Chapter 4

Radiocarbon Dating of Holocene Sediments at the Mawaki Site by Accelerator Mass Spectrometry

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Abstract

^{14}C dating by accelerator mass spectrometry was conducted for sediment cores B3, C3, C4, C5, C6 and C8, as well as for wood samples collected from an outcrop of trench site along C-Line (D2), around the Mawaki archeological site, middle of the Noto Peninsula, in Noto-town, Hosu-gun, Ishikawa Prefecture, to analyze paleoenvironmental change, especially the temporal progression of the Holocene marine transgression and the successive retreat. The calibrated ^{14}C ages of the cored sediments ranged from 10,400 cal BP to 900 cal BP. Additionally, several carbonaceous fractions were separated from dolphin bones excavated at the Mawaki site for ^{14}C dating. The ^{14}C ages and their calibrated ages for the alkali-treated fractions from the dolphin bone ranged around 5,230-5,270 BP and 5,580-5,650 cal BP, respectively. The temporal change of the correction value for the local marine carbon reservoir effect, ΔR, was analyzed using the ^{14}C ages measured for sediments from cores C4, C5 and C6, and it was recognized that the ΔR values tended to be more negative during the Holocene marine transgression period (6,000~7,000 cal BP). It means that the ^{14}C age differences between marine and terrestrial samples are smaller here at the Mawaki site compared with the average difference value established worldwide. The negative trend of the ΔR values can be explained by a higher supply of well-mixed surface ocean water from the warm Kuroshio Current.

4.1 Introduction

Age determination is very important for understanding the chronological sequence of environmental changes and human activities at archaeological sites. The chronological sequence of transitions of pottery types constructed by archaeologists is very effective for establishing the chronology of the site and comparing its order to with that of other sites. However, numerical age determination is more useful and important than estimating chronological order

because it allows determination of the specific ages of material or strata. Radiocarbon (^{14}C) dating is one of the most trustworthy age determination methods for establishing absolute ages from several tens of thousands of years ago to present. ^{14}C age determination began in the late 1940's, when Professor Willard Libby detected ^{14}C in nature (Figure 4.1), confirmed a relation known as the decay curve of ^{14}C abundance in a carbon sample, and determined the age of the sample, the time passed since the living material became dead (Arnold and Libby, 1949; Figure 4.2). ^{14}C dating can be applied to carbon containing materials such as wood, other plant material, shell, and so on. Since that time, the techniques for implementing the ^{14}C method have advanced greatly. In this section, we briefly describe the principles and application techniques of the ^{14}C dating method. We then report the results of an application of the ^{14}C dating method using accelerator mass spectrometry (AMS) to several types of remains excavated at the Mawaki Archaeological Site.

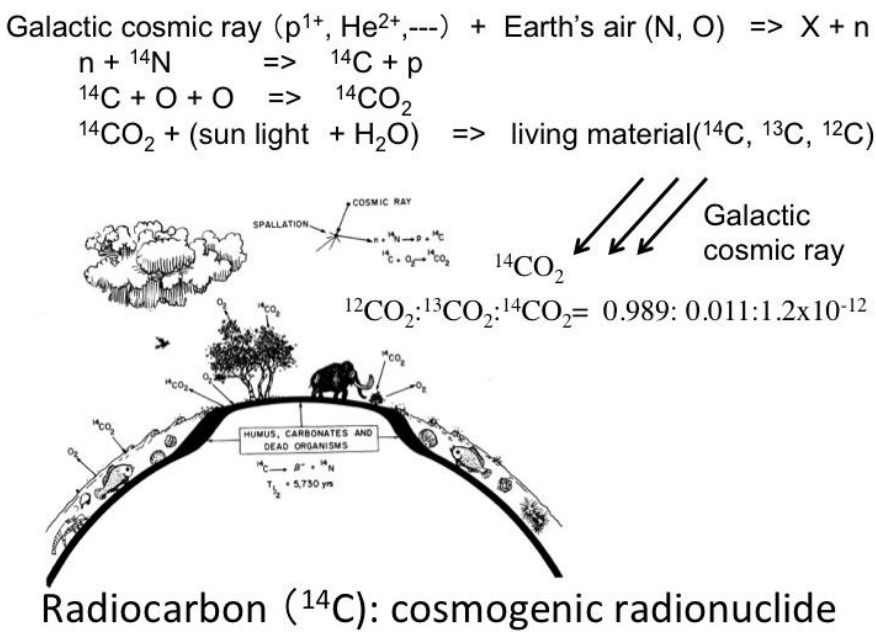

Figure 4.1 *Production, decay and distribution of ^{14}C on the earth.*

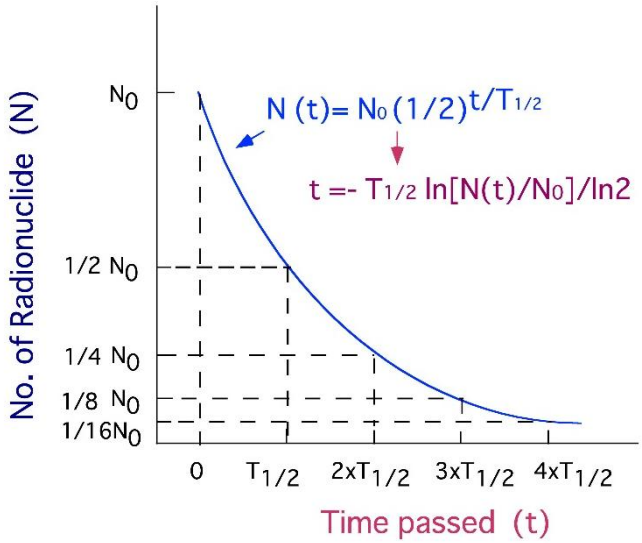

Figure 4.2 *Relationship between number of radionuclide and time passed.*

4.2 Two Methods of ^{14}C Dating

^{14}C dating is one of the radiometric methods based on the radioactive decay of radionuclides in the environment. The method utilizes the cosmogenic radionuclide, ^{14}C, which has a half life of 5,730±30 years. ^{14}C is produced continuously in the Earth's atmosphere by galactic cosmic rays, at a rate of almost two atoms per second per cm^2 of earth surface. Measurement of ^{14}C in nature was first conducted first by Prof. Libby and his colleagues at the University of Chicago during the late 1940s. To be a suitable material for ^{14}C dating, a sample must contain carbon originally fixed by the incorporation of atmospheric CO_2 through photosynthesis and must have a clear relationship in its geological context to the event to be dated. The material also must have been preserved well during the time period from carbon fixation to ^{14}C measurement. Materials commonly measured include wood (cellulose), seeds, pollen, charcoal, bone, peat, chitin, and carbonate shells (Figure 4.3).

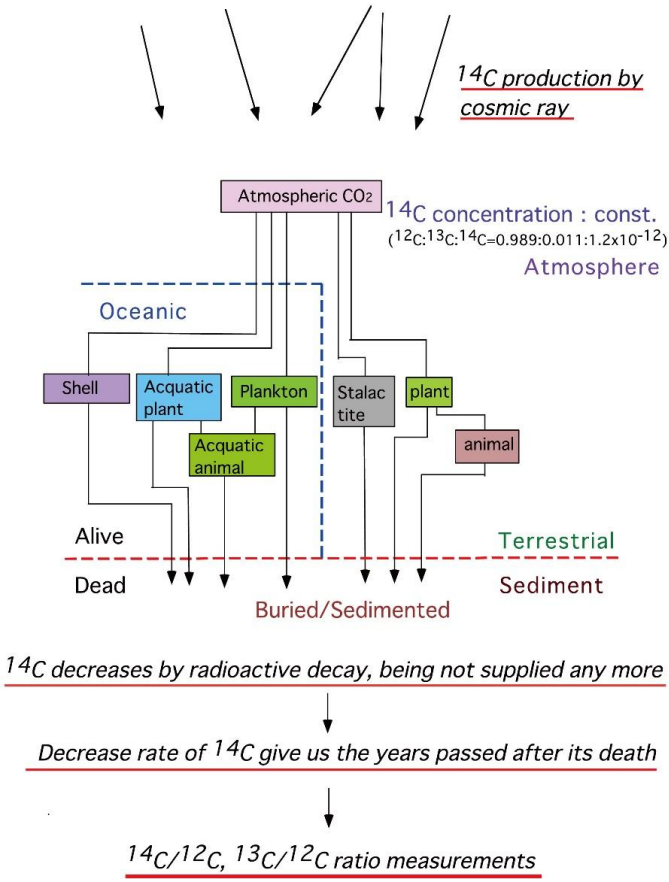

Figure 4.3 *Principle of ^{14}C dating for carbonaceous materials on the earth.*

^{14}C dating is applicable to organic matter containing carbon that was fixed photosynthetically from atmospheric CO_2 within the past 50,000 to 60,000 years. The reliability of age determination by the ^{14}C dating method has been improved by calibration of ^{14}C ages to calendar dates and by taking account of the inevitable temporal variations of the ^{14}C content of atmospheric CO_2 in the past (Reimer et al., 2013). Additionally, improved accuracy of ^{14}C content analysis and appropriate selection of specific samples during the field surveys have contributed to the high reliability of ^{14}C dating analysis.

Two different methods for measuring the ^{14}C content of carbonaceous

materials are in use. In the first method, the ^{14}C activity of a sample is measured by counting the beta particles emitted through the decay of ^{14}C, by using a gas proportional counter for carbonaceous gases such as CO_2, CH_4, C_2H_2, or rarely C_2H_6, or by using a liquid scintillation counter using benzene or ethanol synthetized from sample carbon. The second method, which has been in use since 1977, is direct ion counting of three carbon isotopes, ^{12}C, ^{13}C and ^{14}C of the carbon sample using accelerator mass spectrometry (AMS) (Figures 4.4, 4.5 and 4.6). AMS uses a tandem electrostatic accelerator to obtain individual carbon ions of ^{12}C, ^{13}C and ^{14}C with energies high enough (several MeV) to be separated clearly from background ions with a mass-analyzing magnet. Individual ions of ^{14}C, which has quite low abundance compared to stable ^{12}C and ^{13}C (even a contemporaneous carbon sample has $^{14}C/^{12}C$ ratio as low as 10^{-12}), are finally identified and counted by a heavy ion ionization detector.

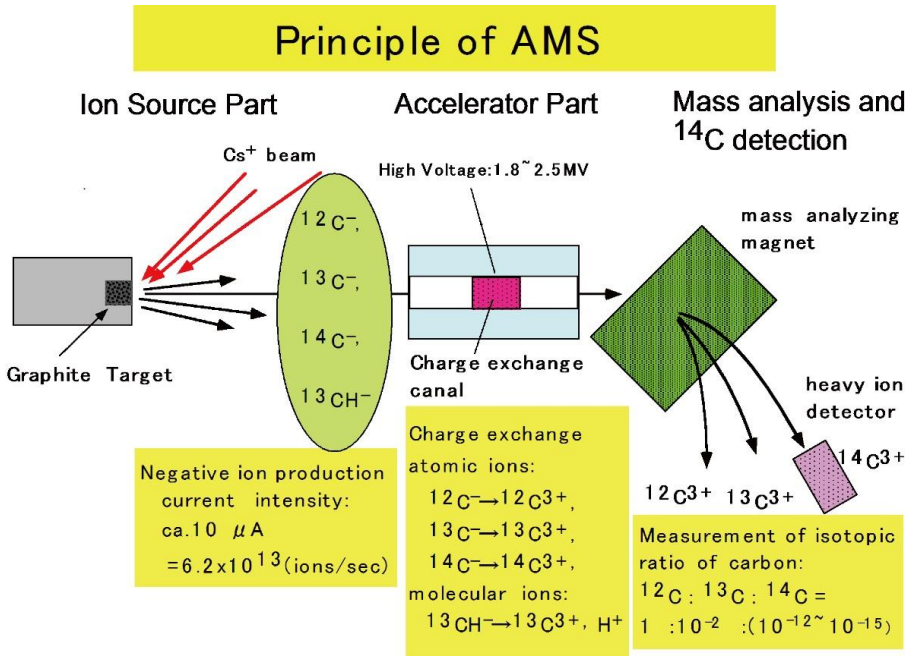

Figure 4.4 *Process of measuring three carbon isotopes, ^{12}C, ^{13}C and ^{14}C with AMS.*

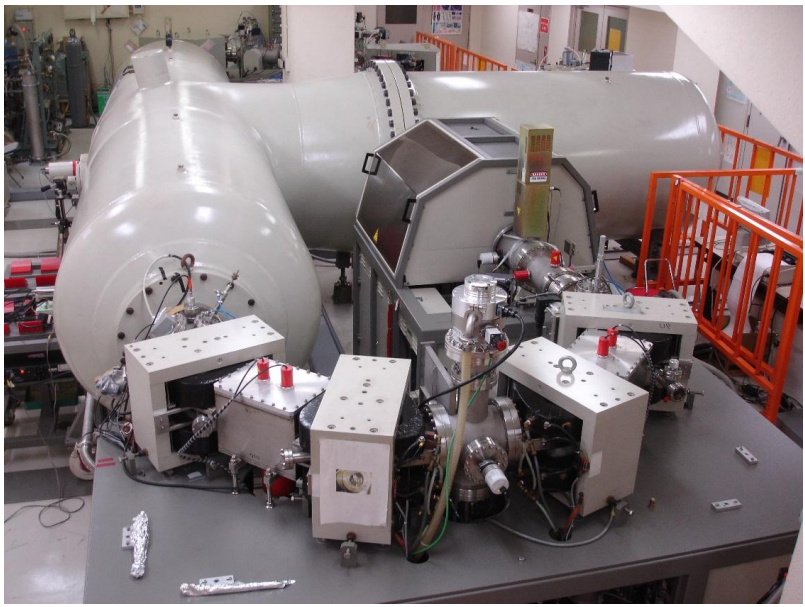

Figure 4.5 *Photo of Tandetron AMS System (Model 4130-AMS) at Nagoya University.*

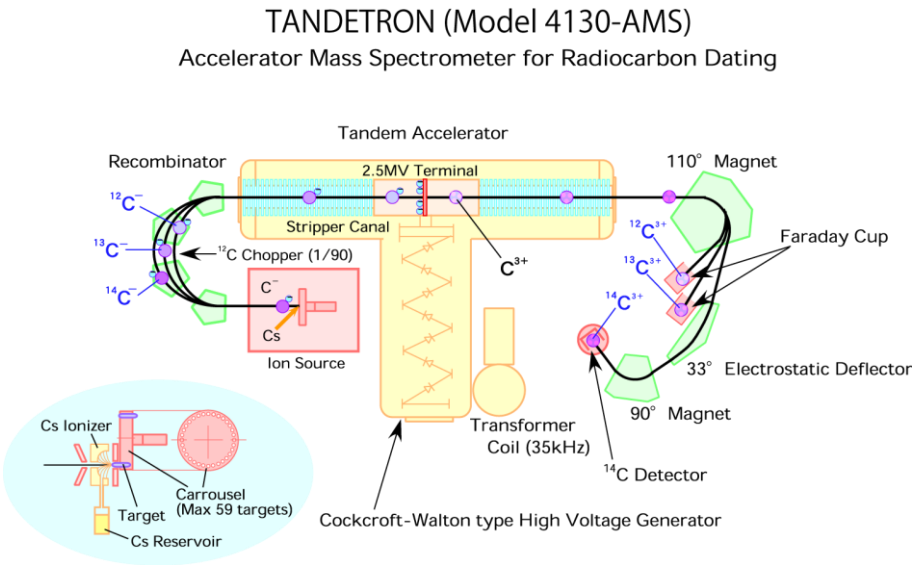

Figure 4.6 *Layout of Tandetron AMS System (Model 4130-AMS) at Nagoya University.*

The characteristics and advantages of AMS ^{14}C age determination compared with beta-ray counting methods include the following; (1) The sample volume required for the AMS method is far less (by three orders of magnitude) than that required for decay counting methods (Figure 4.7). AMS allows routine measurements for carbon samples ranging from 100 μg and 1.5 mg, whereas decay counting methods usually require a minimum of several grams of carbon. (2) Because a small amount of sample can be used in AMS, replicate measurements of the same sample and measurements of specific fractions of the sample are possible. (3) AMS can also measure older material (ca. 50 to 60 ka BP). The procedures required for ^{14}C dating of geological and archeological samples are summarized in Figure 4.8, which describes the processes from selection of adequate sample materials that are deeply related to the events to be dated, to the reporting of the ^{14}C dating results.

Item	AMS system	Radioactivity method
Carbon necessary	0.1 ～ 1.5 mg	2 ～ 5 g
Measurement error (±1σ)	±20 ～ ±40 yr	±80 yr
Oldest age measurable	ca. 60,000 yr BP	35,000 ～ 40,000 yr BP
Measurement time	20 ～ 40 min. (for sample only)	16 ～ 20 hr (for sample only)

Figure 4.7 *Comparison of performances in ^{14}C dating by AMS system and radioactivity method.*

Process	Checks and operations
Selection of sample material to be dated	・sample material that clearly shows the event to be solved ・selection of carbonaceous materials suitable for dating ・removal of foreign carbon contamination ・sample preparation
^{14}C measurement	・high precision measurement ・high accuracy measurement ・reduction of ^{14}C blank, as low as possible
Calculation of ^{14}C age	・estimate the initial ^{14}C abundance in the sample material ・correction for carbon isotopic fractionation
Calibration to calendar date	・calibration with an appropriate IntCal dataset ・correction for local ocean carbon reservoir effect, and calibration with Marine dataset
Report of ^{14}C dating results	・conventional ^{14}C age ・$\delta^{13}C$ value (carbon stable isotope ratio) ・calibrated calendar dates

Figure 4.8 *Procedure of calendar age determination by AMS ^{14}C dating.*

4.3 Process of Calendar Age Determination and Evaluation of Marine Reservoir Effect

^{14}C ages of terrestrial samples can be calibrated to calendar dates by using international calibration datasets (Reimer et al., 2013), IntCal or SHCal, depending on the location in the Northern or Southern Hemisphere where the sample formed by the incorporation of atmospheric CO_2 through photosynthesis or by the acquisition of carbon via a food chain. On the other hand, the ^{14}C ages of marine samples are calibrated to calendar dates differently than those of terrestrial samples. It is well known that ocean deep water forms in the North Atlantic Ocean and circulates in the deeper layers of the ocean through the Atlantic, Antarctic, Indian, and Pacific oceans before finally upwelling in the northern Pacific Ocean and returning at the ocean surface to the North Atlantic Ocean, with a cycle time of more than 1,500 years (Stuiver and Braziunas, 1993). The circulation of ocean deep water causes marine samples to become eventually depleted in ^{14}C (marine carbon reservoir effect: R in Figure 4.9). The ^{14}C ages of marine materials is globally older by an average of 400 ^{14}C years

(<R>) (Stuiver and Braziunas, 1993), than those of terrestrial samples that incorporate atmospheric CO_2 directly. In areas where the upwelling of deep water is strong, the surface water, and of course the oceanic carbonaceous materials, are more depleted in ^{14}C than the average value of <R>, which is known as the local ^{14}C reservoir effect of surface ocean water. Along with the global average effect, this additional local reservoir effect, i.e., correction value of the local marine reservoir effect denoted as ΔR, is normally not negligible for precise calibration of ^{14}C ages of marine samples (Hughen et al., 2004).

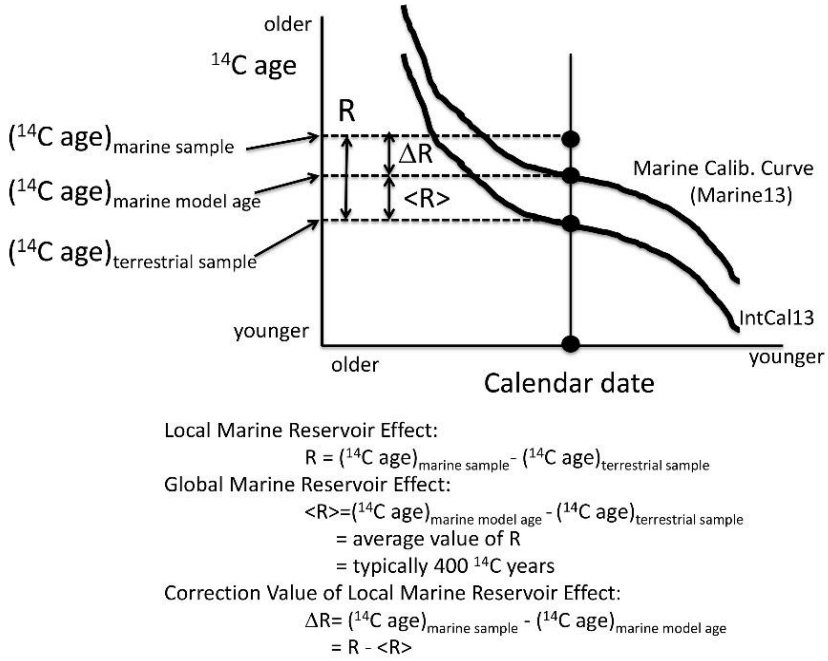

Figure 4.9 *Marine carbon reservoir effect, its local effect and correction value of the local effect.*

The marine carbon reservoir effect R at a local point is expressed by the difference in ^{14}C age between the marine sample and a contemporaneous atmospheric sample collected in the same area (Stuiver and Polach, 1977; Stuiver et al., 1986; Stuiver and Braziunas, 1993). However, the correction

value of the local marine reservoir effect is sometimes expressed by ΔR, as stated above, and defined as (1) the age difference between the local marine reservoir value R and the average value <R> for global contemporaneous ocean materials (Hughen et al., 2004), or more directly, as (2) the difference between the ^{14}C age of the marine sample and the corresponding optimum marine global ^{14}C age at the sample calendar age given by the Marine13 calibration curve (Figure 4.9; Reimer et al., 2013). We used the second calculation method noted as (2) above to calculate the correction value ΔR, as discussed later in this text.

In the southwestern part of the Japanese Archipelago, well-mixed surface ocean water is supplied from the warm Kuroshio Current, which flows northward along the western rim of the Pacific Ocean and partly into the Sea of Japan. The correction value of the local reservoir effect, ΔR, is rather negative in this region.

4.4 Sediment Samples from the Mawaki Site for ^{14}C Dating

Table 4.1 *Organic fractions separated and their yields, CO_2 yields, C/N ratios, $\delta^{13}C$ and ^{14}C age values, calibrated age ranges and Lab. code no. of ^{14}C measurements, for dolphin bone samples collected from the Mawaki site.*

No.	Organic fraction	yield	CO_2 yield	C/N ratio	$\delta^{13}C$ by RIMS	^{14}C age (± 1σ)	calbrated age range (±2σ)	Lab code #
		(%)	(%)		(‰)	(yr BP)	(cal yr BP)	(NUTA2-)
1	SC	0.07	38.20	8.3	-17.5±0.1	4910±35	5318-5065 (95.4%)	1447
2	Insol. Res. after GC ext	-	22.00	4.9	-19.1±0.1	5015±35	5454-5285 (95.4%)	1448
3	GC-DB	1.65	36.80	3.4	-14.4±0.1	5120±35	5578-5388 (94.5%)	1446
4	A-DB(2h)	4.43	22.30	3.5	-15.0±0.1	5220±35	5656-5477 (95.4%)	1448
5	A-DB(48h)	2.34	26.40	3.9	-15.3±0.1	5185±30	5606-5462 (95.4%)	1559
6	GC-A-DB(2h)	1.20	35.10	3.1	-13.5±0.1	5225±30	5656- 5490 (95.4%)	1553

No.	Organic fraction	yield	CO_2 yield	C/N ratio	$\delta^{13}C$ by RIMS	^{14}C age (± 1σ)	calbrated age range (±2σ)	Lab code #
		(%)	(%)		(‰)	(yr BP)	(cal yr BP)	(NUTA2-)
7	GC-A-DB(48h)	0.35	37.90	-	-13.6±0.1	5275±30	5705- 5574 (95.4%)	1557
8	GC-A-DB(48h-A.C.)	0.48	30.10	3.2	-13.5±0.1	5245±30	5692- 5550 (95.4%)	1560
9	XAD-GC-DB	-	40.70	-	-12.8±0.1	5235±30	5680- 5520 (95.4%)	1561

The Mawaki archeological site, located in the middle of the Noto Peninsula, in Noto-town, Hosu-gun, Ishikawa Prefecture (Figure 4.10), is situated on an alluvial coastal plain with an area of about 1.2×10^5 m^2 bordered in the south by Noto bay, and surrounded by hills in the other three directions. As a result of excavation surveys conducted from 1982 to 1983, it was found that the site had been inhabited by humans almost continuously for about 3,500 years, from the early Jomon (around 6,000 years ago) to the latest Jomon (ca. 2,500 years ago).

Fifteen years after the first excavation survey, in 1997, the second survey program was initiated. To obtain a general understanding of the human settlement and the natural environment at the site, in addition to the essential direct excavations, several sediment cores were collected first from the large alluvial plain, normally composed from bottom to top of a sequence of terrestrial, marine and terrestrial layers. We collected wood and plant fragments, charcoal, shell, and bone samples from top to the bottom of the C3, C4, C5, C6, and C8 boring cores (Figures 4.11 and 4.12, and Tables 4.2~4.6), which were taken at intervals of 10 m from north to south in the middle of the alluvial plain. A few samples were collected from core B3 and from an outcrop at the trench dug along C-line (Figure 4.11 and Table 4.7). The shell samples were mixed, containing both spiral gastropods and bivalves.

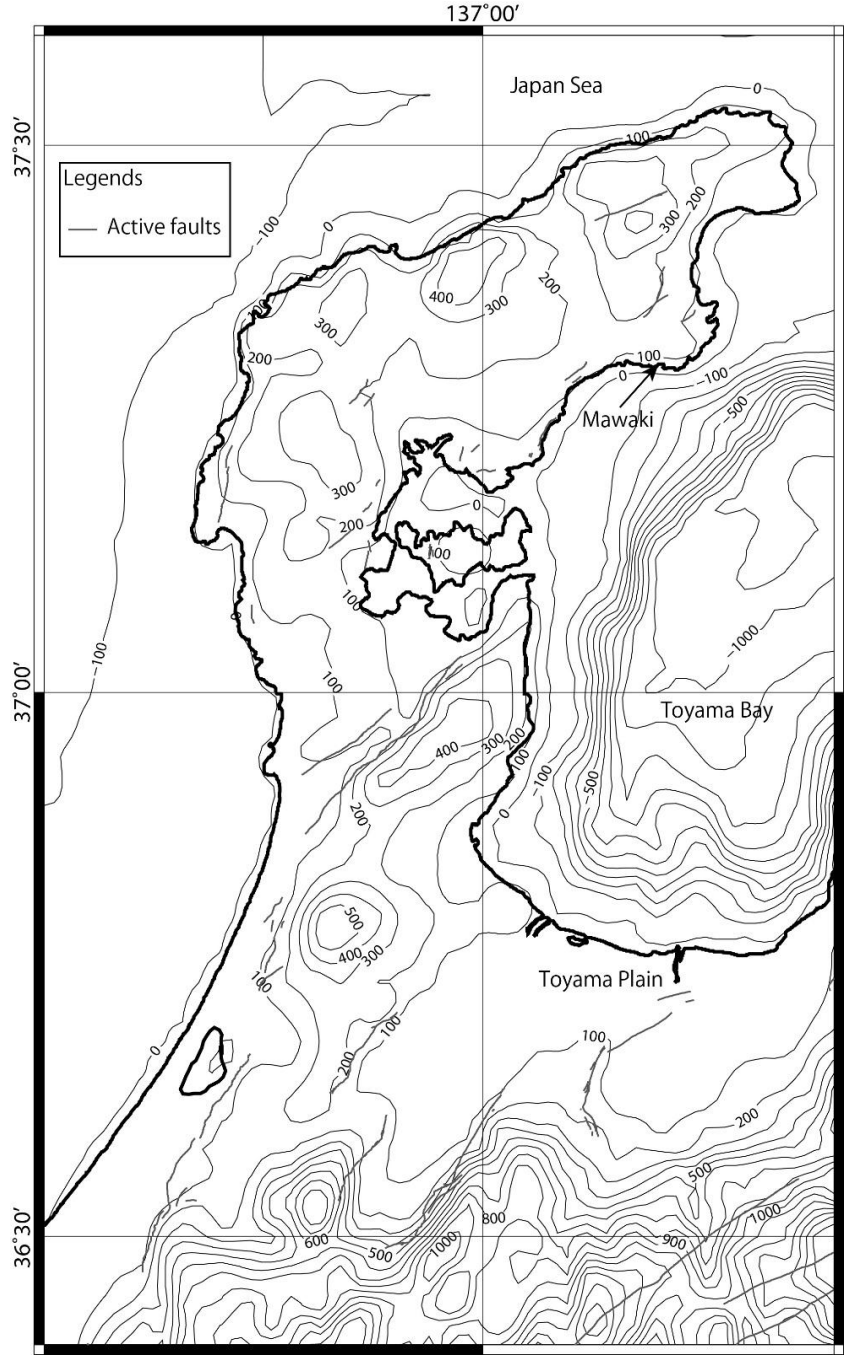

Figure 4.10 *Location of Mawaki archaeological site.*

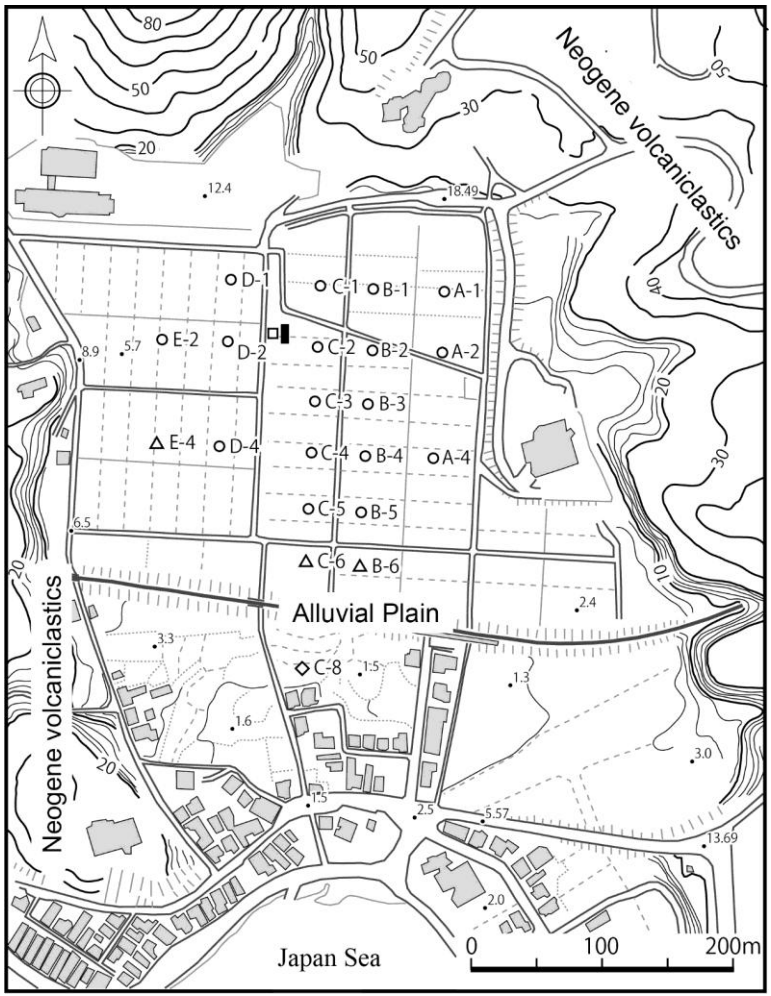

Figure 4.11 *Drilling locations at Mawaki Site.*

Unfortunately, we could not identify the species of the shell samples. Because shell fragments were rare in the cored sediments and no shell mound was observed at the Mawaki site, we assumed that the shell fragments from these core samples were of natural origin and not transported there by human activities. We also collected samples of dolphin bones, which were very common in the deeper sediments. It is considered that the resident people caught dolphins periodically from the sea and used them as food.

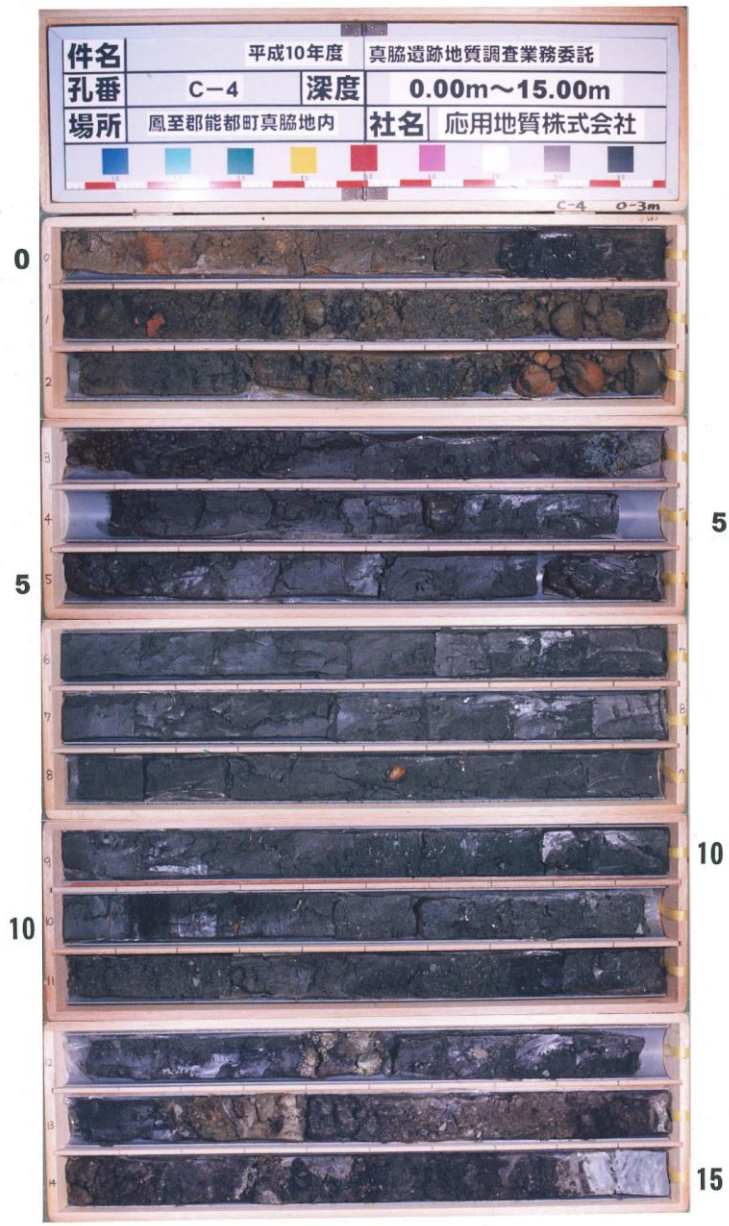

Figure 4.12 *Example of cored sample. Japanese explanations on the core box: Subject: Geological Research at Mawaki Site (2008), Borehole No.: C-4, Depth: 0.00m – 15.00m, Location: Mawaki, Noto Town, Operation: Oyo Corporation Co., Ltd.*

Table 4.2 *Age data from cored sediments of C-3.*

No.	Sample No.	Core No.	Depth	Height above sea level	Sample Material	$\delta^{13}C$ by AMS
			(m)	(m)		(‰)
			0.00	4.59		
1	C3-1W	Core 3	2.53	2.06	Wood	
2	C3-2B	Core 3	3.50	1.09	Bone	
3	C3-3B	Core 3	3.90	0.69	Bone	
4	C3-4C	Core 3	4.40	0.19	Charcoal	
5	C3-5W	Core 3	5.46	-0.87	Wood	
6	C3-6W	Core 3	6.10	-1.51	Wood	
7	C3-7C	Core 3	7.76	-3.17	Charcoal	
8	C3-8W	Core 3	8.43	-3.84	Wood	

Table 4.2 *Continue.*

No.	$\delta^{13}C$ by IRMS	^{14}C age (±σ)	Calibrated age (mean±σ)	Calibrated age range (±2σ)	Lab No.
	(‰)	(yr BP)	(cal yr BP)	(cal yr BP)(Prob.)	(*Beta-)
1	-28.2±0.1	4310±50	4900±70	5040-4820 (95.4%)	*123714
2	-16.4±0.1	5730±40	6140±60	6255-6014 (95.4%)	*123715
3	-17.1±0.1	5620±50	6020±70	6160-5906 (95.4%)	*123716
4	-28.7±0.1	6080±50	6950±90	7156-7098 (9.8%) 7086-7076 (1.0%) 7070-7044 (2.7%) 7030-6795 (81.9%)	*123717
5	-28.4±0.1	6280±60	7200±80	7408-7401 (0.4%) 7325-7005 (95.0%)	*123718
6	-25.2±0.1	6210±60	7110±80	7258-6960 (95.4%)	*123719
7	-27.7±0.1	6700±60	7570±50	7668-7469 (95.4%)	*123720
8	-27.9±0.1	6920±50	7760±60	7918-7904 (1.6%) 7858-7664 (93.8%)	*123721

Table 4.3 *Age data from cored sediments of C-4.*

No.	Sample No.	Core No.	Depth	Height above sea level	Sample Material	$\delta^{13}C$ by AMS
			(m)	(m)		(‰)
			0.00	4.00		
9	C4-1W	Core C4	3.65	0.35	Wood	-24.2±1.0
10	C4-2S	Core C4	3.65	0.35	Shell	1.2±1.0
11	C4-3S	Core C4	5.05	-1.05	Shell	1.3±1.0
12	C4-4W	Core C4	5.48	-1.48	Wood	-26.4±1.0
13	C4-5S	Core C4	7.15	-3.15	Shell	0.0±1.0
14	C4-6W	Core C4	7.52	-3.52	Wood	-27.3±1.0
15	C4-7W	Core C4	8.28	-4.28	Wood	-26.5±1.0
16	C4-8S	Core C4	8.50	-4.50	Shell	0.3±1.0
17	C4-9W	Core C4	9.30	-5.30	Wood	-29.3±1.0
18	C4-10S	Core C4	9.30	-5.30	Shell	0.9±1.0
19	C4-11W	Core C4	10.30	-6.30	Wood	-27.6±1.0
20	C4-12S	Core C4	10.38	-6.38	Shell	-0.7±1.0

Table 4.3 *Continue.*

No.	$\delta^{13}C$ by IRMS	^{14}C age (±σ)	Calibrated age (mean±σ)	Calibrated age range (±2σ)		Lab No.
	(‰)	(yr BP)	(cal yr BP)	(cal yr BP)	(Prob.)	(NUTA2-)
9		5596±30	6370±40	6436-6306	(95.4%)	5608
10		5853±30	6270±40	6350-6190	(95.4%)	946
11		4953±29	5300±50	5423-5228	(95.4%)	945
12		6011±32	6850±50	6944-6777 6764-6754	(93.5%) (1.9%)	5609
13		6445±29	6930±50	7040-6831	(95.4%)	987
14		6139±32	7050±70	7158-6948	(95.4%)	5610
15		6407±32	7350±40	7418-7272	(95.4%)	5613
16		6575±29	7090±50	7188-6990	(95.4%)	990
17		6818±33	7650±30	7694-7589	(95.4%)	5614
18		7106±33	7580±40	7654-7508	(95.4%)	947
19		7107±34	7930±40	8004-7917 7904-7856	(69.4%) (26.0%)	7107
20		7461±30	7920±40	7990-7842	(95.4%)	991

Table 4.4 *Age data from cored sediments of C-5.*

No.	Sample No.	Core No.	Depth	Height above sea level	Sample Material	$\delta^{13}C$ by AMS
			(m)	(m)		(‰)
			0.00	3.67		
21	C5-1P	Core 5	4.05	-0.38	Plant	-27.0±1.0
22	C5-2S	Core 5	4.05	-0.38	Shell	1.5±1.0
23	C5-3W	Core 5	4.35	-0.68	Wood	-30.0±1.0
24	C5-4W	Core 5	4.35	-0.68	Wood	-25.5±1.0
25	C5-5S	Core 5	4.97	-1.30	Shell	2.2±1.0
26	C5-6P	Core 5	6.50	-2.83	Plant	-28.9±1.0
27	C5-7S	Core 5	6.50	-2.83	Shell	2.8±1.0
28	C5-8W	Core 5	6.58	-2.91	Wood	
29	C5-9S	Core 5	7.54	-3.87	Shell	2.4±1.0
30	C5-10S	Core 5	8.15	-4.48	Shell	2.2±1.0
31	C5-11P	Core 5	8.43	-4.76	Plant	-28.3±1.0
32	C5-12S	Core 5	8.83	-5.16	Shell	1.5±1.0
33	C5-13P	Core 5	9.10	-5.43	Plant	-27.1±1.0
34	C5-14S	Core 5	9.62	-5.95	Shell	0.9±1.0
35	C5-15S	Core 5	10.63	-6.96	Shell	-0.4±1.0
36	C5-16S	Core 5	11.85	-8.18	Shell	0.9±1.0
37	C5-17S	Core 5	12.13	-8.46	Shell	-0.1±1.0
38	C5-18W	Core 5	12.57	-8.90	Wood	-31.4±1.0
39	C5-19W	Core 5	12.60	-8.93	Wood	

Table 4.4 *Continue.*

No.	$\delta^{13}C$ by IRMS	^{14}C age (±σ)	Calibrated age (mean±σ)	Calibrated age range (±2σ)		Lab No.
	(‰)	(yr BP)	(cal yr BP)	(cal yr BP)	(Prob.)	(NUTA2-)
21		4373±31	4940±50	5038-4998 4982-4857	(11.9%) (83.5%)	5866
22		4166±28	4250±60	4364-4139	(95.4%)	1205
23		4500±30	5170±80	5296-5046	(95.4%)	5616
24		5291±32	6080±60	6183-5989 5963-5951	(93.1%) (2.3%)	
25		5004±29	5360±40	5440-5285	(95.4%)	1206
26		5228±31	5980±60	6174-6155 6112-6079 6022-5914	(3.4%) (6.9%) (85.1%)	5617
27		5483±29	5860±50	5930-5752	(95.4%)	1207
28	-28.6±0.1	5430±50	6230±60	6314-6172 6155-6110 6079-6058 6052-6020	(85.2%) (6.1%) (1.5%) (2.6%)	*123722
29		6066±30	6490±50	6588-6398	(95.4%)	1208
30		6067±30	6490±50	6588-6398	(95.4%)	1209
31		5933±31	6760±40	6846-6814 6801-6672	(8.3%) (87.1%)	5618
32		6275±30	6730±50	6825-6641	(95.4%)	1210
33		6037±32	6880±50	6970-6790	(95.4%)	5619
34		6545±33	7060±50	7156-6956	(95.4%)	1242
35		6896±34	7410±40	7480-7322	(95.4%)	1251
36		7289±34	7750±50	7837-7662	(95.4%)	1252
37		7337±40	7800±50	7908-7695	(95.4%)	1320
38		7058±32	7890±30	7959-7832	(95.4%)	5622
39	-31.6±0.1	7050±40	7890±40	7958-7818 7812-7794	(91.7%) (3.7%)	*123723

Table 4.5 *Age data from cored sediments of C-6.*

No.	Sample No.	Core No.	Depth	Height above sea level	Sample Material	$\delta^{13}C$ by AMS
			(m)	(m)		(‰)
			0.00	3.10		
40	C6-1P	Core 6	5.89	-2.79	Plant	-27.2±1.0
41	C6-2S	Core 6	5.89	-2.79	Shell	0.8±1.0
42	C6-3P	Core 6	7.16	-4.06	Plant	-25.9±1.0
43	C6-4S	Core 6	7.16	-4.06	Shell	0.8±1.0
44	C6-5P	Core 6	9.31	-6.21	Plant	-27.7±1.0
45	C6-6S	Core 6	9.31	-6.21	Shell	0.6±1.0
46	C6-7P	Core 6	10.28	-7.18	Plant	-31.2±1.0
47	C6-8S	Core 6	10.28	-7.18	Shell	1.1±1.0
48	C6-9P	Core 6	10.88	-7.78	Plant	-40.1±1.0
49	C6-10S	Core 6	10.88	-7.78	Shell	0.4±1.0
50	C6-11P	Core 6	12.03	-8.93	Plant	-37.3±1.0
51	C6-12S	Core 6	12.03	-8.93	Shell	1.8±1.0
52	C6-13P	Core 6	12.58	-9.48	Plant	-30.6±1.0
53	C6-14S	Core 6	12.58	-9.48	Shell	-2.2±1.0
54	C6-15P	Core 6	13.20	-10.10	Plant	-25.8±1.0
55	C6-16S	Core 6	13.20	-10.10	Shell	-0.2±1.0
56	C6-17P	Core 6	14.24	-11.14	Plant	-27.9±1.0
57	C6-18S	Core 6	14.24	-11.14	shell	-0.2±1.0

Table 4.5 *Continue.*

No.	$\delta^{13}C$ by IRMS	^{14}C age (±σ)	Calibrated age (mean±σ)	Calibrated age range (±2σ)	Lab No.
	(‰)	(yr BP)	(cal yr BP)	(cal yr BP)(Prob.)	(NUTA2-)
40		4170±36	4710±70	4834-4780 (20.3%) 4770-4580 (75.1%)	5969
41		4468±37	4660±70	4790-4529 (95.4%)	5964
42		4688±36	5420±70	5577-5537 (11.7%) 5478-5318 (83.7%)	5972
43		5042±37	5390±50	5505-5291 (95.4%)	5965
44		5687±38	6470±50	6626-6586 (2.7%) 6568-6398 (92.7%)	5973
45		5978±38	6390±50	6480-6291 (95.4%)	5966
46		5947±37	6780±50	6880-6870 (2.3%) 6860-6676 (93.1%)	6538
47		6099±33	6530±50	6626-6430 (95.4%)	6542
48		6034±58	6890±90	7153-7118 (2.4%) 7024-6730 (93.0%)	6539
49		6293±33	6750±50	6848-6654 (95.4%)	6543
50		6619±68	7510±50	7607-7423 (95.4%)	6540
51		6501±34	7010±60	7134-6905 (95.4%)	6544
52		6460±37	7370±40	7434-7292 (95.4%)	6541
53		6781±34	7310±40	7398-7238 (95.4%)	6546
54		7080±39	7910±40	7978-7834 (95.4%)	5974
55		7057±40	7540±40	7618-7454 (95.4%)	5967
56		7061±39	7890±40	7965-7825 (94.1%) 7807-7798 (1.3%)	5975
57		7455±40	7910±50	8000-7824 (95.4%)	5968

Table 4.6 *Additional newly measured data from cored sediments of C-8.*

No.	Sample No.	Core No.	Depth	Height above sea level	Sample Material	$\delta^{13}C$ by AMS
			(m)	(m)		(‰)
			0.00	1.96		
58	C8-1P	Core C8	0.91	1.05	Plant	-24.4±1.0
59	C8-2P	Core C8	2.26	-0.30	Plant	-24.2±1.0
60	C8-3P	Core C8	7.15	-5.19	Plant	-29.4±1.0
61	C8-4P	Core C8	10.63	-8.67	Plant	-17.6±1.0
62	C8-5P	Core C8	14.62	-12.66	Plant	-26.6±1.0
63	C8-6P	Core C8	15.34	-13.38	Plant	-24.9±1.0
64	C8-7P	Core C8	16.36	-14.40	Plant	-24.3±1.0
65	C8-8P	Core C8	20.76	-18.80	Plant	-26.2±1.0
66	C8-9P	Core C8	27.40	-25.44	Plant	-28.8±1.0

Table 4.6 *Continue.*

No.	$\delta^{13}C$ by IRMS	^{14}C age (±σ)	Calibrated age (mean±σ)	Calibrated age range (±2σ)	Lab No.
	(‰)	(yr BP)	(cal yr BP)	(cal yr BP)(Prob.)	(NUTA2-)
58		998±23	910±40	962-904 (80.6%) 858-828 (12.6%) 810-802 (2.2%)	16194
59		2886±25	3020±40	3140-3126 (1.8%) 3108-3094 (1.9%) 3079-2928 (91.7%)	16186
60		4761±28	5510±60	5588-5464 (91.6%) 5358-5354 (0.6%) 5348-5333 (3.2%)	16187
61		6528±29	7450±30	7504-7416 (94.3%) 7349-7339 (1.1%)	16195
62		7474±30	8290±50	8372-8276 (58.3%) 8269-8200 (37.1%)	16189
63		7434±30	8260±40	8337-8186 (95.4%)	16190
64		7941±31	8810±100	8979-8824 (42.8%) 8814-8642 (52.6%)	16191
65		8046±31	8930±80	9025-8930 (57.2%) 8924-8859 (17.7%) 8834-8778 (20.5%)	16192
66		9222±33	10380±70	10497-10267 (95.4%)	16193

4.5 Fundamental Procedures of Sample Preparation

4.5.1 Preparation of Dolphin Bone

A fossil dolphin bone collected during the excavation of the Mawaki site in 1983 was analyzed by ^{14}C dating. The procedure of the sample treatment for ^{14}C dating of the dolphin bone is described briefly in the following, as summarized in Figure 4.13 (Muto, 2001; Minami et al., 2004). The bone was decalcified with 0.5M HCl and divided into two fractions: the acid soluble component (SC) and the acid insoluble component (DB: decalcified bone). Gelatin was extracted from the DB component by heating in acidic solution at 90 ℃. The gelatin solution obtained was separated with a centrifuge and then lyophilized (GC-DB). The insoluble residue after gelatin removal (Insol. Res. after GC ext.) was also retained for ^{14}C measurement. A portion of the gelatin thus obtained was hydrolyzed with 6 M HCl at 110 ℃ for 24 h. Then, the solid part was removed by centrifugation, and the filtered hydrolysate was treated with XAD-2 resign. The XAD-treated component was eluted with HCl, evaporated, and lyophilized (XAD-GC-DB). Two aliquot parts of the DB component were treated with 0.1 M NaOH, one for 2h (A-DB (2h)) and the other for 48 h at room temperature, to get rid of any humic acid contamination. In addition, the 48 h NaOH treatment was performed in two ways: one without changing the NaOH solution (A-DB (48h)) and one in which the NaOH solution was changed once during the treatment (A-DB (48h-A.C.). Gelatin components were extracted from A-DB (2h), A-DB (48h) and A-DB (48h-A.C.) using a method similar to the one described above, and labeled as GC-A-DB (2h), GC-A-DB (48h) and GC-A-DB (48h-A.C.), respectively. Finally, all of these carbonaceous fractions were combusted in a sealed evacuated bottle with CuO as an oxidizer at 900 ℃ and changed to CO_2 (Figure 4.14 and 4.15). The liberated CO_2 was purified cryogenically using liquid N_2 and other coolants. The purified CO_2 was then reduced to graphite using a powder iron catalyst under a hydrogen atmosphere, and the mixture of graphite

and iron powder was pressed into an aluminum cathode for ^{14}C analysis by AMS.

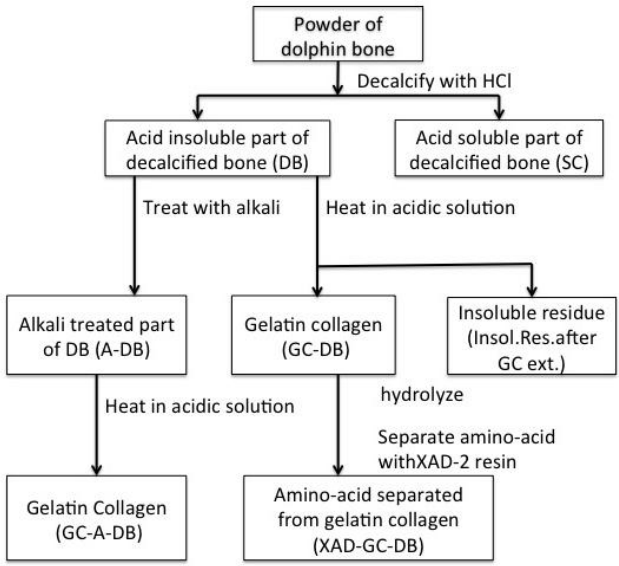

Figure 4.13 *Procedure of extracting carbonaceous fractions from dolphin bones for AMS ^{14}C dating.*

4.5.2 Preparation of Plant, Wood and Shell Samples

Typical samples for ^{14}C dating, such as shell, plant, wood and charred wood samples were pretreated in a routine way (Minami and Nakamura, 2000; Nakamura et al., 2004; Nakamura et al., 2013). (Figures 4.14 and 4.15). Shell samples were cleaned with distilled water as well as diluted HCl (0.6 M) in an ultrasonic cleaner, and then dried and powdered. The shell powder was decomposed with 85% H_3PO_4 in an evacuated bottle to produce CO_2 (Nakamura et al., 2007). Plant, wood and charred wood samples were processed chemically with a 1.2 M HCl-1.2 M NaOH solution-1.2 M HCl (acid-base-acid) treatment and combusted to CO_2. The liberated CO_2 was then converted to graphite as described in the previous section.

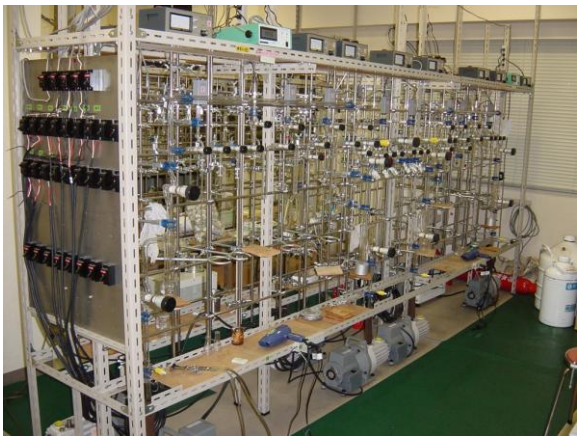

Figure 4.14 *Photo of glass-line vacuum system used for sample preparation.*

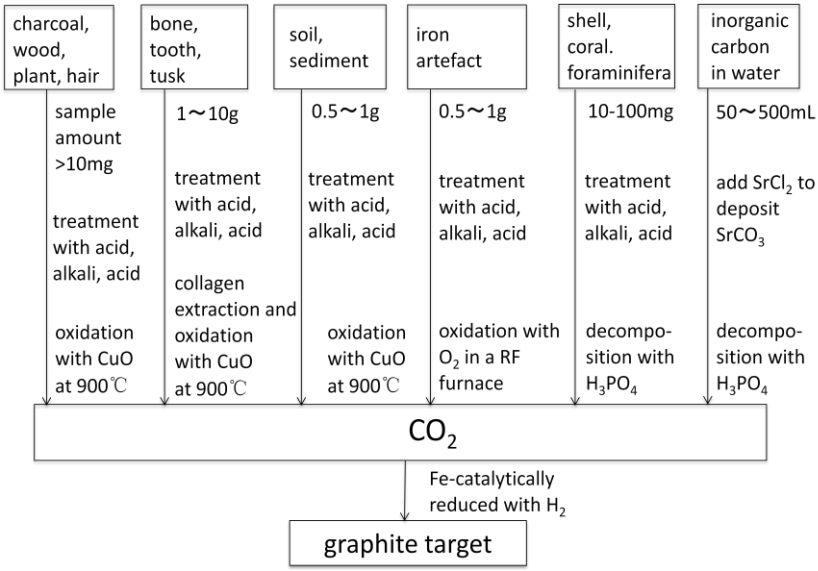

Figure 4.15 *Sample preparation for ^{14}C measurement with AMS.*

4.6 ^{14}C Measurement by AMS

All three carbon isotopes, ^{12}C, ^{13}C and ^{14}C, of the graphite targets prepared from the unknown-age sample, with the NIST HOxII standard and ^{14}C blank material (commercially available oxalic acid synthesized from fossil fuel,

No. 57952 from Kishida Ltd., Japan), were measured with an AMS system (HVEE Model-4130 AMS) at Nagoya University (Nakamura et al., 2004). The measured $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios were used to correct carbon isotopic fractionation and to calculate the sample conventional ^{14}C age. The obtained ^{14}C age was calibrated to a calendar date using the calibration program OxCal 4.2.4 (Bronk Ramsey, 2009) and the IntCal13 or Marine13 calibration dataset (Reimer et al., 2013). We estimated the correction value of the local marine carbon reservoir effect, ΔR, for the sediment samples from cores C4, C5 and C6, as is discussed later in the section. The obtained ΔR values were somewhat unreliable with rather large errors, but because the ΔR values were almost consistently zero, within ±1σ error, we adopted ΔR=0 for calibration of the marine samples collected from the Mawaki site.

4.7 Results

4.7.1 Age Determination of Dolphin Bones

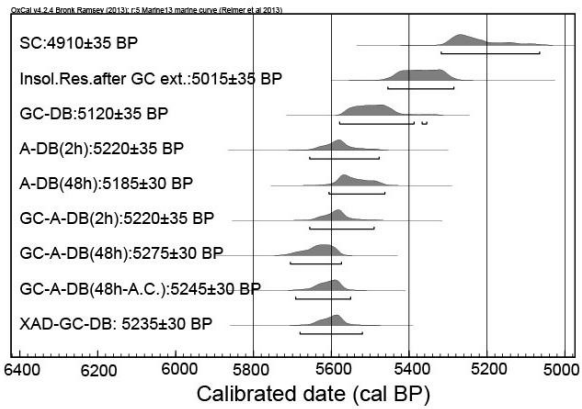

Figure 4.16 *Calibrated ^{14}C ages for nine different carbonaceous fractions separated from dolphin bones excavated at the Mawaki site.*

For ^{14}C measurements of dolphin bone samples, nine carbonaceous fractions collected by the treatment method shown in Figure 4.13 were used. The fraction

yield, CO_2 yield, C/N ratio, $\delta^{13}C$ value by IRMS, ^{14}C age, and calibrated age ranges for each carbonaceous fraction are listed in Table 4.1 and the probability density distributions against calendar date of ^{14}C ages obtained for the nine carbonaceous fractions are shown in Figure 4.16. The ^{14}C ages and their calibrated ages converged to 5,230-5,270 ^{14}C BP and 5,580-5,650 cal BP, respectively, when the carbonaceous fractions that were dated were separated from more essential and genuine parts of the dolphin bones.

4.7.2 Core Samples

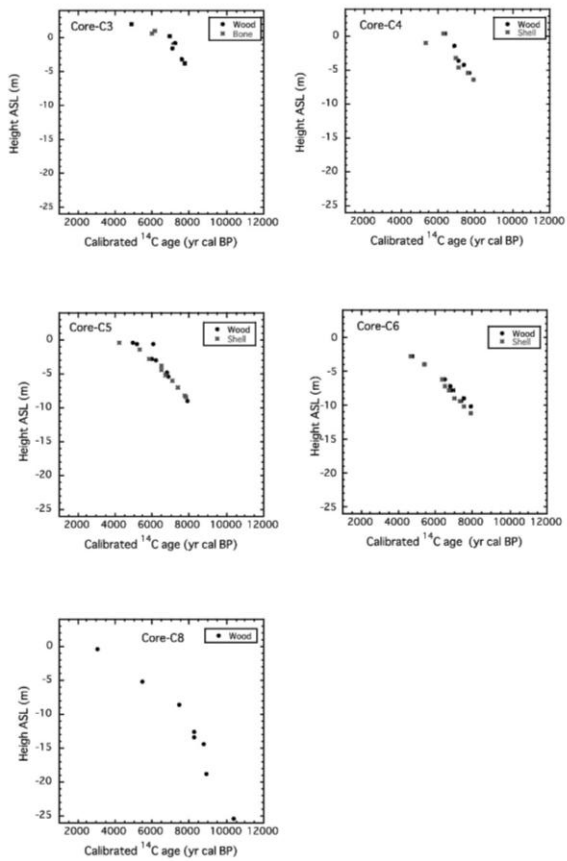

Figure 4.17 *Calibrated age vs height for terrestrial and marine samples from sediments C-3, C-4, C-5, C-6 and C-8 cored at the Mawaki site.*

The ^{14}C ages and the calibrated dates of terrestrial material (wood, plant, charcoal), marine shells and dolphin bones collected from core sediments C3, C4, C5, C6, C8 and B3, as well as wood samples from an outcrop at a trench dug along the C-line drilling (D2 in Figure 4.11) are listed in Tables 4.2, 4.3, 4.4, 4.5, 4.6 and 4.7. The calibrated ages are plotted against sample height above mean sea level (ASL) in Figure 4.17. The sample height ranged from +2 m ASL to -25.5m ASL, and the calibrated ages ranged from 3,000 cal BP to 10,400 cal BP, covering the full Holocene period.

Table 4.7 *Additional newly measured data from B3 and D2.*

No.	Sample No.	Core No.	Depth	Height above sea level	Sample Material	$\delta^{13}C$ by AMS
			(m)	(m)		(‰)
			0.00	4.59		
67	B3-1S	Core B3	3.12	1.47	Shell	-0.7±1.0
68	B3-2S	Core B3	3.38	1.21	Shell	0.8±1.0
69	D2-1W	C-Line trench		3.15	Wood	-24.8±1.0
70	D2-2W	C-Line trench		3.16	Wood	-26.5±1.0
71	D2-3W	C-Line trench		3.13	Wood	-27.5±1.0
72	D2-4W	C-Line trench		3.16	Wood	-24.6±1.0

Table 4.7 *Continue.*

No.	$\delta^{13}C$ by IRMS	^{14}C age (±σ)	Calibrated age (mean±σ)	Calibrated age range (±2σ)	Lab No.
	(‰)	(yr BP)	(cal yr BP)	(cal yr BP)(Prob.)	(NUTA2-)
67		4832±26	5140±70	5258-5024 (95.4%)	21532
68		6314±27	6770±50	6866-6682 (95.4%)	22221
69		1149±27	1060±60	1174-1157 (7.6%) 1150-979 (87.8%)	21689
70		2959±29	3120±50	3211-3020 (93.9%) 3015-3005 (1.5%)	21690
71		2959±29	3120±50	3211-3020 (93.9%) 3015-3005 (1.5%)	21691
72		2245±28	2240±60	2341-2296 (27.9%) 2269-2155 (67.5%)	21694

4.8 Discussion

4.8.1 Age of Dolphin Bones

As listed in Table 4.1 and shown in Figure 4.16, the ^{14}C ages and also their calibrated ages converged to 5,230-5,270 ^{14}C BP and 5,580-5,650 cal BP, respectively, when the carbonaceous fractions dated were collected from more genuine part of the dolphin bones. The SC fraction in the dolphin bone, collected as the acid soluble part just after decalcification with 0.5 M HCl, showed evident contamination with younger carbonaceous materials. The acid insoluble fraction after decalcification (Insol. Res. after GC ext. in Figure 4.13) was also contaminated with younger carbonaceous materials, and the contaminants could not be removed even by gelatin collagen separation (GC-DB). The GC-DB fraction showed younger age than the alkali treated fractions (A-DB, GC-A-DB) or amino-acid fraction separated with XAD treatment (XAD-GC-DB). Normally, alkali treatment removes humic acid contaminants from bone samples, and alkali treatment seemed essential for the chemical cleaning of the dolphin bone sample from the Mawaki site. As mentioned previously, the ^{14}C ages and the calibrated ages of the dolphin bone from the Mawaki site ranged from approximately 5,230-5,270 BP and 5,580-5,650 cal BP, respectively. This age of dolphin bone is consistent with the chronology established with other samples from the cored sediments, which is discussed by Takemura et al. (this volume).

4.8.2 Age-Height Relation Plot of Bored Sediment Samples

Using the ^{14}C ages and the calibrated dates of charcoal, wood and plant fragment samples that were collected from the C3, C4, C5, C6 and C8 cored sediments, height-age relations were obtained for the sediments. In the calibration of the ^{14}C ages to calendar dates for the marine samples, the correction value of the local marine carbon reservoir effect, ΔR, peculiar to the

area of the Mawaki site was assumed to be zero, and this assumption produced no particular temporal discrepancy. Because the height-age relations were smooth, except for a few ^{14}C ages, we considered that the obtained relations are acceptable (Figure 4.17). Some exceptional ages may be the result of reworking of the samples during sedimentation.

The age-height relations for sediment samples from cores C3, C4, C5, C6 and C8, which correspond to the most distant to the most proximal from the seashore (Figure 4.11), are summarized in Figure 4.18. Sediments older than 8,000 yr cal BP accumulated only at C8. Additionally, C8 sediments accumulated until less than 1,000 cal yr cal BP. Contemporaneous sediments accumulated at higher horizons as the location of sedimentation moved away from the shoreline, although the age-height relations for sedimentation in cores C6 and C8 are almost identical for overlapping periods.

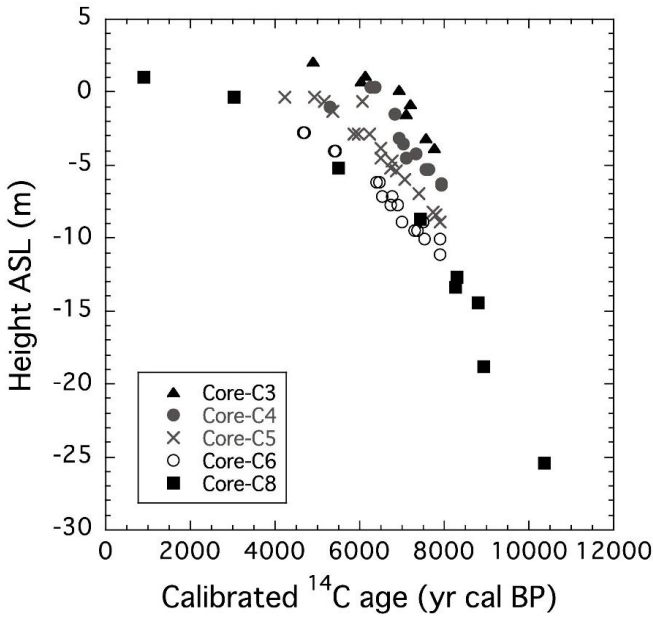

Figure 4.18 *Age-height relation of sediment samples from bored core C3, C4, C5, C6, C8.*

4.8.3 Comparison of ^{14}C Ages of Terrestrial and Marine Materials

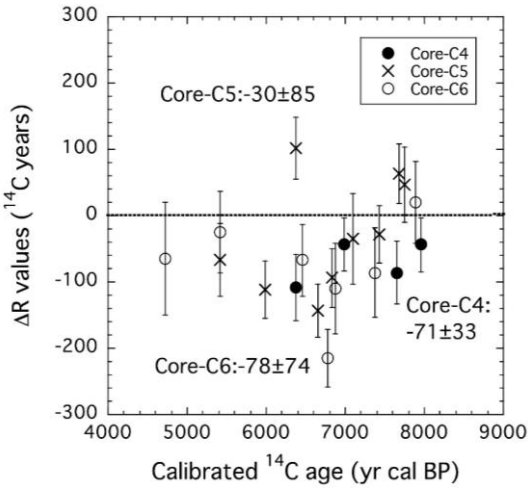

Figure 4.19 *Time dependence of the ΔR values for C4, C5 and C6 cored sediments.*

Based on the ^{14}C ages of terrestrial materials, height-age relations were determined for the sediments of cores C4 and C5. As the height-age relations were considerably smooth, with the exception of a few ^{14}C ages, we accepted that the obtained height-age relations describe the real relations. Then, the terrestrial ^{14}C ages were estimated at the depths where shell samples were collected, and pairs of terrestrial and marine ^{14}C ages were prepared. From the terrestrial ^{14}C ages thus obtained by interpolation, marine model ^{14}C ages were calculated and compared with real marine ^{14}C ages of shell samples to evaluate the local marine reservoir correction value ΔR (Figure 4.9). For core C6 sediment, both terrestrial and marine samples were selected from the identical horizons (Table 4.5), and the local marine reservoir correction values, ΔR, were calculated in the similar way. The results are illustrated in Figure 4.19. From the Mawaki samples, we obtained the time dependence of the ΔR values in the temporal range covered by the cored sediments (4,600-8,000 cal BP), as shown in Figure 4.19. The ΔR values tend to be more negative during the Holocene marine transgression period (6,000-7,000 cal BP), except for one ΔR value for

C5 core (Itoh et al., 2011). The well-mixed surface ocean water supplied by the warm Kuroshio Current might have contributed to this negative value of ΔR (weaker marine carbon reservoir effect). The average ΔR values for cores C4, C5 and C6 were calculated, excluding the unacceptable values more negative than -300 ^{14}C years that are quite different from the global marine reservoir correction value (ΔR = 0), to be -71±33, -30±85 and -78±74 ^{14}C years, respectively. Recent studies on the marine carbon reservoir effect for samples from Japan are summarized in Nakamura et al. (2016).

4.9 Summary

We measured ^{14}C ages for sediment cores B3, C3, C4, C5, C6 and C8, as well as for wood samples collected from an outcrop at a trench dug along the C-line drilling, to analyze paleoenvironmental change around the Mawaki archeological site, especially the temporal progression of Holocene ocean transgression and successive retreat. To also make use of ^{14}C ages for marine samples, we checked the local marine carbon reservoir effect and discovered that the reservoir effect is negligible at the moment, because the obtained correction values of the local marine carbon reservoir effect, ΔR, were consistent with zero within large experimental errors. We thus reached the following conclusions.

(1) Core C8 located nearest the seashore accumulated Holocene sediments from 10,400 cal BP until 900 cal BP.

(2) The ^{14}C ages obtained from several carbonaceous fractions collected from dolphin bone suggested that alkali treatment is essential to chemically clean dolphin bone samples from the Mawaki site. The ^{14}C ages and their calibrated ages for the alkali-treated fractions from the dolphin bone collected at the Mawaki site ranged 5,230-5,270 ^{14}C BP and 5,580-5,650 cal BP, respectively.

(3) The temporal change of the correction value of the local marine carbon

reservoir effect ΔR was analyzed for sediments from cores C4, C5, and C6, and it was recognized that the ΔR values tend to be more negative during the Holocene marine transgression period (6,000-7,000 cal BP).

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