AMS ^{14}C DATING OF IRON ARTIFACTS: DEVELOPMENT AND APPLICATION

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ABSTRACT. We have developed a prototype carbon extraction system for accelerator mass spectrometry (AMS) radiocarbon dating of archaeological iron remains by combusting them with a RF induction furnace. We have also successfully tested and used a method of carbon extraction from iron using a $CuCl_2$ solution. Modifications to our carbon extraction systems and methods provide us acceptable performances; carbon yield is normally around 80% and the ^{14}C background level is as low as 42–48 ka BP in ^{14}C apparent age. We have also conducted an iron refining experiment to examine the sources for carbon ^{14}C age derived from iron, using established AMS ^{14}C dating and carbon extraction systems. Our refining experiment was conducted on iron slag, which are by-products formed during iron smelting methods in the 7th century AD, and using modern charcoal as fuel. The aim of the experiment was to determine whether original carbon characteristics in the original iron materials would be preserved, or if the carbon signature would be replaced to some degree by the modern charcoal. AMS ^{14}C measurements on the refined iron yielded ^{14}C ages equivalent to those of the modern charcoal fuel. The result indicates that the original carbon signatures in the iron slag from 7th century production was replaced completely by modern carbon used in our experiment. The experiment confirms the assumption that ^{14}C ages on iron products are associated with the fuel source of the iron smelting or refining process. We also report on the dating of iron slag materials excavated from the Gennaitouge iron smelting site, where ^{14}C dates were consistent with the age of the site estimated by archaeological evidence.

INTRODUCTION

The timing of the introduction of ancient iron manufacture from China or Korea to Japan remains uncertain. Direct radiocarbon dating on archaeological iron remains is one of the most promising tools to investigate the history of iron introduction in Japan. The ages of ancient iron manufacture sites are usually determined by typological estimation, based on the shape and decoration on the surface of pottery, or ^{14}C dating of charred wood collected from the layers in which iron-related remains were excavated. Such indirect methods, however, are not applicable for sites where pottery is absent or where charcoal deposits in relevant horizons may have been mixed with those of different horizons.

Van der Merwe and Stuiver (1968) first reported on the ^{14}C dating of iron samples. However, their method was not practical because it required iron samples of 1 kg or more. In the 1980s, accelerator mass spectrometry (AMS) techniques were widely used to date various kinds of carbon-containing materials, and required an average of 1 mg of carbon. The ^{14}C ages of iron artifacts were measured directly with AMS for the first time by Cresswell (1991, 1992) at the IsoTrace Laboratory, Toronto, Canada. Since then, AMS ^{14}C dating has been applied widely for iron materials (Yoshida 1992; Igaki et al. 1994; Nakamura et al. 1995; Yokoi et al. 1998; Ono et al. 1999; Yamada et al. 1999; Yamada et al. 2001; Cheoun et al. 2001; Cook et al. 2001; Craddock et al. 2002; Cook et al. 2003a; Cook et al. 2003b; Hüls et al., forthcoming). Developments over that time on the complex apparatus developed originally by Cresswell (1991, 1992), wherein iron samples were melted and carbon was extracted under vacuum, was a simple carbon extraction method for iron based on a sealed tube combustion with CuO in quartz, which was introduced successfully by Cook et al. (2001) and further modified by Hüls et al. (forthcoming). In addition, the possibility of exact dating on carbon contained in the rusty part of iron artifacts was shown by Cook et al. (2003a, 2003b).

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We have applied AMS ^{14}C dating to archaeological iron materials at Nagoya University since 1994. We developed a prototype of a carbon extraction system from iron samples by combusting them with a radio-frequency (RF) induction furnace in 1994. Since 1998, we have also successfully tested and applied a method of carbon extraction by dissolving iron materials in $CuCl_2$ solution. We have since modified both carbon extraction systems and now the 2 methods provide us acceptable performances, as will be described below. Our test experiments had 3 stages: first, we checked ^{14}C contamination levels introduced by carbon extraction based on combustion of iron with a RF induction furnace (Nakamura et al. 1995) and iron dissolution by $CuCl_2$ solution (Oda et al. 1999); second, we refined ancient iron slag materials in a furnace using modern charcoal blocks to clarify the sources of carbon in the newly produced iron; third, we measured the ^{14}C ages of ancient iron slag and charcoal remains from an archaeological site, of which the period of intense occupation is clearly known. These experiments clarify whether iron artifacts can be dated directly to estimate their production ages.

SAMPLE DESCRIPTIONS

Materials used are described to estimate ^{14}C contamination introduced during carbon extraction by the RF combustion method and $CuCl_2$ dissolution.

Iron and Charcoal Materials Used to Estimate [14]C Contamination in Carbon Extraction Procedures

We used a standard iron (LECO-501-024) supplied by LECO Corporation, which is traceable to the National Institute of Standards and Technology (NIST), to test the existence of detectable ^{14}C contamination that may be introduced during carbon extraction by the RF combustion method and $CuCl_2$ dissolution. The LECO standard iron is granular and contains 3.35% carbon (dead carbon). Charcoal used to test the ^{14}C background level of the RF combustion system was prepared from wood fragments that were extracted from a pyroclastic flow deposit (Aso-4) formed at 85–90 ka (Shimoyama et al. 1994), and derived from Aso Volcano located in Central Kyushu, Japan.

Refining of Ancient Iron Materials with Modern Charcoal Fuel

The archaeological iron slag remains used for iron-refining experiments were collected from the Gennaitouge site, which was one of the iron smelting sites active during the second half of the 7th century AD, located in Otsu City, Shiga prefecture, Japan (Figure 1). Modern charcoal blocks used as fuel for the refining experiment were sourced from a 20- to 25-yr-old oak tree, from Zhejiang Province, People's Republic of China, in 2001.

Ancient Iron Products and Charcoal Remains from Archaeological Sites of Known Age

AMS ^{14}C ages were measured for iron slag and charcoal remains collected from the Gennaitouge site, which the iron ore probably originated. Charcoal samples were extracted from the blocks of iron slag, ensuring that the charcoal fragments tested were the remains of the fuel used in iron smelting at the site. In addition, oven remains and pottery fragments related with the iron smelting activities have been excavated (Shiga Preservation of Cultural Assets Association 2001).

EXPERIMENTS

Iron Refining Experiment

In 2001, the refining experiment was repeated twice on archaeological iron slag materials. We constructed a handmade oven, 60 cm high and 13 cm in inner diameter and made of diatomaceous earth.
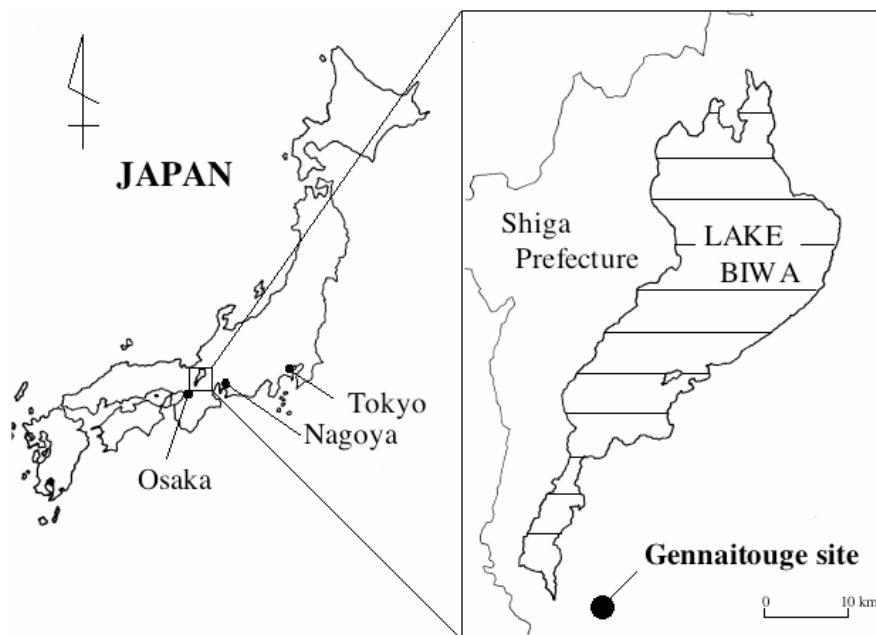
Figure 1 Location of the Gennaitouge site

The oven was first fired with charcoal. After being heated up to 1000 °C, fragmented charcoal and iron slag materials were put into the oven alternately. Air was supplied into the oven by a blower and the temperature inside the oven was maintained at 1400–1500 °C for about 5 hr. In the first run, 263.6 g of iron metal was obtained from 5.6 kg of iron slag materials and 8.9 kg of charcoal. In the second run, 222.7 g of iron metal was obtained from 3.2 kg of iron slag materials and 16.1 kg of charcoal.

Chemical Pretreatments and Graphite Preparation for AMS [14]C Dating

Charcoal Materials

To process charcoal samples for AMS ^{14}C dating, the charcoal was first broken into small fragments of about 1 mm^3 and treated with 1.2N HCl solution at 60 °C for 2 hr to eliminate carbonate and other impurities. Next, the sample was treated with 1.2N NaOH solution at 60 °C for 2 hr to remove humic acid and other organic contaminants. A final treatment with 1.2N HCl solution was repeated under similar conditions. The samples were rinsed with distilled water and dried. Samples of about 7 mg were put in the Vycor glass tubes with about 700 mg of copper oxide wire. The glass tubes were evacuated, sealed with a torch, and then heated at 850 °C for 6 hr in an electric furnace. The resulting CO_2 gas was separated cryogenically and the amount of CO_2 collected was determined. The CO_2 gas was reduced to graphite by hydrogen under an iron catalyst (Kitagawa et al. 1993) and used for ^{14}C analysis by AMS.

Iron Materials

To prepare iron samples for AMS ^{14}C dating, we first checked the existence of metallic iron in the samples, because metallic iron preserves original carbon that was incorporated during iron production and, therefore, is suitable for ^{14}C dating. We cut the iron sample into small pieces of several

mm^3 by using a metal cutting tool with a whetstone blade. The iron pieces were treated with 1.2N NaOH solution at 60 °C for 1 hr to eliminate humic acid and other organic contaminants. The samples were then treated with 1.2M HCl solution at 60 °C for 5–10 min to eliminate carbonate. Finally, the samples were rinsed with distilled water and dried.

CO$_2$ Extraction from Iron Samples by the RF Combustion Method

To accelerate combustion, a mixture of about 1.0 g of treated iron sample and 1.0 g of iron chips (LECO-502-231, high-purity iron chip accelerator with carbon content <8 ppm, LECO Corporation, USA) was placed in a preheated alumina crucible at 1000 °C for 10 hr. In order to remove carbonaceous contaminants from air dust, the crucible and contents were heated at 500 °C for 30 min in an electric oven. The sample was then taken from the oven and placed in a RF induction furnace (HF-10, LECO Corporation) that was connected to a glass vacuum line system used to purify the resultant CO$_2$. The iron sample and iron chips were heated to melting by RF induction for 4 min in a flow of ultra-high-purity oxygen (CO<0.1 ppm, CO$_2$<0.1 ppm, THC<0.1 ppm, Taiyo-toyo-sanso Co Ltd., Japan) at a flow rate of 200 mL/min, to ensure that all carbon in the iron sample was converted to CO$_2$. A schematic diagram of the glass line system used to purify CO$_2$ produced is shown in Figure 2. The vacuum system was evacuated in advance for 1 hr. Next, the combustion gas was passed through Pt/CuO at 450 °C to convert any remaining CO to CO$_2$. The CO$_2$ was then condensed with 3 cold traps aligned successively and cooled by liquid nitrogen, and the residual gas (mainly O$_2$) was pumped out slowly. The remaining CO$_2$ was further separated from water with an ethanol trap at −78 °C, then from any SO$_2$ that resisted a MnO$_2$ trap (Figure 2) with a normal pentane trap at −130 °C. The amount of CO$_2$ collected was measured volumetrically by a manometer. The CO$_2$ was reduced to graphite for analysis in the AMS ^{14}C dating system.
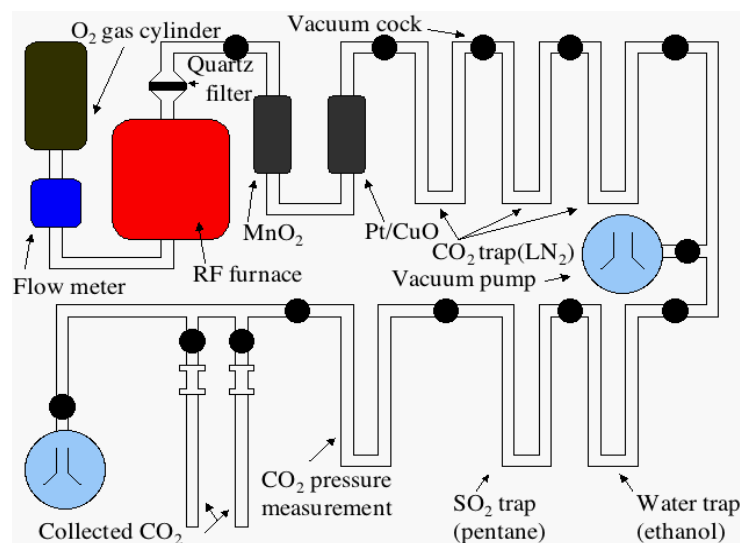

Figure 2 A schematic diagram of a RF induction furnace used to combust iron remains, and a glass line system used to purify CO$_2$ produced from iron remains.

The RF combustion method efficiently utilizes the O$_2$ and iron chips to combust iron samples completely. However, we recognized that both the O$_2$ and iron chips could possibly introduce modern carbon contamination to the CO$_2$, and a potential leak of the vacuum line system used for the iron combustion and purification of the produced CO$_2$ may do the same. Therefore, we tested for ^{14}C con-

tamination by changing the amounts of iron chips (0–2000 mg) and the O_2 flow rate (100–300 mL/min), as shown in Table 1 and 2, respectively. Charcoal with dead carbon derived from the Aso-4 volcanic deposits was also treated in the RF combustion system as well as by the routine combustion procedure in a Vycor tube to compare the apparent ^{14}C ages of graphite prepared by both procedures, as shown in Table 3.

Table 1 Yield of carbon and carbon-isotope ratios vs. amount of iron chip, for carbon extractions from standard iron using the RF combustion method. O_2 gas was supplied at a constant flow rate of 200 mL/min during the combustion period of 4 min.

Sample[a] code nr	Sample amount [mg]	Iron chip amount[b] [mg]	Carbon yield [mg C] (%)[c]	$\delta^{13}C$ [‰]	R [($^{14}C/^{12}C$)sa/ ($^{14}C/^{12}C$)st]	^{14}C age [BP]	Lab code [NUTA2-]
LECO Fe 1-1	501.61	0.00	14.27 (89.4)	−25.7 ± 0.1	0.0041 ± 0.0002	44,170 ± 450	5664
LECO Fe 1-2	501.59	0.00	14.86 (88.4)	−25.8 ± 0.1	0.0033 ± 0.0002	45,780 ± 550	5666
LECO Fe 1-3	501.61	0.00	14.27 (84.9)	−25.7 ± 0.1	0.0021 ± 0.0002	49,590 ± 790	6081
LECO Fe 2-1	501.92	500.32	15.49 (92.1)	−25.0 ± 0.1	0.0035 ± 0.0002	45,510 ± 540	5667
LECO Fe 2-2	500.87	500.56	15.07 (89.8)	−25.0 ± 0.1	0.0032 ± 0.0002	46,110 ± 580	5668
LECO Fe 3-1	500.27	750.76	14.67 (87.5)	−25.2 ± 0.1	0.0031 ± 0.0002	46,380 ± 580	5669
LECO Fe 3-2	500.38	750.73	14.69 (87.6)	−25.3 ± 0.1	0.0025 ± 0.0002	48,110 ± 700	5670
LECO Fe 4-1	500.71	1000.28	16.00 (95.4)	−25.6 ± 0.1	0.0024 ± 0.0002	48,400 ± 730	5671
LECO Fe 4-2	500.67	1000.31	15.19 (90.6)	−25.6 ± 0.1	0.0031 ± 0.0002	46,420 ± 600	5672
LECO Fe 4-3	500.71	1000.28	16.00 (54.4)	−25.6 ± 0.1	0.0024 ± 0.0002	48,590 ± 730	6082
LECO Fe 5-1	500.43	1250.85	11.17 (66.6)	−25.4 ± 0.1	0.0030 ± 0.0002	46,630 ± 600	5674
LECO Fe 5-2	500.37	1250.67	11.39 (67.9)	−25.5 ± 0.1	0.0030 ± 0.0002	46,540 ± 590	5675
LECO Fe 6-1	500.71	1500.63	14.65 (87.3)	−25.6 ± 0.1	0.0036 ± 0.0002	45,240 ± 520	5676
LECO Fe 6-2	500.68	1500.21	15.01 (89.5)	−25.6 ± 0.1	0.0031 ± 0.0002	46,370 ± 590	5677
LECO Fe 7-1	500.61	1750.19	15.73 (93.8)	−25.5 ± 0.1	0.0028 ± 0.0002	47,320 ± 640	5678
LECO Fe 7-2	500.60	1750.21	15.70 (93.6)	−25.4 ± 0.1	0.0032 ± 0.0002	46,060 ± 560	5679
LECO Fe 8-1	500.82	2000.23	9.84 (58.7)	−25.9 ± 0.1	0.0042 ± 0.0002	43,960 ± 460	5680
LECO Fe 8-2	500.01	2000.71	10.34 (61.7)	−26.0 ± 0.1	0.0039 ± 0.0002	44,570 ± 490	5681
LECO Fe 8-3	500.82	2000.23	9.84 (58.7)	−25.9 ± 0.1	0.0032 ± 0.0002	46,130 ± 580	6083
		<Av.>[d]	**13.90 (82.9)**	**−25.5 ± 0.3**	**0.0031 ± 0.0006**	**46,280 ± 1430**	

[a]LECO standard iron (LECO-501-024): 3.35% C, 0.065% S.
[b]LECO Pure iron chip accelerator (LECO-502-231): C<8 ppm, S<15 ppm.
[c]Carbon collection efficiency in percent against total carbon contained in an Fe-standard material.
[d]Errors quoted are 1 standard deviation.

Table 2 Yield of carbon and carbon-isotope ratios vs. amount of O_2 gas, for carbon extractions from standard iron using the RF combustion method. The flow rate of O_2 gas was changed from 100 to 300 mL/min. The combustion period was 4 min and no iron chips were added.

Sample[a] code nr	Sample amount [mg]	O_2 [mL/min × 3 min]	Carbon yield [mg C] (%)[b]	$\delta^{13}C$ [‰]	R [($^{14}C/^{12}C$)sa/ ($^{14}C/^{12}C$)st]	^{14}C age [BP]	Lab code [NUTA2-]
LECO Fe 100-1	450.13	100	11.21 (74.1)	−28.9 ± 0.0002	0.0040 ± 0.0002	44,390 ± 470	5683
LECO Fe 100-2	450.12	100	12.46 (82.6)	−27.2 ± 0.0002	0.0032 ± 0.0002	46,230 ± 560	5684
LECO Fe 100-3	450.13	100	12.65 (83.9)	−27.2 ± 0.0002	0.0030 ± 0.0002	46,590 ± 580	5685
LECO Fe 200-1	450.16	200	13.67 (90.6)	−25.3 ± 0.0002	0.0034 ± 0.0002	45,680 ± 540	5686
LECO Fe 200-2	450.24	200	13.64 (90.4)	−25.4 ± 0.0002	0.0030 ± 0.0002	46,800 ± 600	5687
LECO Fe 200-3	450.11	200	13.45 (89.2)	−25.4 ± 0.0002	0.0031 ± 0.0002	46,300 ± 570	5688
LECO Fe 300-1	450.06	300	10.99 (72.9)	−25.9 ± 0.0002	0.0028 ± 0.0002	47,120 ± 610	5689
LECO Fe 300-2	450.22	300	14.49 (96.1)	−25.91± 0.0002	0.0028 ± 0.0002	47,200 ± 610	5691
LECO Fe 300-3	450.18	300	14.10 (93.5)	−25.2 ± 0.0003	0.0033 ± 0.0003	45,910 ± 530	6080
		<Av.>[c]	**12.96 (86.0)**	**−26.2 ± 0.0004**	**0.0032 ± 0.0004**	**46,200 ± 940**	

[a]LECO standard iron (LECO-501-024): 3035% C, 0.064% S.
[b]Carbon collection efficiency in percent against total carbon contained in an Fe standard material.
[c]Errors quoted are 1 standard deviation.

Table 3 Yield of carbon and carbon-isotope ratios for carbon extractions from charcoal (dead carbon) using the RF combustion method and a routine procedure of combustion and purification.

Sample[a] code nr	Sample amount [mg]	Iron chip amount[b] [mg]	O_2 [mL/min × 3 min]	Carbon yield [mg C] (%)[c]	$\delta^{13}C$ [‰]	R [$(^{14}C/^{12}C)$sa/ $(^{14}C/^{12}C)$st]	^{14}C age [BP]	Lab code [NUTA2-]
Aso4-Dry1	6.42	500.98	200	2.94 (45.8)	−25.7 ± 0.1	0.0049 ± 0.0002	42,790 ± 390	5869
Aso4-Dry2	5.79	500.96	200	5.11 (88.3)	−25.7 ± 0.1	0.0038 ± 0.0002	44,700 ± 470	5895
Aso4-Dry3	5.77	500.26	200	5.03 (87.2)	−25.8 ± 0.1	0.0044 ± 0.0002	43,520 ± 410	5896
Aso4-Dry4	5.47	500.21	200	4.61 (84.3)	−25.8 ± 0.1	0.0039 ± 0.0002	44,620 ± 460	5897
Aso4-Dry5	5.14	500.31	200	4.21 (81.9)	−25.7 ± 0.1	0.0047 ± 0.0002	43,140 ± 390	5901
Aso4-Dry6	5.85	500.04	200	4.70 (80.3)	−25.8 ± 0.1	0.0038 ± 0.0002	44,680 ± 450	5902
			<Av.>[d]	**4.43 (78.0)**	**−25.8 ± 0.1**	**0.0043 ± 0.0005**	**43,870 ± 870**	
Aso4-Line1	6.45	—	—	5.57 (86.4)	−25.7 ± 0.1	0.0028 ± 0.0002	47,190 ± 570	5903
Aso4-Line2	5.74	—	—	5.24 (91.3)	−25.5 ± 0.1	0.0030 ± 0.0002	46,570 ± 560	5904
Aso4-Line3	6.12	—	—	5.08 (83.0)	−25.9 ± 0.1	0.0033 ± 0.0002	46,000 ± 520	5905
Aso4-Line4	5.85	—	—	5.48 (93.7)	−25.6 ± 0.1	0.0023 ± 0.0002	48,920 ± 690	5906
Aso4-Line5	4.79	—	—	3.59 (74.9)	−25.7 ± 0.1	0.0023 ± 0.0002	48,870 ± 700	5910
Aso4-Line6	5.69	—	—	4.73 (83.1)	−25.9 ± 0.1	0.0023 ± 0.0002	48,720 ± 690	5911
			<Av.>[d]	**4.95 (85.4)**	**−25.7 ± 0.1**	**0.0027 ± 0.0004**	**47,620 ± 1300**	

[a] Aso4-Dry1-6 were prepared by the FR-combustion method. Aso4-Line1-6 were prepared with a purification line used routinely for charcoal and wood samples.
[b] LECO Pure iron chip accelerator (LECO-502-231): C<8 ppm, S<15 ppm.
[c] Carbon collection efficiency in percent against total weight of charcoal (Aso-4).
[d] Errors quoted are 1 standard deviation.

CO_2 Extraction from Iron Samples by the Dissolution Method

^{14}C contamination for the dissolution method was estimated with an iron standard (cast iron with carbon content of 3.35%) supplied by LECO Corporation. Both HCl and $CuCl_2$ solutions were used to dissolve iron samples. First, standard iron samples of about 200 mg (nr 1–3 in Table 4) were treated with 4N HCl at room temperature for about 2 weeks to be dissolved completely. The carbon residue was collected on quartz wool in a glass funnel of 6 mm outer diameter. Next, standard iron samples of about 200 mg were dissolved in $CuCl_2$ solutions of different concentrations (2.4–31.1 g of $CuCl_2 \cdot 2H_2O$ per 70 mL of water, nr 4–9 in Table 4) at 60 °C. A mixture of standard iron and $CuCl_2 \cdot 2H_2O$ was added with 70 mL of distilled water to dissolve the iron. Carbon in the iron was then precipitated as an aggregated colloid and metallic copper was deposited. The deposited copper was dissolved with 4N HCl at 60 °C, and the carbon residue was collected on quartz wool by filtration. We also tested the $CuCl_2$ solution that was filtered through a quartz wool filter before dissolving 200 mg of standard iron, to eliminate any possible carbon contaminants in the $CuCl_2 \cdot 2H_2O$ (nr 10–14 in Table 4). The separated solid carbon recovered by the quartz wool filter was combusted to produce CO_2. After purification, the CO_2 was converted to graphite and analyzed for ^{14}C age by AMS.

^{14}C Analysis with AMS

The graphite prepared from carbon samples (as described above) was pressed into an aluminum holder and used as a target for ^{14}C dating with a Tandetron AMS system (model 4130-AMS, HVEE, the Netherlands) at the Center for Chronological Research, Nagoya University (Nakamura et al. 2000). R = $[(^{14}C/^{12}C)_{spl}/(^{14}C/^{12}C)_{std}]$ was used to represent the carbon isotope ratio for a sample $[(^{14}C/^{12}C)_{spl}]$ in the ratio to the NIST oxalic acid standard $[(^{14}C/^{12}C)_{std}]$, after being corrected for machine ^{14}C background and carbon isotopic fractionation, and then multiplied by a constant to normalize R=1.0 to represent the value of a sample formed in AD 1950 (Mook and van der Plicht 1999). Conventional ^{14}C ages were also calculated from R, and calibrated to calendar yr using the INTCAL98 data sets (Stuiver et al. 1998). All errors quoted are ±1 σ.

Table 4 Yield of carbon and carbon-isotope ratios for carbon extractions from standard iron using the dissolution method. HCl solution was used for sample nr 1–3; non-filtrated $CuCl_2$ solution with different $CuCl_2 \cdot 2H_2O$ concentration for sample nr 4–9; and filtrated $CuCl_2$ solution with different $CuCl_2 \cdot 2H_2O$ concentration for sample nr 10–14. The $CuCl_2 \cdot 2H_2O$ used was from the same lot nr, except for 2 samples (nr 9 and 14).

Sample nr	Sample code nr	Filtration[a] [yes or no]	$(CuCl_2 \cdot 2H_2O)/Fe$ [g/g]	Iron amount [mg]	Carbon yield [mg C] ([%])[b]	$\delta^{13}C$ [‰]	R $[(^{14}C/^{12}C)sa/(^{14}C/^{12}C)st]$	^{14}C age [BP]	Lab code [NUTA2-]
1	HCl-1	—	0.0	201.18	3.00 (44.5)	−25.0 ± 0.1	0.0037 ± 0.0002	44,900 ± 480	6057
2	HCl-2	—	0.0	201.51	3.00 (44.4)	−25.1 ± 0.1	0.0040 ± 0.0002	44,280 ± 460	6058
3	HCl-3	—	0.0	201.43	2.99 (44.3)	−25.2 ± 0.1	0.0040 ± 0.0002	44,450 ± 460	6059
			<Av.>c		**(44.4)**	**−25.1 ± 0.1**	**0.0039 ± 0.0002**	**44,560 ± 360**	
4	$CuCl_2$-nf-1	no	12.0	200.67	4.83 (71.8)	−24.4 ± 0.1	0.0045 ± 0.0002	43,440 ± 420	6060
5	$CuCl_2$-nf-2	no	36.0	200.97	5.99 (84.9)	−24.6 ± 0.1	0.0064 ± 0.0003	40,530 ± 320	6065
6	$CuCl_2$-nf-3	no	60.0	200.43	6.27 (93.4)	−24.7 ± 0.1	0.0093 ± 0.0003	37,500 ± 250	6066
7	$CuCl_2$-nf-4	no	96.0	201.68	6.12 (90.6)	−24.7 ± 0.1	0.0117 ± 0.0003	35,730 ± 220	6067
8	$CuCl_2$-nf-5	no	180.0	115.36	3.49 (90.3)	−24.4 ± 0.1	0.0225 ± 0.0004	30,490 ± 150	6068
9	$CuCl_2$-nf-6	no	155.0	201.63	5.56 (82.3)	−24.6 ± 0.1	0.0127 ± 0.0003	35,070 ± 210	6079
			<Av.>c		**(86.2)**	**−24.6 ± 0.1**	**0.0112 ± 0.0064**	**35,070 ± 7070**	
10	$CuCl_2$-f-1	yes	12.0	201.05	6.23 (92.5)	−24.6 ± 0.1	0.0033 ± 0.0002	45,950 ± 550	6069
11	$CuCl_2$-f-2	yes	36.0	200.46	6.04 (89.9)	−24.7 ± 0.1	0.0036 ± 0.0002	45,300 ± 510	6074
12	$CuCl_2$-f-3	yes	60.0	200.81	5.86 (87.1)	−24.6 ± 0.1	0.0036 ± 0.0002	45,130 ± 510	6075
13	$CuCl_2$-f-4	yes	96.0	200.33	6.15 (91.6)	−24.7 ± 0.1	0.0046 ± 0.0002	43,160 ± 410	6076
14	$CuCl_2$-f-5	yes	156.5	200.76	5.92 (88.0)	−24.7 ± 0.1	0.0052 ± 0.0002	42,180 ± 370	6077
			<Av.>c		**(89.8)**	**−24.7 ± 0.1**	**0.0039 ± 0.0008**	**44,640 ± 1580**	

[a] Yes or no indicates with or without filtration of $CuCl_2$ solution during the Fe sample preparation procedure.
[b] Carbon collection efficiency in percent against total carbon contained in Fe standard material.
[c] Errors quoted are 1 standard deviation.

RESULTS AND DISCUSSION

Carbon Collection Efficiency from Iron

To test any possible dependence of the ^{14}C background level on iron chip amounts (Table 1) and O_2 flow rates (Table 2) in the RF combustion system, and $CuCl_2$ amounts for the dissolution method (Table 4), an iron standard (LECO-501-024) with carbon content of 3.35% was used. The tests resulted in a carbon collection efficiency of about 83–86% on average for both carbon-extraction methods, as shown in relevant tables. Though about 15% of carbon was lost, we detected no dependence of $\delta^{13}C$ values on the carbon collection efficiency for the separated carbon. Thus, no carbon isotopic fractionation was evident in our sample preparation procedures.

Three Types of Verifications for the RF Combustion Method

The R value was dependent on neither the amount of the iron chips nor the flow rate of O_2 gas used for carbon extraction by the RF combustion method (Tables 1, 2), i.e., an increase in contamination by modern carbon was not evident when using larger amounts of iron chips (less than 2000 mg) or O_2 gas (flow rate less than 300 mL/min). On the other hand, the average value of R for carbon which was extracted from charcoal (Aso-4) by the RF combustion method was 0.0043 ± 0.0002, and that for carbon converted from charcoal by using an ordinary preparation line (a sealed-tube combustion with CuO in Vycor glass) was 0.0027 ± 0.0002 (Table 3). Thus, we detected a small increase in ^{14}C contamination from a leak in the glass line system used for the RF combustion procedure. However, the increase in contamination corresponds to only about a 4-yr shift towards a younger age when dating a sample of around 2000 BP. Thus, in case of dating archaeological iron products in Japan, the contamination effect was within the range of measurement error. Therefore, we conclude that the RF combustion method used at Nagoya University is applicable to ^{14}C dating of archaeological iron artifacts.

Verifications for the Dissolution Method

It was clear that $CuCl_2$ used in the experiment contained a small but detectable amount of modern carbon (nr 4–9 in Table 4). In fact, the R value increased from 0.0045 ± 0.0002 to 0.0225 ± 0.0002 when the maximum amount of $CuCl_2$ (30.7 g) was used for iron dissolution. The modern carbon contamination in $CuCl_2$ could, however, be considerably reduced by filtration of the $CuCl_2$ solution with a quartz wool filter (nr 10–14 in Table 4). In the measurement of archaeological products, the effect of residual modern carbon contamination, after the purification of the $CuCl_2$ solution, was estimated to be about a 3-yr shift to a younger age in dating a sample of around 2000 BP and was within the range of ^{14}C measurement error. Therefore, the dissolution method using prefiltrated $CuCl_2$ solution is applicable to archaeological iron materials.

Iron Refining Experiment

The refining experiment suggested that the R values for 7 pieces of newly produced iron fragments selected randomly (an average value of R [<R>] = 1.245 ± 0.007, nr 32–38 in Table 5) were completely different from those for 8 pieces of original iron fragments (<R> = 0.838 ± 0.002, nr 15–22 in Table 5). They have changed from the original value to that of modern charcoal used as fuel for the refining (<R> = 1.193 ± 0.004, nr 23–28 in Table 5). The R values for refined iron samples were almost consistent with, or a bit larger than, those for the modern charcoal mixture, as shown in Figure 3. However, the former values were within the range of the R values (1.108 ± 0.003 to 1.569 ± 0.003, nr 29–31 in Table 5) with respect to annual growth rings of wood from which the modern charcoal used for the refining was produced. The results of this experiment and of an iron

smelting experiment conducted by Yamada et al. (1999) suggested that carbon in the iron products was replaced with carbon from fuel charcoal that had been used for iron smelting or refining.
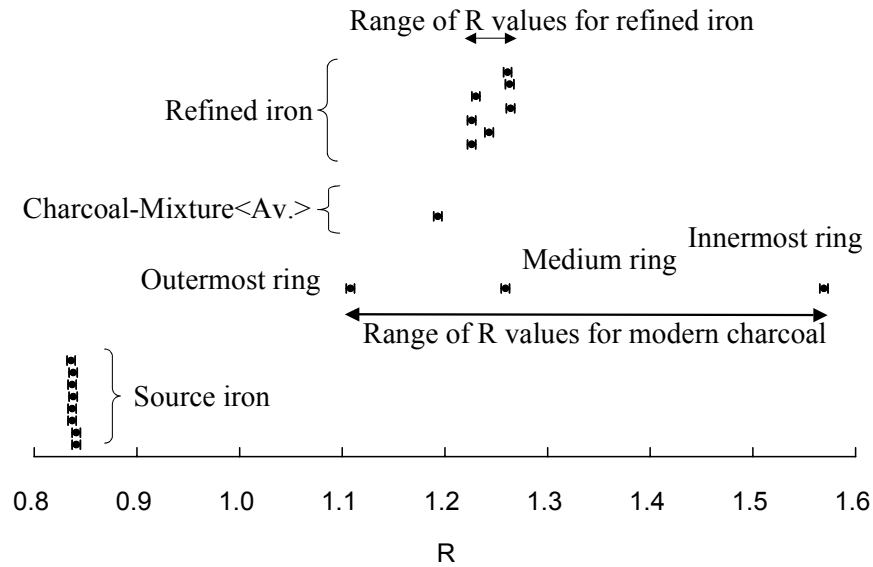

Figure 3 Comparison of R values for source iron and modern charcoal used as fuel for the refining experiment, and for produced iron. R = (^{14}C/^{12}C)spl/(^{14}C/^{12}C)std to indicate the ^{14}C concentration for sample carbon, as defined in the text.

Dating of Iron Slag and Charcoal Remains from Archaeological Sites

^{14}C ages of iron slag and charcoal remains from the Gennaitouge site were dated from 1385 ± 31 BP to 1441 ± 29 BP and from 1365 ± 28 BP to 1609 ± 30 BP, respectively (Table 6). The calibrated ^{14}C ages of these samples ranged from the second half of the 6th to the 7th century AD, except for 1 charcoal sample (nr 11), and were consistent with the occupation period (around 7th century) of the site as estimated by archaeological evidence. The charcoal (nr 11) may have been derived from the inner part of a large tree, thus showing an old wood effect. Some charcoal samples were collected from the inside of iron slag blocks to certify that the charcoal fragments were the remains of charcoal blocks that were used as fuel for the iron smelting. Among such charcoal and iron slag pairs, the ^{14}C ages of charcoal samples were older by 26 to 111 yr than those of iron slag samples for 5 pairs (nr 2, 3, 4, 7, and 8 in Table 6). The charcoal ages were younger by 54 and 39 yr for 2 pairs (nr 9 and 10). In general, the ^{14}C ages for charcoal samples appeared older than those for iron slag materials, but the ^{14}C ages for the pairs (nr 4, 7, 8, 9, and 10) were quite consistent with each other. These findings suggest that we can estimate the ages of iron remains directly by dating the carbon extracted from the remains. The archaeological relevance of ^{14}C ages of iron materials from the Gennaitouge site will be discussed in a future publication.

CONCLUSION

We have estimated the ^{14}C contamination levels, i.e., the amounts of modern carbon contamination induced by the RF combustion and dissolution procedures in extracting carbon components from iron materials for AMS ^{14}C dating. The average values of R which implied the ^{14}C contamination level were 0.0043 ± 0.0002 ($43,870 \pm 870$ BP in ^{14}C age; Table 3) and 0.0039 ± 0.0008

Table 5 Change in ^{14}C concentration of carbon components from original iron to newly-produced iron by the iron-refining experiment. Yield of carbon and carbon-isotope ratios are shown for the carbon extractions using the RF combustion method from original iron (sample nr 15–22) and from produced iron (nr 32–38), as well as those using the routine charcoal preparation method from modern charcoal used as fuel (nr 23–31).

Sample nr	Sample name[a]	Sample amount [mg]	Carbon yield [mgC]	$\delta^{13}C$ [‰]	R $[(^{14}C/^{12}C)sa/(^{14}C/^{12}C)st]$	Lab code [NUTA2-]
15	Iron[1]-2D	729.51	1.18	−33 ± 1	0.842 ± 0.003	3393
16	Iron[1]-3D	384.92	1.28	−29 ± 1	0.841 ± 0.003	3394
17	Iron[1]-4D-1	500.72	10.10	−27.7 ± 0.1	0.837 ± 0.003	3395
18	Iron[1]-4D-2	692.73	1.54	−20.8 ± 0.1	0.837 ± 0.003	3409
19	Iron[2]-1D	257.31	0.78	−25 ± 1	0.838 ± 0.003	3396
20	Iron[2]-2D	581.62	1.27	−27 ± 1	0.837 ± 0.003	3397
21	Iron[2]-3D	555.72	1.18	−31 ± 1	0.838 ± 0.003	3398
22	Iron[2]-4D	908.30	6.47	−26.1 ± 0.1	0.836 ± 0.003	3401
			\<Av.\>[b]	**−27.5 ± 3.7**	**0.838 ± 0.002**	
23	Charcoal-Mix-1	6.46	4.79	−26.3 ± 0.1	1.187 ± 0.005	3088
24	Charcoal-Mix-2	6.54	4.55	−25.5 ± 0.1	1.191 ± 0.005	3089
25	Charcoal-Mix-3	6.61	4.58	−26.1 ± 0.1	1.185 ± 0.005	3090
26	Charcoal-Mix-4	6.48	5.32	−26.0 ± 0.1	1.187 ± 0.005	3104
27	Charcoal-Mix-5	6.58	6.00	−26.5 ± 0.1	1.194 ± 0.004	3462
28	Charcoal-Mix-6	6.58	6.03	−26.5 ± 0.1	1.212 ± 0.004	3463
			\<Av.\>[b]	**−26.3 ± 0.2**	**1.193 ± 0.010**	
29	Charcoal-innermost ring	7.35	6.98	−27 ± 1	1.569 ± 0.005	3658
30	Charcoal-medium ring	7.46	6.89	−25 ± 1	1.259 ± 0.004	3659
31	Charcoal-outermost ring	7.21	6.73	−24 ± 1	1.108 ± 0.004	3660
32	Refined iron[1]-1D	1162.77	17.32	−23.0 ± 0.1	1.226 ± 0.005	3094
33	Refined iron[1]-2D	1099.81	2.40	−20.9 ± 0.1	1.243 ± 0.005	3098
34	Refined iron[1]-3D	697.31	7.54	−26.5 ± 0.1	1.226 ± 0.005	3097
35	Refined iron[2]-1D	1115.18	7.82	−25.8 ± 0.1	1.264 ± 0.005	3095
36	Refined iron[2]-2D	1099.81	13.42	−27.8 ± 0.1	1.230 ± 0.005	3096
37	Refined iron[2]-3D	1366.64	21.11	−29.6 ± 0.1	1.263 ± 0.004	3410
38	Refined iron[2]-4D	1059.06	23.11	−31.4 ± 0.1	1.261 ± 0.004	3411
			\<Av.\>[b]	**−26.4 ± 3.6**	**1.245 ± 0.018**	

[a]The iron refining experiment was done 2 times (indicated superscript 1 and 2). "Charcoal-Mix" was a portion of shuffled and comminute mixture from 1 modern charred wood with about 20–25 annual rings. Charcoal-innermost ring, -medium ring, and -outermost ring indicated charcoal samples collected from innermost, medium, and outermost annual rings of 1 modern charred wood.

[b]Errors cited are 1 σ.

(44,640 ± 1580 BP; Table 4) for graphite targets prepared by the RF combustion and dissolution procedures, respectively. The contamination corresponded to only about a 3- to 4-yr shift towards a younger age in dating a sample of around 2000 BP. In dating archaeological iron artifacts, the effect of contamination was within the error range.

We described here the tests conducted using an iron standard with high carbon content (3.35%). However, we believe that we can also prepare wrought-iron samples in our RF combustion system. We can melt up to 1 g of an iron sample mixed with the same weight of an iron chip accelerator, and can date the sample if 1 mg of carbon will be recovered from it. In fact, we have collected around 1 mg of carbon for several iron slag samples and obtained consistent ^{14}C concentrations and ^{14}C ages as shown in Table 5 (nr 15, 16, 18, 19, 20, and 21) and Table 6. Of course, we consider that more systematic studies are necessary for iron samples with low carbon content (wrought-iron samples).

Table 6 AMS ^{14}C ages and calibrated calendar yr for iron slag and charcoal remains collected from the Gennaitouge archaeological site, Otsu city, Shiga prefecture, Japan.

Sample nr	Sample code nr[a]	Sample amount [mg]	Carbon yield [mg C]	δ^{13}C [‰]	[14]C age[b] [BP]	Calibrated age range[b] [cal AD]	Lab code [NUTA2-]
1-1	Charcoal included[1]-1	6.75	4.15	–27.4 ± 0.1	1498 ± 29	540(563,590,596)604,612()616	3007
2-1	Iron[1]-2	729.51	1.18	–33 ± 1	1385 ± 31	643(657)664	3393
2-2	Charcoal included[1]-2	6.57	4.23	–25.6 ± 0.1	1487 ± 29	542(599)619	3009
3-1	Iron[1]-3	384.92	1.28	–29 ± 1	1387 ± 32	642(657)663	3394
3-2	Charcoal included[1]-3	6.81	5.93	–26.4 ± 0.1	1498 ± 29	540(563,590,596)604,612()616	3450
4-1	Iron[1]-4-1	500.72	10.10	–27.7 ± 0.1	1430 ± 29	604(640)654	3395
4-2	Iron[1]-4-2	692.73	1.54	–20.8 ± 0.1	1428 ± 30	604(641)655	3409
4-3	Charcoal included[1]-4	6.35	4.58	–26.7 ± 0.1	1465 ± 33	561()594,595 (603) 641	3091
5-1	Charcoal-free[1]-5	6.43	4.69	–27.5 ± 0.1	1503 ± 29	539(561,595)602	3013
6-1	Charcoal-free[1]-6	7.31	4.52	–27.0 ± 0.1	1482 ± 29	543()553,556(600)621,634()636	3451
7-1	Iron[2]-1	257.31	0.78	–25 ± 1	1423 ± 30	613(642)656	3396
7-2	Charcoal included[2]-1	6.40	4.22	–26.7 ± 0.1	1490 ± 29	541(598)618	3008
8-1	Iron[2]-2	581.62	1.27	–27 ± 1	1430 ± 29	604(640)654	3397
8-2	Charcoal included[2]-2	6.44	4.78	–25.6 ± 0.1	1456 ± 30	598(617)642	3012
9-1	Iron[2]-3	555.72	1.18	–31 ± 1	1419 ± 30	617(643)657	3398
9-2	Charcoal included[2]-3	6.55	6.50	–26.5 ± 0.1	1365 ± 28	654(661)673	3454
10-1	Iron[2]-4	908.30	6.47	–26.1 ± 0.1	1441 ± 29	601(623,628,638)647	3401
10-2	Charcoal included[2]-4	8.20	8.20	–26.1 ± 0.1	1402 ± 29	625()626,639(651)660	3455
11-1	Charcoal[2]-free-5	5.34	2.79	–27.9 ± 0.1	1609 ± 30	416(428)440,451()46 485()486,504()506,519()528	3014
12-1	Charcoal-fre[2]e-6	10.76	6.40	–27.6 ± 0.1	1485 ± 28	543(599)620	3456

[a]All samples were excavated from the same horizon, but from 2 different locations, as indicated by superscript 1 and 2. Charcoal samples were included in iron slags, except for charcoal-free samples nr 5-1, 6-1, 11-1, and 12-1.
[b]Errors quoted are 1 standard deviation.

We also conducted an iron refining experiment and confirmed that carbon in the iron products had been replaced with fuel charcoal that had been used for iron smelting or refining. Finally, we applied these methods to the measurement of ^{14}C ages of iron slag and charcoal remains from the Gennaitouge iron production site in Shiga Prefecture, Japan. The calibrated ^{14}C ages of these samples ranged from the second half of the 6th to the 7th century AD and were consistent with their archaeological ages. We conclude that the carbon extraction system from archaeological iron materials developed at Nagoya University is reliably applicable to estimate production ages of archaeological iron artifacts.

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