14C DATING OF THE EARLY NATUFIAN AT EL-WAD TERRACE, MOUNT CARMEL, ISRAEL: METHODOLOGY AND MATERIALS CHARACTERIZATION

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ABSTRACT. The Natufian (15–11.5 kyr BP) sites in the southern Levant are characterized by a lack of macrobotanical remains, including charcoal, and poor preservation of bone collagen. As a result, only about 30 reliable radiocarbon dates are available for building a chronology of the Natufian period. Here, we present new ^{14}C data from the Natufian site of el-Wad terrace that fall in the range of the Early Natufian period. Using Fourier transform infrared (FTIR) analysis, we investigated the environmental factors that influenced the preservation of material for ^{14}C dating of the site, and we tested a modified pretreatment method for poorly preserved charcoal samples. The normal pretreatment protocol for ^{14}C samples (W-ABA) removed more charcoal material than the modified method, which omits the first acid treatment (W-BA). This first acid step seems to enhance the extraction of humic substances during the subsequent base step. We found that the poor preservation of charcoal could be attributed to the presence of calcite, and therefore an alkaline pH of sediments. The most important factor determining bone collagen preservation may have been the hydrological setting, i.e. fluctuating water levels due to oversaturation of the dense sediments after rainfall.

INTRODUCTION

The transition from a nomadic way of life to the establishment of permanent settlements is one of the most influential cultural and economic changes in prehistory. This transition is manifested in the Natufian culture in the Levant from about 15,000 to 11,500 yr cal BP. The reasons for the establishment of Early Natufian (15–13 kyr BP) sedentism, as well as its demise and the introduction of agriculture during the following Neolithic period, are still under debate (e.g. Bar-Yosef 1998, 2002).

The Natufian sites in the southern Levant are characterized by a conspicuous almost total absence of macrobotanical remains such as charcoal (Weinstein-Evron 1998). Information about the type of vegetation that dominated the landscape or was used by the Natufians, respectively, is limited to a few pollen and phytolith remains (Weinstein-Evron 1998; Rosen 2004, 2007; Weinstein-Evron et al. 2007; Portillo et al. 2010). On the other hand, charcoal is abundant in the Natufian sites of the northern Levant (Deckers et al. 2009). It is not known if the absence of macrocharcoal is a result of climatic conditions, human behavior, or chemical degradation. There is evidence, though, that the presence of charcoal is related to its mode of production or formation, its nature, and the environmental conditions of its deposition.

The extent of charcoal degradation depends on the nature of the fuel and the charring temperature (e.g. Baldock and Smernik 2002). Degradation processes involve microbial breakdown (Hamer et al. 2004) or oxidative processes and chemical degradation of its organized graphite-like phase into humic acids (Cohen-Ofri et al. 2006). The chemical degradation is a process that is also influenced by the pH of the environment and the presence of certain minerals. While the presence of Ca^{2+} in soils was supposed to protect charred material from degradation (Clough and Skjemstad 2000), it was shown by Rebollo et al. (2008) that alkaline conditions are responsible for structural degradation of charcoal because oxidative promoting cations such as Fe^{2+} are not removed from the charcoal structure, unless the pH was acidic (Rebollo et al. 2008). A consequence of the structural insta-

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bility of charcoal is a high weight loss during pretreatment for ^{14}C dating. Braadbaart et al. (2009) suggested physical degradation of charcoals due to the intercalation of Ca^{2+} ions between the aromatic sheets. The preservation of charcoal is therefore mediated by an alkaline pH and/or the presence of calcite, although the mechanisms of preservation are controversial.

Preservation of bone collagen in Natufian sites is also rather poor. The processes that lead to the preferential preservation of collagen in some sites are not well studied and understood. It seems that the hydrological setting of a site where a bone was deposited has the largest influence on its preservation (Nielsen-Marsh and Hedges 2000), but also a high clay content in sediments could protect bone collagen, as reported by Weiner and Bar-Yosef (1990) and Yizhaq et al. (2005) for other sites in Israel.

A result of the scarcity of radiocarbon datable material is that only about 30 reliable ^{14}C dates from the Natufian are available for constructing a chronology of this period, which would enable a better synchronization of archaeological and environmental data. A key question of Natufian research is if and to what extent past climate changes influenced the lifestyle of the Natufian communities (Bar-Yosef and Belfer-Cohen 1989; Bar-Yosef 2002; Balter 2010). The prerequisite for the correlation of cultural and environmental events in time are accurate chronologies, so that events can be placed in order (Blockley et al. 2007). Therefore, a chronological framework with dates from well-defined contexts and samples of good quality is essential for the investigation of the Natufian.

In this study, we use the Natufian site of el-Wad terrace, Israel, to obtain information about the state of preservation of the ^{14}C-dated samples, and about possible environmental factors that influenced their preservation. The preliminary results of our ongoing dating program at the site are also presented and further discussed in relation to intrasite stratigraphy and architecture in Weinstein-Evron et al. (these proceedings). We analyzed sediments, as well as charcoal and bone samples using Fourier transform infrared (FTIR) and applied prescreening methods to select bone samples that were most suitable for ^{14}C dating. The charcoal samples were treated with the acid-alkali-acid method and a modified pretreatment method previously proposed by Rebollo et al. (2008) in order to gain information about their state of preservation by measuring the amount of charcoal lost as humic acids, and to test if the modified treatment would allow ^{14}C dating of small and poorly preserved samples.

MATERIAL AND METHODS

Site Description

El-Wad terrace is the open-air portion of the major site of el-Wad Cave on the southern escarpment of Nahal Mearot (Valley of the Caves) at the western slope of Mount Carmel (Israel). Both Early and Late/Final Natufian assemblages have been excavated at the site. Together with el-Wad Cave, the site contains one of the longest and most complete Natufian sequence in the Levant (Garrod and Bate 1937; Valla et al. 1986; Weinstein-Evron 1998, 2009; Weinstein-Evron et al. 2007, in press). The archaeological stratigraphy is described in Weinstein-Evron et al. (2007 and these proceedings). To date, only 3 reliable ^{14}C dates were obtained from the inner part of the cave (Weinstein-Evron 1991), and none were available from the terrace.

The Natufian layer at el-Wad terrace (Unit 2, correlated with Garrod's layer B) is composed of very compact sediment, which is dominated by limestone and clay loam and extremely rich in lithic artifacts and faunal remains. This unit was excavated to a depth of ~1 m, and its base is yet unattained. Unit 2 is overlain by Unit 1, containing disturbed Natufian and post-Natufian findings, ~50 cm thick. Previous micromorphological investigations showed that *Terra Rossa* soil aggregates have been incorporated into the calcareous clay matrix. The presence of manganese (Mn) concretions indicated sporadic standing water at the site (Weinstein-Evron et al. 2007).

Sampling

Eighteen sediment samples were collected from the Early Natufian layer in the Western area: 2 samples from a round stone circle (Locus 57, P 10b/O10c, 421/424 cm depth) and controls outside (stone-poor compact matrix south Locus 57, P9b, 416/421 cm); 2 samples from a stony living floor (SL I, O7b/O7d, 403/408 cm) and controls (stone-poor compact matrix north and south SL I, O8a/O6c, 398/417 cm); sediments associated with a human burial (H 132; sediments under a skull in Q8c and femur in Q7b, and control; for locations see Figure 1). Sediments were also collected from a 70-cm-long section in 10-cm intervals, covering the Natufian and younger Holocene layers in square O11 (369–436 cm depth).

Figure 1 Position of bone sample (EWT 19; RTT-6114) and sediment samples at burial H 132: sediments under skull (EWT 16), under femur (EWT 17), and control (EWT 18).

The charcoal and bone samples (12 charcoals and 34 bones, of which 6 charcoals and 5 bones were dated) were derived from seemingly well-preserved living surfaces, dwellings, and burials. The Early Natufian living surfaces were identified as such based on the distinct arrangements of stones, the presence of built installations and walls, and preservation of delicate findings (e.g. articulated tortoise shells) showing minimal postdepositional movement (Yeshurun et al., in press). All samples derive from a depth between 314 to 446 cm. The stratigraphic position and description of the samples selected for ^{14}C dating is given in Table 1. Bone samples were taken either from the assemblages collected in previous years or sampled in 2009. The charcoal samples were collected during several excavation seasons (2004–2009).

Infrared Spectroscopy

Sediment, bone, and charcoal samples were ground and homogenized in an agate mortar and pestle. In each case, a subsample was mixed with KBr, ground again, and pressed into a pellet using a hydraulic press. Infrared spectra were obtained by scanning in absorbance mode in the range of 250–4000 cm^{-1} using a Fourier transform infrared (FTIR) spectrometer (Nicolet™ 380) and the OMNIC data software. The infrared splitting factors (IRSF) for bone samples were calculated from the infrared spectra as described by Weiner and Bar-Yosef (1990).

Table 1 Radiocarbon-dated samples, their archaeological location and context, stable isotope ratio, ^{14}C age, and calibrated ranges (OxCal v 4.1; Bronk Ramsey 2009; using IntCal09 data, Reimer et al. 2009) for the dated charcoal and bone samples from el-Wad terrace. Samples are arranged in stratigraphic order and by location.

Sample nr (RTT-)	Material	Treatment	Square/ Basket/ Locus	Depth below datum (cm)	Unit/Phase/Level	Remarks (collection year)	δ^{13}C ‰ PDB	^{14}C age ±1 σ yr BP	cal BP ±1 σ	cal BP ±2 σ
6095-1	Charcoal	W-BA	Q7d 50	314–319	Unit 2 W-1 or W-2 (Center)	Associated with a few stone installations (2004)	–25.6	12,040 ± 80	13,980–13,800	14,080–13,740
6095-2	Charcoal	W-ABA					–25.5	11,610 ± 80	13,570–13,350	13,660–13,280
6096-1	Charcoal	W-BA	P6b 66	348–353	Unit 2 W-5 level I (Center)	Well-preserved level with stone-built features (2007)	–25.6	12,505 ± 80	14,880–14,400	15,000–14,200
6096-2	Charcoal	W-ABA					–25.5	12,340 ± 85	14,560–14,080	14,800–14,000
6098-1	Charcoal	W-BA	Q6a 94 loc 46	355–361	Unit 2 W-6 level IV (Center)	Stone with adhering charcoal, in a stony living floor, probably inside structure (2008)	–23.6	12,575 ± 85	15,050–14,500	15,100–14,250
6098-2	Charcoal	W-ABA					–23.6	12,430 ± 80	14,660–14,220	14,950–14,100
6097-1	Charcoal	W-BA	O6c 84 loc 55	383–388	Unit 2 W-6 level VII (Center)	Stony living floor, probably inside structure (2009)	–26.4	13,085 ± 105	15,660–15,250	15,900–15,100
6097-2	Charcoal	W-ABA					–26.4	14,150 ± 140	17,200–16,550	17,550–16,350
6106	Bone	ABA	Q8c 37	343–347	Unit 2 W-3 (North)	Well-preserved level with stone-built features (2008)	–19.5	11,840 ± 100	13,820–13,580	13,910–13,440
6105	Bone	ABA	O9d 20	396–400	Unit 2 W-5 level II (North)	Well-preserved level with stone-built features (2006)	–20.1	11,935 ± 100	13,920–13,690	14,030–13,560
6107	Bone	ABA	Q8d 85 loc 58	392–393	Unit 2 W-6 level VII (North)	Concentration of artifacts and small stones with concretions, above burial H132 (2009)	–19.2	12,350 ± 100	14,590–14,100	14,900–14,000
6117-1	Charcoal	W-BA	Q9a 54	408–408	Unit 2 W-7 level VIII (North)	Above a large pile of stones and flint artifacts, loc 63 (2009)	–25.5	12,290 ± 70	14,310–14,020	14,650–13,950
6117-2	Charcoal	W-ABA					–25.3	12,300 ± 70	14,350–14,030	14,700–13,950
6115	Bone	ABA	M8c 96	442–446	Unit 2 W-7 level IX (East)	Well-preserved level with architecture (2007)	–18.9	11,570 ± 75	13,490–13,300	13,620–13,260
6114	Bone	ABA	Q7b 124 H132	397–397	Unit 2 W-6 (Burial)	Burial H132, human femur (2009)	–18.7	11,570 ± 75	13,490–13,300	13,620–13,260
6116	Charcoal	W-ABA	N4b 25 H101	321–329	Unit 2 (Burial)	Associated with burial H101 (1997)	–24.5	11,640 ± 70	13,590–13,390	13,680–13,320

Prescreening of Bone Collagen Content and Quality

Before preparing the bone samples for dating, the amount and quality of collagen in 34 bones were tested. About 200–300 mg of powdered mineral bone material was dissolved in 1N HCl and washed with nanopure water. The insoluble fraction (IF) was weighed to calculate its proportion and analyzed using FTIR to determine the presence and quality of collagen.

Bone Collagen Extraction and Purification

The cleaning procedure for the collagen samples chosen for dating was based on the acid-base-acid (ABA) technique and ultrafiltration as described in Yizhaq et al. (2005). First, the bone surface was cleaned of attached sediment and from encrusting material, which was kept separately. About 2 to 10 g of bone material was crushed, ground, and homogenized with an agate mortar and pestle; 1N HCl was added to the powder until the mineral bone components dissolved. The acidic solution was centrifuged for 3 min at 3000 rpm, the supernatant was removed, and the pellet was rinsed with nanopure water to pH 7. The insoluble fraction was treated with 10 mL 0.1N NaOH for 15 min and centrifuged, with this procedure repeated 3 times. The atmospheric CO_2 adsorbed during the alkali treatment was removed by adding 10 mL of 1N HCl for 30 min. The sample was washed until the solution reached pH 3. The resulting collagen was gelatinized to purify and concentrate the protein components by heating the sample at 70 °C for 20 hr in pH 3 solution. The gelatin was subsequently purified by filtration through a polyethylene filter (100 μm Ezee-filter™). The filtrate was pipetted into an ultrafilter (Sartorius Vivaspin 20™ centrifugal concentrator, 30 kDa MWCO) and centrifuged for 25 min at 3000 rpm. After freeze-drying the filtrate, the purified gelatin sample was weighed.

Charcoal Purification

Charcoal was identified by using a binocular microscope and FTIR. The selection of charcoal samples was based on the mass of charred material and the purity of charcoal and absence of clay or other minerals. Out of 35 samples collected as charcoal particles, 12 samples were identified as pure charcoal, from which 6 charcoal samples were processed for ^{14}C dating based on their archaeological context and the available mass of material.

The samples were pretreated using the acid-base-acid (ABA) method (Yizhaq et al. 2005). Before treatment, the charcoal was slightly crushed to powder and homogenized. Five samples were divided into 2 subsamples (12–28 mg per subsample) that were inserted into separate glass tubes. Sample RTT-6116 was too small and was therefore treated only by the W-ABA method.

One subsample was treated with the original method with an additional preceding cleaning step with water (W-ABA): (1) 3 mL nanopure H_2O; (2) 3 mL 1N HCl; (3) 3 mL 0.1N NaOH, 3 times; (4) 3 mL 1N HCl in hot water bath (80 °C). The other subsample was treated with a modified method, where the first HCl step was omitted (W-BA): (1) 3 mL nanopure H_2O; (2) 3 mL 0.1N NaOH, 3 times; (3) 3 mL 1 N HCl in hot water bath (80 °C).

During every step, the samples were treated for 30 min. After every step, the sample was centrifuged for 5 min at 3000 rpm and rinsed with nanopure water until the solution was neutral. Then the sample was dried in an oven at 105 °C to determine the weight loss and to analyze the remaining charcoal material using FTIR in order to identify potential contaminants.

Target Preparation and AMS Analysis

The samples prepared for dating were combusted to CO_2 in quartz tubes containing ~200 mg of copper oxide (Fluka) at 900 °C for 200 min. The CO_2 was divided into 3 aliquots and each was reduced

to graphite using about 1 mg of cobalt (Fluka) as a catalyst and hydrogen, and then heated to 700 °C for 20 hr. The graphite samples were analyzed for ^{14}C content at the NSF-AMS Radiocarbon Laboratory in Tucson, Arizona, USA. The ^{14}C ages were calibrated to calendar years BP using the latest calibration curve (Reimer et al. 2009) and the software OxCal v 4.1 (Bronk Ramsey 2009).

RESULTS

Sediments

The sediments showed similar attributes for all samples, and no differences could be found between the archaeological structures and the controls outside. Clay was dominant, while calcite was present only in low amounts. Quartz and apatite were also present in all samples. The FTIR spectra of the Natufian sediments and the overlying younger (Holocene) sediments did not show any differences, which can be explained by a similar origin from *Terra Rossa* soil material. The presence of calcite is an indicator for a neutral to alkaline pH. No macrocharcoal was found in the investigated Natufian sediment samples, while bones were ubiquitous.

Charcoal Pretreatment

On average, about one-third (29%) of the sample material could be recovered after the W-ABA treatment (Table 2). Mineral material (calcite, clay), fulvic acids, and other contaminants that were removed after the water and the first acid treatment accounted for an average of 40% of the lost material. The recovery was better for the treatment that omitted the first HCl step, where 57% of the sample material was left after the final HCl. After the NaOH treatments, the supernatant of all samples after centrifugation was deep brown. The supernatant was removed and humic acids were precipitated with HCl. The proportion of material lost only during the NaOH treatment after the first acid step (W-ABA), which is considered humic acid, varied between samples, from 5 to 45% (average 26%). Without the first HCl treatment (W-BA), the proportion of humic acids was 9–16% (average 12%).

Table 2 Weight % of the recovered charcoal material after the pretreatment steps (W-ABA and W-BA) in relation to the untreated charcoal sample, the proportion of material lost during the alkaline (NaOH) treatments after HCl (W-ABA) or H_2O (W-BA) as humic acids, and the organic carbon (C_{org}) concentration of charcoal after treatment.

Lab nr (RTT-)	Treatment	after H_2O %	after HCl %	after 3rd NaOH %	after final HCl %	Humic acids %	C_{org} %
6095-1	W-BA	93		83	56	10	67.7
6095-2	W-ABA	85	55	39	33	16	69.0
6096-1	W-BA	83		73	58	10	67.9
6096-2	W-ABA	86	62	39	35	23	68.0
6097-1	W-BA	91		75	52	16	69.7
6097-2	W-ABA	84	59	36	32	23	69.0
6098-1	W-BA	77		62	42	15	62.0
6098-2	W-ABA	85	54	10	8	45	52.0
6116	W-ABA	88	62	19	17	43	68.0
6117-1	W-BA	86		76	76	9	68.8
6117-2	W-ABA	87	65	60	49	5	70.0

The FTIR spectra of the charcoal samples showed that the untreated charcoal was dominated by carboxylate groups (COO^-). During the first acid treatment, the carboxylic groups became protonated by the addition of H^+ ions and converted to carboxylic acids. During the alkaline treatment, the charcoal structure dissolved into humic acids, and the peaks of the recovered charcoal material shifted again to the deprotonated stage. The humic acid precipitates after addition of HCl, and its FTIR spectra showed the same distribution of peaks as the charcoal, which suggests that the structure is re-assembled after re-addition of protons. During the W-BA procedure, the FTIR spectra did not indicate any changes of functional groups in charcoals after water and NaOH treatment. Only after the last HCl treatment are the charcoals protonated, as the charcoals that were treated by the W-ABA method.

The organic carbon (C_{org}) concentrations in 5 samples were similar and did not differ between the applied treatment methods (68–70%). Sample RTT-6098 yielded lower proportions of C_{org} after the W-ABA (62%) and W-BA (52%) treatment. The FTIR spectra of all samples showed the presence of pure charcoal after pretreatments. Calcite compounds were removed completely, even when the first HCl treatment was omitted, and thus all samples were suitable for ^{14}C dating.

Bone Prescreening and Pretreatment

We pre-examined 34 bones for the presence of collagen. The selection was based on archaeological context and stratigraphy. The recovered acid-insoluble fractions, which are collagen and clay, were small (<2% of mass). The FTIR spectra of the insoluble fractions showed that collagen is present in 27 samples, of which 13 displayed a very clear collagen signal, which is indicated by peaks at about 1640, 1540, and 1455 cm^{-1}.

Out of the 13 samples containing collagen, 11 bones were selected and treated to extract the collagen by filtration after dissolution of the mineral part (Table 3). Four bones contained clay, mainly in fissures or other cavities, but it was possible to remove the clay completely during filtration. A sufficient amount of collagen for dating could be extracted from 5 bones (4–22 mg). For those 5 bones, the proportion of extracted collagen to bone material was between 0.17 to 0.35%.

Table 3 Bone samples from el-Wad terrace that showed a clear collagen signal in the FTIR spectra of the HCl-insoluble fraction (prescreening). The table shows the infrared splitting factor (IRSF) of the bulk bone material, if clay was present in bone pores or cracks (+), the proportion of the fraction not soluble by HCl (IF) in the bone crust, and how much collagen was extracted after ultrafiltration (in mg and in relation to the amount of bone material). The samples that were selected for ^{14}C dating are indicated by their RTT number.

Lab code (RTT-)	Sample (Square)	IRSF	Clay in bone	IF bone crust (%)	Collagen extracted (mg)	Collagen extracted (%)
6105	O9d (20)	3.0	+	16	22	0.23
6106	Q8c (37)	3.3		4	17	0.35
6107	Q8d (85)	3.3		23	14	0.24
6114	Q7b (124)	3.7		25	4	0.20
6115	M8c (96)	3.5	+	19	11	0.17
	P5ab (35)	3.2		21	0	0.02
	Q6a (68)	3.4		25	0	0.00
	O6a (56)	3.5	+	23	0	0.00
	O7c (60)	2.8		14	1	0.01
	P7a (82)	3.2	+	27	0	0.00
	M4 (24)	3.5		25	0	0.00

The splitting factors of the 11 bones, which were analyzed in crushed bone material, varied between 2.8 and 3.7. One bone was in the region of fresh bone material (2.6–2.9), 5 were in the region of slightly altered bones (3.0–3.3), and 5 were in the range of well-altered fossil bones (3.4–4.0) (Berna et al. 2004).

Most bones were covered by a hard crust of clay-rich material (Figure 2). The FTIR spectra of the bone crust showed that the mineral composition of the crust was dominated by calcite, followed by clay (Figure 3A), in contrast to the sediment in which clay was the main component (Figure 3B). A microscopic inspection of the bone crust of sample RTT-6114 (human femur) showed that it did not contain any pseudomorphs, phytoliths, or other fossils.

Figure 2 Bone fossil related to sample RTT-6114 (burial 132, human femur), showing the hard mineral crust surrounding the bone. Note that the flint artifact is attached to the crust; it is not sitting in the bone itself.
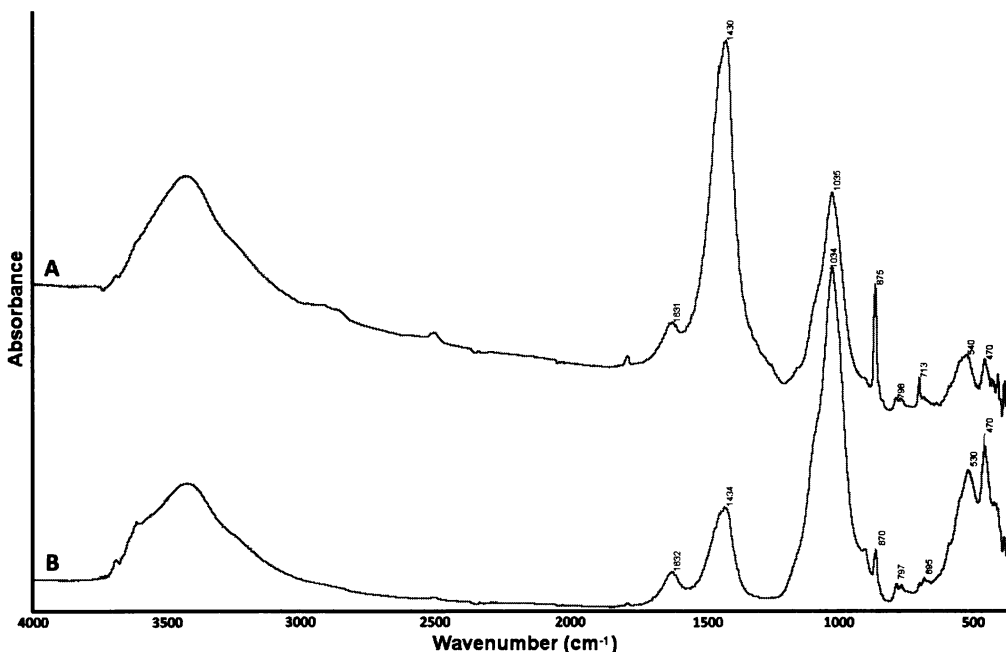

Figure 3 FTIR spectra of bone crust (A) and sediment (B) related to bone sample RTT-6114 (burial 132, human femur)

Radiocarbon Ages

We dated 6 charcoal samples, of which 5 were divided into 2 subsamples that were pretreated according to the W-ABA method and the modified W-BA method. An additional 5 bone samples contained a sufficient amount of collagen to be ^{14}C dated.

All ^{14}C ages are in the range of 14,150 ± 140 to 11,570 ± 75 ^{14}C yr BP (17,200–16,550 to 13,490–13,300 cal BP). Most dates fall into the Early Natufian period (15–13 cal kyr BP); only 1 charcoal (RTT-6097) delivered older ages (Table 1). The ages of charcoal sample RTT-6097 showed the largest discrepancy between the 2 pretreatment procedures (–1065 ^{14}C yr), followed by RTT-6095 (+430 ^{14}C yr), while the age differences for the 3 other sample pairs were between –10 to +165 ^{14}C yr (Figure 4).
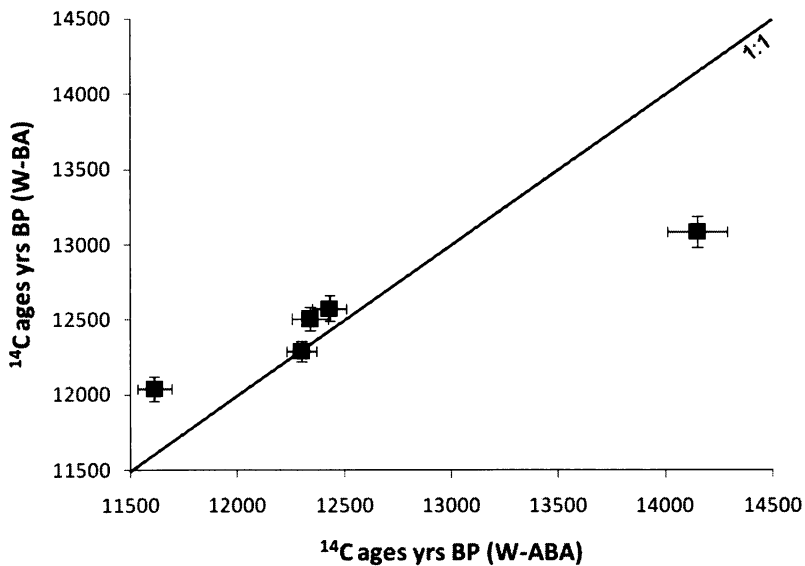

Figure 4 AMS ^{14}C ages (uncalibrated) of charcoal samples after original W-ABA and modified W-BA treatment. Two samples show a significant discrepancy in age between the 2 different procedures.

DISCUSSION

Preservation of Charcoal

Macrocharcoal remains are rare in el-Wad terrace, so that only a few pieces were available for ^{14}C dating. The presence of more abundant macrocharcoals in the adjacent el-Wad Cave enabled the only study that, to date, has investigated the species of wood charcoals found in an Early Natufian site in the southern Levant. This study showed that the burnt wood came from tree species that were typical of a Mediterranean forest or maquis, and for marshes or other wet habitats (Lev-Yadun and Weinstein-Evron 1994). The scarcity of macrocharcoal in el-Wad terrace hence cannot be a result of a lack of wood fuel due to environmental or climatic factors. This is supported by pollen (Weinstein-Evron 1994; Weinstein-Evron et al. 2007) and phytolith (Portillo et al. 2010) studies at the site and the uninterrupted presence of several woodland mammal taxa in both the Early and Late Natufian of el-Wad and other Natufian sites in the region indicating the presence of Mediterranean maquis in the vicinity of the site (Bar-Oz et al., in press; Weissbrod et al., in press).

Human exploitation of small branches or twigs as fuel, rather than using large pieces of wood, may explain the rarity of macrocharcoal at the sites. However, if macrocharcoal was present onsite, the conditions of its production and the environment of its deposition affected its preservation over time (e.g. Czimczik and Masiello 2007). An important factor for charcoal preservation is the pH of the sediments surrounding the charcoal, and it has been shown that alkaline conditions can degrade charcoal either chemically or lead to physical degradation (Cohen-Ofri et al. 2006; Rebollo et al. 2008; Braadbaart et al. 2009).

The pretreatment procedure of charcoal for ^{14}C dating exposes charcoal to changes in pH, as might be the case for archaeological sites, although the pH values there are not as extreme as in the laboratory. The application of the 2 different pretreatment methods showed that the charcoal pieces found on the site were degraded, although to different degrees. The pH change during W-ABA treatment from acidic to alkaline solution resulted in a higher loss of charcoal material in the form of humic acids as was the case during the W-BA treatment.

The first acid treatment, when the carboxylic groups become protonated, seems to be crucial for the disruption of the charcoal structure (Rebollo et al. 2008). Up to now, humic acids were considered a fraction of soil organic matter that intruded and contaminated the charcoal, but it was shown that humic acids are rather an autochthonous element of the charcoal itself, and that the loss of charcoal material as humic acids can be a measure of charcoal diagenesis (Cohen-Ofri et al. 2006; Ascough et al. 2010).

The investigated charcoals from el-Wad, however, were better preserved than charcoal samples from other Natufian sites. In Hayonim Cave, where the Natufian sediments are dominated by calcite-rich ash, macrocharcoal particles are rarely present and only 5% of the total mass of 5 tested charcoal samples was recovered after the W-ABA treatment (unpublished data).

We cannot exclude that the lack of charcoal is a result of repeated and intensive fires in the settlement area, which could have completely combusted the charcoal (Czimczik et al. 2005). There is evidence for the repeated lighting of fires on pre-existing bone and other refuse in the excavated living floors, resulting in indirect charring of bones (Yeshurun et al., in press). It is, however, very likely that sediment pH is responsible for its scarcity, according to the model of Rebollo et al. (2008). The abundant presence of bones indicates that the sediment pH was generally alkaline, although fluctuating water levels in the sediments might have temporarily changed the pH on the site due to the dissolution of carbonates. The presence of water facilitated the oxidation of charcoal and the dispersion and removal of resulting humic acids. Furthermore, cycles of drying and wetting break down soil aggregates, a process that promotes the decomposition of organic matter in general (Denef et al. 2001). It should be noted that the size of the samples was too small to do additional analyses in order to control the effect of the W-BA treatment on the charcoal structure.

Preservation of Bone Collagen

The preservation of bone collagen was poor at the site. However, the collagen that could be extracted was very pure and of high quality. The amount of collagen that remained after ultrafiltration was not related to the results of the prescreening, nor to the splitting factor, the amount of crust on the bones, or to the amount of clay in the bones. The proportion of calcite (HCl-soluble fraction) in the bone crust material shows no correlation ($R^2 = 0.378$; $p = 0.044$) with the amount of collagen extracted.

The processes of collagen preservation are not well understood. Weiner and Bar-Yosef (1990) examined the preservation of bone collagen from a variety of prehistoric sites in the Near East and found

that a high clay content of the sediments on a site could protect the bones from exposure to water and therefore collagen degradation. Yizhaq et al. (2005) reported similar results for bones from the Early Pre-Pottery Neolithic (PPNB) site of Motza, Israel, which also contained low amounts of well-preserved collagen that might have been protected by clay intrusions.

Hydrological conditions on a site are influential for the preservation of bone material, which is better preserved when the water levels are steady (Nielsen-Marsh and Hedges 2000). Fluctuating water, especially where oxic and anoxic phases alternate, facilitates the degradation of bone material. During oxygen-rich conditions, collagen is broken down by higher activity of microorganisms (Bocherens et al. 1997). In phases of higher water levels, the organic molecules leach out of the bones, thus increasing bone porosity and subsequently the accessibility for microorganisms in dry periods (Collins et al. 2002; Reiche et al. 2003). Percolating water could also hamper bone degradation, when water carries mineral sediment particles like clay into the bone pores, where they could act as a diffusion barrier and shield the bone collagen from leaching (Reiche et al. 2003). Under permanently waterlogged and reducing conditions, the bone material would be degraded at the surface but well preserved in the center of the bone.

Most bones from el-Wad terrace were covered by a hard crust of clay-rich material (Figure 2). Previously investigated micromorphology sections on bones showed that also their cavities were filled with clay, and that they were coated with secondary calcite material. The bone crusts are therefore indicators for calcitic neoformation on the site. Furthermore, micromorphological investigations of the Natufian sediments showed that Mn concretions are present (Weinstein-Evron et al. 2007). El-Wad terrace is an open site that is annually affected by seasonal rainfall. Mn concretions form when Mn oxides precipitate in aerobic zones, after the sediments have been temporarily waterlogged and reduced Mn has been soluble. Fluctuating water levels due to standing water in cavities in the rock and oversaturation of the dense clay-rich sediments after rainfalls might have dissolved sediment calcite, which precipitated on the bones after the water evaporated and built up the bone crust. The lack of pseudomorphs in the crust might indicate that the calcite material did not derive from ash. The bones that still contain collagen might have been protected by their microenvironmental position from the influence of periodic water on the site. It is also possible that clay or other mineral particles in the soil pore water precipitated in the bone or on its surface, and physically protected the collagen from microbial degradation.

Radiocarbon Data

The calibrated ^{14}C ages, both bone collagen and charcoal ages, fall within the range of the Early Natufian period (15–13 kyr BP), with the exception of charcoal RTT-6097-2, which yielded an older age (Table 1). The ^{14}C ages of W-ABA treated charcoals (except RTT-6097-2) and bone collagen cover the same range, so that an old-wood effect can be excluded for the dated charcoal samples. The ages obtained are in accordance with the stratigraphic position of the samples, with the exception of bone sample RTT-6115, which is younger than indicated by its stratigraphic position. A detailed discussion of the contextual implication and stratigraphic positions of the dates is given in Weinstein-Evron et al. (these proceedings).

The differences between the ages of the charcoal subsamples that have been treated with the W-ABA and the W-BA method do not show a clear trend. While 1 sample pair yielded a difference of −10 ^{14}C yr, 2 sample pairs had a difference of +145 and +165 ^{14}C yr, while the other 2 sample pairs yielded ages that differed by +430 and −1065 ^{14}C yr, respectively. Three samples treated with W-BA yielded older ages, while for the sample that showed the largest difference (RTT-6097), the W-BA

treated charcoal was younger. The differences in age demonstrate that the 2 treatments did not result in a similar composition of charcoal compounds, which therefore yielded different ^{14}C ratios.

Considering that the W-BA treatment resulted in 3 older ages, and 1 which is only 10 yr younger, sample RTT-6097 could be considered an outlier. Thus, the modified treatment removed younger organic contaminations more efficiently than the W-ABA method, which resulted in ages that reflect more stable charcoal compounds, without damaging the charcoal structure. An explanation for the large offset between samples RTT-6097-1 and -2 might, however, be that in this case contaminating organic substances have not been removed efficiently enough with our modified treatment, so that the sample yielded a younger age. The C_{org} concentrations did not indicate the presence of additional contaminants; there was no difference in the amount of organic matter between both samples. The C_{org} concentrations of sample RTT-6098, contrastingly, were different after the pretreatments have been applied, but the yielded ^{14}C ages are very close (145 ^{14}C yr). Mineral contaminants could have diluted the W-ABA treated sample, which did not affect the ^{14}C ratio.

CONCLUSIONS

The ^{14}C-dated charcoal and bone samples from el-Wad terrace fall in the range of the Early Natufian period, with the exception of 1 charcoal sample that yielded an older age. The application of rigorous prescreening methods allowed the selection of suitable samples for ^{14}C dating despite the small sample sizes. The preservation of charcoal samples was poor, most probably due to chemical degradation because of the alkaline conditions of the sediments. The amount of extractable bone collagen was small because fluctuating water tables on the site might have triggered the degradation of bone organic matter. Bones were encrusted with clay and calcite-rich sediment that could have protected the collagen from complete degradation. The application of a modified pretreatment method (W-BA) of charcoal resulted in higher yields of dateable charcoal material and, in most cases, in older ages. The modified W-BA method is a promising tool for dating charcoal samples, but needs further testing with larger numbers of samples pairs from different environments especially concerning the structural changes.

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