiocarbon evidence of the Middle to Upper Paleolithic transition in southwestern Europe. *Trabajos de Prehistoria* 60: 15–38.
- Kuijt I. 2003. Between foraging and farming; critically evaluating the archaeological evidence for the southern Levantine early Pre-Pottery Neolithic period. *Turkish Academy of Sciences Journal of Archaeology* 6:7–25.
- Kuijt I, Goring-Morris N. 2002. Foraging, farming, and complexity in the Pre-Pottery Neolithic of the southern Levant: a review and synthesis. *Journal of World Prehistory* 16:361–440.
- Law IA, Hedges REM. 1989. A semi-automated bone pretreatment of older and contaminated samples. *Radiocarbon* 31(3):247–53.
- Mook WG, Waterbolk-Groningen HT. 1985. Handbooks for Archaeologists Number 3, Radiocarbon Dating. Strasbourg: European Science Foundation.
- Rollefson GO. 1998. The Aceramic Neolithic. In: Henry DO, editor. *The Prehistoric Archaeology of Jordan*. Oxford: British Archaeological Reports International Series 705:102–26.
- Stafford TW, Jull AJT, Brendel K, Duhamel RC, Donahue D. 1987. Study of bone radiocarbon dating accuracy at the University of Arizona NSF Accelera-

tor Facility for Radioisotope Analysis. *Radiocarbon* 29(1):24-44.

- Stuckenrath R, Lawn B. 1969. University of Pennsylvania radiocarbon dates XI. Radiocarbon 11(1):150–62.
- Stuiver M, Reimer PJ, Bard E, Beck JW, Burr GS, Hughen KA, Kromer B, McCormac G, van der Plicht J, Spurk M. 1998. IntCal 98 radiocarbon age calibration, 24,000–0 cal BP. *Radiocarbon* 40(3):1041–84.
- Tuinstra F, Koenig JL. 1970. Raman spectra of graphite. Journal of Chemical Physics 53:1126–30.
- van Klinken GJ. 1999. Bone collagen quality indicators for paleodietary and radiocarbon measurements. *Jour*nal of Archaeological Science 26:687–95.
- Weiner S, Bar-Yosef O. 1990. State of preservation of bones from prehistoric sites in the Near East: a survey. *Journal of Archaeological Science* 17:187–96.
- Wyckoff RWG. 1972. The Biochemistry of Animal Fossils. Bristol: Scientechnica LTD. 152 p.
- Yang Y, Wang T. 1997. Fourier transform Raman spectroscopic characterization of humic substances. *Vibrational Spectroscopy* 14:105–12.
- Yizhaq M. 2004. Characterizing and dating the early PPNB layer at the site of Motza [M.Sc. thesis]. Rehovot, Israel: Weizmann Institute of Science.
- Zhiyu G, Kexin L, Xiangyang L, Hongji M, Kun L, Sixum Y. 2000. The use of AMS radiocarbon dating for Xia-Shang-Zhou chronology. *Nuclear Instruments* and Methods in Physics Research B 172:72–31.
- Zilhão J, d'Errico F. 1999. The chronology and taphonomy of the earliest Aurignacian and its implications for the understanding of Neanderthal extinction. *Journal of World Prehistory* 13:1–68.
- Ziv V. 1991. Crystal sizes in normal and osteopetrotic rat bone [M.Sc. thesis]. Rehovot, Israel: Weizmann Institute of Science.