Radiocarbon Dating of Archaeological Materials Excavated at Kaman-Kalehöyük: Initial Report.

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1 INTRODUCTION

Few absolute dating studies have been carried out on archaeological materials from Kaman-Kalehöyük. Hirao (1995) reported absolute dates by radiocarbon dating of thirty-six charcoal samples from the site, and Huber (1995) summarized the results of dendrochronological dating of Iron Age materials. There is some discrepancy between the results, and it has not yet been possible to determine the absolute dates of each stratum (Matsumura 1996). Absolute radiocarbon dating of high accuracy can be obtained through Accelerator Mass Spectrometry (AMS). The purpose of this study is to correlate absolute AMS radiocarbon dates with the relative stratigraphy of the site, and thereby date the cultural phases of the site. In this paper, we report absolute dates of Middle-Late Bronze Age to Ottoman Period layers.

2 SAMPLE DESCRIPTION

Twenty-five samples of charred grain, human bone, and animal bone were ^{14}C dated by AMS; 17 samples are from the 2005 excavation season, while 8 are from earlier seasons. The samples were carefully selected from each stratum so as to strictly correlate the absolute ages with the relative sequences of building levels. The archaeological provenance data for each sample are listed in Table 1.

3 EXPERIMENTAL

3.1 Pretreatment of bone materials

Bone comprises an inorganic fraction and a protein fraction. The inorganic fraction is not reliable for dating because of the difficulty of removing the secondary carbonates originating from soil and ground water. Protein such as collagen can be separated easily from contamination and the inorganic fraction. For radiocarbon dating, gelatin collagen extracted from a bone sample is normally used.

The bone sample was washed ultrasonically, treated with 0.6 M sodium hydroxide (NaOH) solution overnight at 4˚C to remove humic acid contaminants, and rinsed with distilled water. The lyophilized bone sample was reduced to powder. In order to dissolve calcium phosphate, the main inorganic constituent of bone, the fine fraction that had been put into a semipermeable membrane bag (cellulose tube) was treated with 0.5 M hydrochloric acid (HCl). The semipermeable membrane can separate the dissolved fraction and the collagen protein. The decalcified component remaining in the bag was transferred to a glass tube, some water added, and heated at 90 ˚C (hydrolysis). Only soluble gelatin collagen can be obtained from other protein fractions, because most of the protein fraction can get changed into insoluble coagulates in hot water. The gelatin collagen was obtained by lyophilizing the solution. This method is discussed in detail in Longin (1971).

3.2 Pretreatment of charcoal and charred grain samples

Acid-alkali-acid treatment (AAA treatment) was performed, the most common pretreatment for radiocarbon dating. In order to remove carbonate contaminants, 1.2 M HCl was added to charcoal or charred grains, and heated at 80˚C for 12h. NaOH solution of 0.1-1.2 M was added to remove humic acid contaminants. The solution was heated until the dark

Table 1 The archaeological provenance data for each sample from Kaman-Kalehöyük

Y. No.	Area	Sector	Grid	Provisional layer	Feature Information	Stratum	material
94001635	North	XXVII	XLVI-52	-	P1156	I	Human bone
95001699	North	XXX	XLVIII-51	②	T23	I	Human bone
95001704	North	XXVIII	XLVIII-52	①	T21	I	Human bone
95001707	North	XXVIII	XLIX-53	-	G29	I	Human bone
05000493	North	XVI	XXXV-53	㉟	H256	IIa	Charred grain
05000494	North	XVI	XXXV-52	㊻	H250	IIa	Charred grain
05000495	North	XIV	XXXVIII-52	㉙	H271	IIa	Charred grain
05000505	North	XV	XXXVI-52	⑨	P1671	IIa	Charred grain
05000511	North	XXXI	XLIV-50	㊴	P2860	IIa	Charred grain
05000513	North	XVI	XXXIV-52	㊿	H252	IIa	Charred grain
05000519	South	XXV	LX-53	-	P607	IIa	Charred grain
05000520	South	LV	LX-51	①	P564	IIa	Charred grain
05000521	South	XXV	LX-53	⑪ⓐ	P543	IIa	Charred grain
05000525	North	XXXII	XLIII-50	⑭	P2717	IIa	Charred grain
05000532	North	XXXII	XLII-51	㊱	P2856	IIa	Charred grain
87001041	North	V	XXXVII-54	-	Pit	IIa	Animal bone
05000497	South	LVI	LIII-49	㉘	H83	IIc	Charred grain
05000508	South	LV	LX-50	-	P590	IId	Charred grain
05000512	North	XXIX	XLVII-50	⑬	H154	IId	Charred grain
05000515	South	LI	LII-53	-	P715	IId	Charred grain
92001527	North	VII	XXXIII-55	⑬ⓐ	Burnt floor	IId	Charcoal
05000500	North	VIII	XXX-55	⑲	R345	IIIb	Charred grain
03001082	North	VIII	XXX-55	㉑	R345	IIIb	Charcoal
05000514	North	VIII	XXXI-55	㊗85	P2886	IIIc	Charred grain
94001631	North	I	XLV-54	㉗	S4	IIIc	Human bone

brown fraction was extracted from the charred samples completely. The samples were treated again with HCl, then washed with distilled water and dried.

3.3 Graphitization

A sample containing about 1.5 mg of carbon, together with an appropriate amount of CuO, was filled into a Vycor tube. The evacuated tube was sealed and heated to 900˚C for 4h combusting the sample. The CO_2 gas was purified cryogenically in a vacuum line. The purified CO_2 gas was reduced to graphite with hydrogen over iron powder as the catalyst at 650 for 6h (Kitagawa *et al*. 1993). Graphite was pressed into an aluminum target holder for ^{14}C measurement.

3.4 ^{14}C age and $\delta^{13}C$ measurement

^{14}C measurements and $\delta^{13}C$ analyses were performed with an AMS system (HVEE, model 4130-AMS) and IR-MS (Finnigan, MAT-252) at the Center for Chronological Research, Nagoya University (Nakamura *et al*. 2004). Oxalic acid (SRM-4990c), an IAEA standard material, was used as a ^{14}C concentration reference.

Conventional radiocarbon dates, calculated by correcting for carbon isotopic fractionation using ^{13}C, were converted to calibrated dates by CALIB 5.0.1 (Stuiver and Reimer 1993) with IntCal04 calibration curve (Reimer *et al*. 2004).

4 RESULTS AND DISCUSSION

The $\delta^{13}C$ value is an index of isotopic fractionation. Although ^{12}C, ^{13}C and ^{14}C are all carbon isotopes and chemically indistinguishable, in any biological pathway there will be a tendency for the lightest isotope ^{12}C to be taken up preferentially. Similarly ^{13}C will be taken up in preference to ^{14}C. This tendency is called isotopic fractionation. It is necessary to correct the obtained ^{14}C age by the $\delta^{13}C$ value, because there are small

Table 2 $\delta^{13}C$, ^{14}C age and calibrated age of the charred plant and bone materials

Y. No.	$\delta^{13}C$ (‰)*	^{14}C age BP ± 1 δ	Lab. Code (NUTA2-)	Calibrated age cal AD/BC (2 σ)	Probability
94001635	-17.8	348 ± 23	10594	1460 - 1530 1540 - 1630	0.418 0.582
95001699	-18.0	323 ± 23	10595	1490 - 1600 1610 - 1640	0.787 0.213
95001704	-17.6	364 ± 23	10598	1450 - 1520 1560 - 1630	0.567 0.434
95001707	-18.0	994 ± 24 943 ± 20	10599 11002		
	Ave.	969 ± 16		1020 - 1050 1080 - 1130 1140 - 1150	0.486 0.401 0.113
05000493	-20.6	2540 ± 25 2533 ± 26	10560 10565		
	Ave.	2537 ± 18		790 - 750 690 - 670 640 - 590 580 - 560	0.495 0.241 0.215 0.048
05000494	-20.6	2552 ± 26	10561	800 - 750 690 - 670 640 - 590 580 - 560	0.595 0.177 0.176 0.051
05000495	-21.4	2555 ± 25	10564	800 - 750 690 - 670 640 - 590 580 - 560	0.658 0.170 0.142 0.031
05000505		2547 ± 25 2492 ± 21	10569 10982		
	Ave.	2520 ± 16		780 - 740 690 - 660 650 - 550	0.263 0.225 0.513
05000511	-22.2	2469 ± 25	10573	760 - 680 670 - 490 460 - 450 440 - 420	0.317 0.615 0.023 0.044
05000513	n.d.	2726 ± 21	10986	910 - 820	1.000
05000519	-20.9	2333 ± 25	10582	480 - 470 420 - 370	0.016 0.984
05000520	-22.6	2449 ± 25	10583	750 - 690 670 - 640 620 - 610 600 - 410	0.273 0.097 0.012 0.617
05000521	-21.6	2525 ± 25	10584	790 - 730 690 - 660 650 - 550	0.309 0.193 0.497
05000525	-21.8	2480 ± 21	10990	770 - 510	1.000
05000532	-22.8	2504 ± 21	10992	780 - 720 690 - 540	0.209 0.791
87001041	n.d.	2491 ± 21	10994	770 - 540 530 - 530	0.998 0.001
05000497	-21.4	2756 ± 26 2723 ± 22	10566 10978		
	Ave.	2740 ± 17		920 - 830	1.000
05000508	-23.8	3074 ± 26	10570	1410 - 1290 1280 - 1270	0.970 0.030
05000512	n.d.	2742 ± 25 2695 ± 22	10574 10985		
	Ave.	2719 ± 17		900 - 820	1.000
05000515	-22.5	3086 ± 26	10576	1430 - 1290	1.000
92001527	-25.2	2878 ± 25 2911 ± 26	10586 10587		
	Ave.	2895 ± 18		1190 - 1180 1130 - 1010	0.010 0.979
05000500	n.d.	3346 ± 26	10568	1730 - 1720 1690 - 1600 1590 - 1530	0.024 0.774 0.201
03001082	-23.2	3360 ± 26 3324 ± 22	10593 10998		
	Ave.	3342 ± 17		1690 - 1610 1580 - 1540	0.866 0.134
05000514	-23.1	3511 ± 26	10575	1910 - 1751	1.000
94001631	-18.5	3473 ± 22	10999	1880 - 1740	0.994

n.d.: not determined
* The error of $\delta^{13}C$ is ± 0.1 ‰

variations from species to species in the degree of this isotopic fractionation. The ^{14}C dates presented here are values corrected for isotopic fractionation by $\delta^{13}C$. It is also possible to interpret the carbon source of carbonaceous materials by $\delta^{13}C$ value in some cases. The reported $\delta^{13}C$ values of charred plant and gelatin collagen of human or animal bone are approximately -28 to -22 % and -22 to -16 %, respectively (Bowman 1990). The $\delta^{13}C$ values of charred plants and bone materials in this study were between -25.2 % and -20.6 % and between -18.5 % and -17.6 % (Table 2), respectively, quite consistent with typical values.

Atmospheric ^{14}C concentration varies with time, so ^{14}C ages (derived from the ^{14}C concentration in a sample) must be calibrated. The IntCal04 data set shows the shift in ^{14}C concentration year by year, and was used to derive the calendar age. The calibration of ^{14}C ages, which is obtained as a Gaussian distribution, was carried out with an uncertainty of 2σ, 95 % probability. Calibrated ages are shown in Table 2. In addition, the calibrated age images obtained by a probability method are shown in Fig. 1. The horizontal axis shows a calibrated age (cal BC), and the vertical line shows probability.

4.1 Ottoman Period: Stratum I

We dated four human bone samples from Stratum I. These samples came from a series of Stratum I remains in Sectors XXVI-XXXI (Omura 1995: Fig. 3). Except for sample 95001707, the absolute dates are approximately 1450-1600 cal AD. This corresponds with the archaeological date of AD 16th to 17th century determined by Chinese ceramic and coin typologies (Omura 2000). The calibrated date of sample 95001707 is 1020-1150 cal AD, approximately 400 years older than the other samples from this stratum. The excavation report about stratum I around these sectors once mentions the possibility of human bones being in disturbed contexts from next phase (Omura 1995). Therefore, it is possible that sample 95001707 belongs to an earlier building level, and its date indicates that there was activity in the 11th century AD at Kaman-Kalehöyük.

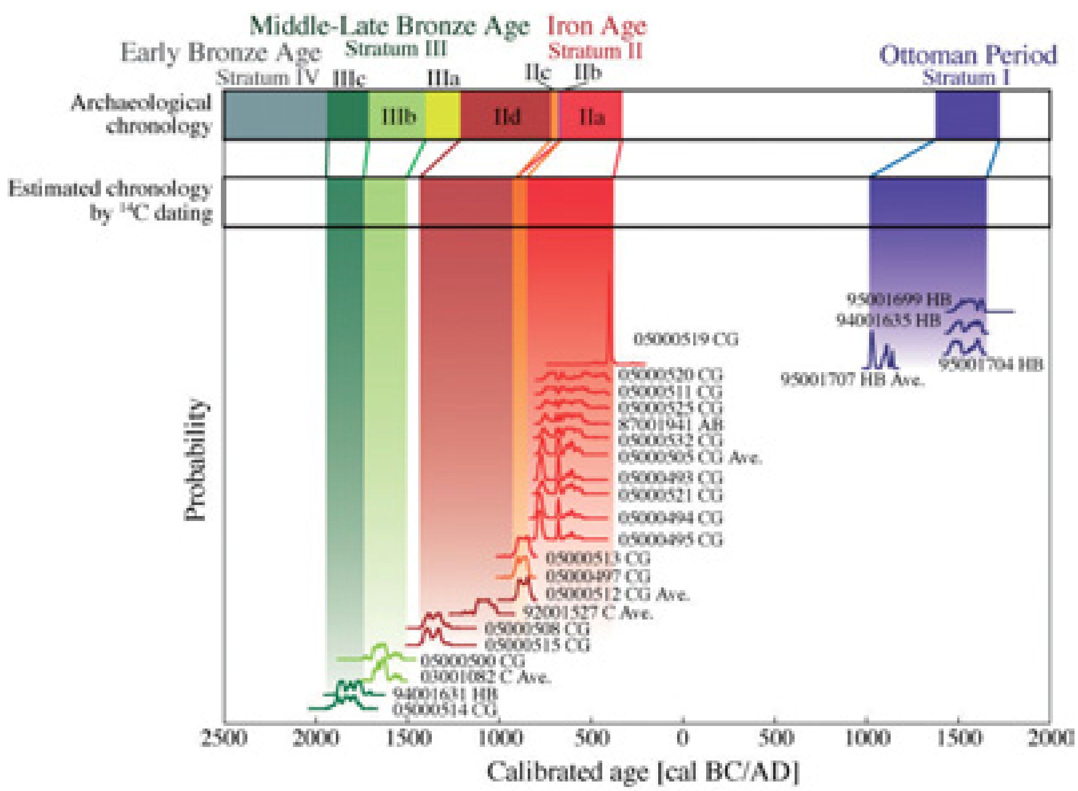

Fig.1 Calibrated ages and relationship between the Archaeological chronology and Estimated chronology by 14 C dating.
CG: Charred Grains, C: Charcoal, HB: Human Bone, AB: Animal Bone

4.2 Iron Age: Stratum IIa

Stratum IIa is dated to the 7th to 4th centuries BC based on pottery typology (Matsumura 1992). We dated eleven charred grains and an animal bone from this stratum, with results in the range from 910 to 370 cal BC. Sample 05000519 was from the first building level of Stratum IIa, exposed after removing the remains of Stratum I (Omura 1998: Fig.11). The end of the Iron Age may be in the 5th to 4th century BC based on the result of 05000519. It is also thought that its boundary is younger than this result, because we could not judge whether this sample belongs to the end of the IIa period or not the whole, although it is possible to obtain the evidence of the life of the IIa period. Similar dates of approximately 8th- 4th centuries BC were obtained from all samples, except 05000513, and are in good agreement with the archaeological dating. The calibrated date of sample 05000513 is about 100 years older than the others. One possible explanation is that H252, the feature from which the sample came, belongs to Stratum IIb, IIc or IId, rather than the final building level of Stratum IIa. Another possibility is that Stratum IIa started earlier than had been determined archaeologically.

4.3 Iron Age: Stratum IIc

We dated charred grains from Stratum IIc. The obtained date is 920 to 830 cal BC. This is older than the date of the major remains of Stratum IIa, and younger than the date of the remains of Stratum IId (see next paragraph). Therefore, the contextual relationship is consistent, but there is a contradiction between the calibrated radiocarbon date and the archaeological date of 8th to 7th centuries BC (Omura 1992).

4.4 Iron Age: Stratum IId

We dated three charred grains and one piece of charcoal from Stratum IId. The suggested date of Stratum IId is 1200-800 BC based on pottery typology and fabric studies (Matsumura 1996). The ^{14}C date of this stratum is 1410-900 cal BC. The IId period tends to indicate that it is older than the archaeological age from the viewpoint of ^{14}C dating, although this probability range of ^{14}C dating overlaps with the archaeological age. At this point, we cannot furthermore discuss about the date of the IId period due to few results.

4.5 Middle-Late Bronze Age: Stratum IIIb

We dated two samples of charred grain and charcoal found in R345 in Sector VIII (Omura 2004, Fig. 37), belonging to Stratum IIIb. The calibrated date is 1730 to 1540 cal BC. This result correlates closely with the archaeological date of 1700 to 1400 BC (Omura 1992).

4.6 Middle-Late Bronze Age: Stratum IIIc

We dated charred grain and human bone from Stratum IIIc to 1910 to 1740 cal BC. This result fully corresponds to the archaeological date of 1930 to 1750 BC (Omura 1992). Sample 05000514 was found while investigating the boundary between Stratum IIIb and IIIc, so its calibrated date provides a clear end date for Stratum IIIc.

5 CONCLUSION

Through AMS ^{14}C dating, we obtained an absolute chronology of Kaman-Kalehöyük that shows good agreement with the archaeological chronology. The result reflects the precise excavation carried out at Kaman-Kalehöyük. However, the boundary date of each stratum is still not clear. In particular, we were not able to date the boundaries of Stratum IIa, IIc and IId at this time. Further ^{14}C dating is needed, based on stratigraphic analysis. Also, we have to reconsider the archaeological provenance of some samples whose radiocarbon dates were older than their expected dates based on archaeological analysis.

Dating of Stratum IId samples from Kaman-Kalehöyük was carried out by Dr. Huber and Dr. Hirao, as stated above. In their results, Stratum IId was dated to approximately the 12th to 10th centuries BC, although there was some scatter. However, these results were not calibrated. Their dates calibrated are 16th to 7th centuries cal BC. The dates obtained from dendrochronology of Iron Age materials were 12th century BC and 6th century BC. The dates obtained in the present AMS study roughly agree with these dates, except for the dendrochronology result of 6th century BC.

Therefore, it seems reasonable to conclude that the date of Stratum IId is 14th to 8th centuries BC. In this way, the comparison between data from more than one laboratory and more than one method is important in determining the date of each stratum at Kaman-Kalehöyük. Further ^{14}C dating will be needed to improve the accuracy of the chronology of Kaman-Kalehöyük, and comparison between this site and others will help to reconstruct the archaeological chronology of Central Anatolia.

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