AMS RADIOCARBON DATING OF ANCIENT ORIENTAL IRON ARTIFACTS AT NAGOYA UNIVERSITY

TOSHIO NAKAMURA,[1] MASAHIRO HIRASAWA,[2] and KENZO IGAKI[3]

ABSTRACT. We present here the current status of AMS dating of iron artifacts at Nagoya University. We initially developed a "wet" method of carbon collection from iron samples, consisting of a resistance furnace and a "wet" trapping of the evolved CO_2 with a saturated $Ca(OH)_2$ solution, in which overall collection efficiency of carbon ranged from 50 to 60%. To improve the carbon-collection efficiency, we more recently constructed a "dry" system, consisting of an induction furnace followed by "dry" separation of the produced CO_2 from combustion gases and conversion of the CO_2 into a graphite target. We describe here mainly the performance of the "dry" separation system, tested using standard steel samples. We also report previously determined ^{14}C dates on three ancient Oriental artifacts using the earlier "wet" procedure.

INTRODUCTION

Recent iron production in blast furnaces utilizes coke from coal and oil, which are ^{14}C-free. In ancient iron production, charcoal was used as a carbon source. Thus, a reliable date may be obtained from the carbon contained in an iron artifact if it is almost contemporaneous with the iron production. The ^{14}C age of carbon in metallic iron artifacts, which essentially implies the date of cutting the source trees for the charcoal (more precisely, the date of formation of annual rings of the trees), can be almost equal to the production date of the metallic iron, considering typical measurement uncertainties for ^{14}C ages of *ca.* ±80 yr in a routine measurement using a Tandetron accelerator mass spectrometer at Nagoya University (Nakamura *et al.* 1985).

Applications of ^{14}C dating by conventional beta-ray counting to iron samples was first initiated by van der Merwe and Stuiver (1968) at the Yale Radiocarbon Laboratory. They used 0.5- and 1.5-liter CO_2 gas proportional counters requiring several hundred milligrams of carbon from hundreds of grams of iron. Despite using small proportional counters (Harbottle, Sayre and Stoenner 1979; Sayre *et al.* 1979), large iron sample sizes of the order of tens of grams were still needed and poor precision was obtained.

Cresswell (1991, 1992) first applied accelerator mass spectrometry (AMS) to ^{14}C dating of iron artifacts at the IsoTrace Laboratory, Toronto, Canada. He constructed a system based on the design of van der Merwe and Stuiver (1968) in which carbon extraction, purification and graphite target preparation was performed in a continuous operation. He obtained reliable ^{14}C dates from ancient iron artifacts on samples of only a few hundred milligrams. In Japan, Yoshida (1992) studied AMS ^{14}C dating of iron artifacts, using an AMS system at the University of Tokyo. However, he used only solid residues from the acid treatment of iron samples and could analyze only high carbon cast-iron samples.

As described by Igaki *et al.* (1994), we developed a carbon extraction system for metallic iron for AMS ^{14}C dating. We initially constructed a "wet" method of carbon collection from iron samples, which uses a saturated $Ca(OH)_2$ solution to trap CO_2 produced by oxidizing iron samples with an electric resistance furnace at 1200°C in a mullite tube in the presence of purified oxygen gas. Carbon from iron trapped as $CaCO_3$ was then changed to CO_2 by thermal decomposition at 850°C in a vacuum line, for routine graphite target fabrication (Kitagawa *et al.* 1993), to perform ^{14}C AMS analyses at Nagoya University. The collection efficiency of carbon was rather low in the "wet" method, ranging from 50 to 60%. To achieve higher collection efficiency, we recently developed another

[1]Dating and Materials Research Center, Nagoya University, Chikusa, Nagoya 464-01 Japan
[2]School of Engineering, Nagoya University, Chikusa, Nagoya 464-01 Japan
[3]Faculty of Engineering, Tohoku University, Aoba, Sendai 980 Japan

simple "dry" method by extracting carbon from iron samples and directly separating CO_2 from the combustion gas. Here we discuss the newly developed "dry" method, and some ^{14}C dates for oriental iron artifacts determined using the earlier "wet" procedure.

SAMPLE COMBUSTION AND CARBON EXTRACTION: "DRY METHOD"

Combustion of Iron Samples

Iron samples were oxidized using an induction furnace in the presence of purified O_2. CO_2 converted from carbon in the iron samples was collected in a gas bag along with O_2. The CO_2 was then separated from O_2 and other impurity gases in a vacuum line.

Figure 1 shows the combustion system for iron samples. An induction furnace, LECO HF-10, LECO Corporation, St. Joseph, Michigan, USA, can oxidize up to 2 g of iron at once. We normally require 1 mg of carbon in the form of CO_2 to produce a graphite target for the Tandetron spectrometer, in which only one cycle of carbon extraction is needed for iron samples with >0.05% carbon content. This restriction in sample size does not affect ancient iron artifact samples, which usually have higher carbon contents.
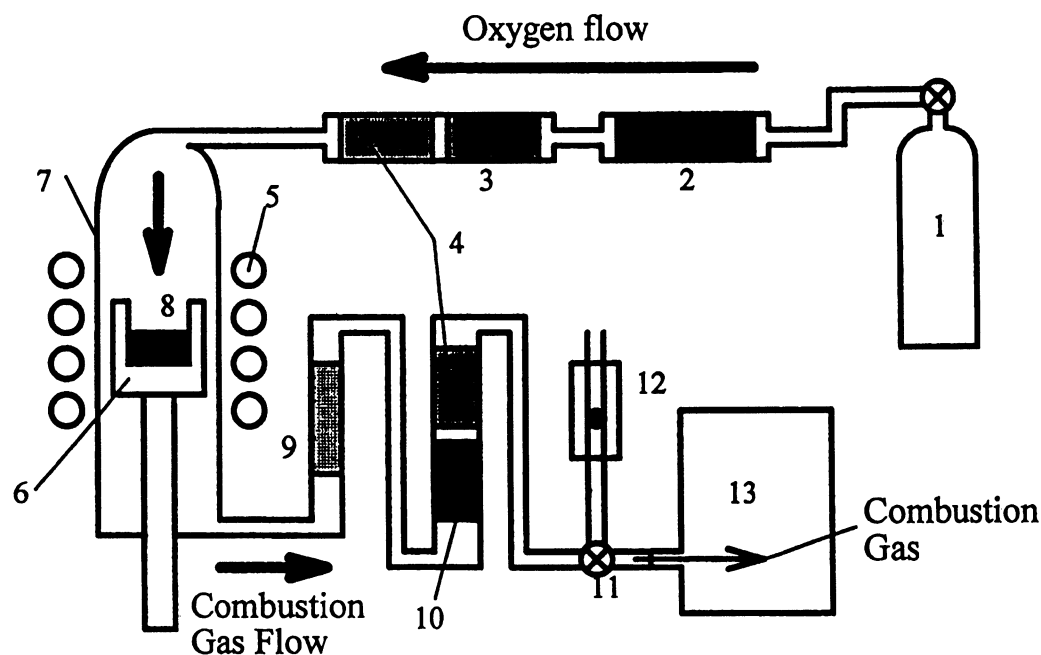

Fig. 1. Schematic diagram of the iron combustion system: 1. oxygen gas cylinder; 2. heated copper oxide; 3. Ascarite to trap CO_2; 4. Anhydrone to trap H_2O; 5. induction coil; 6. crucible; 7. quartz reaction tube; 8. molten oxide bath; 9. quartz wool to trap dust; 10. manganese oxide to trap SO_2 and SO_3; 11. three-way valve; 12. flow meter; 13. gas bag.

Normal-grade and grade-A high-purity oxygen gas were tested for the combustion of iron samples. Possible carbon contamination of the oxygen gas was eliminated by passing the oxygen through a CuO wire mesh at 500°C, as well as a set of CO_2 and water vapor absorbers (Ascarite of *ca.* 8–20 mesh and Anhydrone of granular $Mg(ClO_4)_2$). Iron- and tungsten-oxide dust was trapped in a quartz wool filter, located just after the furnace. Sulfur oxide gases (SO_2, SO_3) and water vapor produced

by the combustion of iron samples were absorbed by granular MnO_2 and Anhydrone, respectively. We used a 10-liter Tedlar bag, equipped with two inlets with rubber O-ring seal stopcocks, to collect combustion gas samples.

We used pure graphite and four standard iron samples of different carbon content (4.67%, 0.13%, 0.05% and 0.0056%) to test the combustion system. Each iron sample was put in a ceramic crucible (#528-018, LECO) preheated at 1100°C for 10 h. The iron sample was placed in the crucible and heated at 600°C for 10 min in an electric oven to eliminate possible carbon contamination. Then we took the crucible out of the oven, added an appropriate amount of combustion accelerant and placed it in the microwave furnace. The gas collection bag was connected to the combustion line via a three-way valve, as shown in Figure 1.

After the iron sample was set in the furnace, residual air in the combustion line was removed by flushing with *ca.* 30 liters of O_2 gas at STP, monitoring the flow rate with a gas flow meter. The gas bag was then flushed by filling it with O_2 and pumping O_2 out three times to eliminate atmospheric CO_2 contamination. When the flushed gas bag was empty, the O_2 flow rate was adjusted to 2 liters per minute and the induction furnace was ignited. The start of oxidation of the iron sample was marked by a decrease in O_2 gas flow rate.

Ten seconds after ignition of the furnace, the combustion gas was directed to the gas bag, and collected for 2–3 min. Following this, the gas bag stopcock was closed and the tube connected to the stopcock was closed with a pinch-cock.

CO_2 Extraction from Combustion Gas and Graphite Preparation

We tried to extract CO_2 from the combustion gas on the same day as the combustion, to keep the gas sample free from any atmospheric CO_2 contamination. However, for some samples, extraction was performed 1–3 days after combustion. The gas bag was connected to the vacuum line system with a rubber tube, and the vacuum system and the connection tube were evacuated (Fig. 2). Once the system was evacuated, water traps 1 and 2 were cooled to −100°C with an ethanol/liquid nitrogen (liq. N_2) mixture, and CO_2 traps 3 and 4 with liq. N_2. (Traps 2, 3 and 4 are U-shaped, 20 mm in diameter and 40 cm long, with many small glass fingers to increase the gas-trapping surface.) The combustion gas was then fed through the traps with a flow rate of 40 ml per minute, regulated by a mass-flow controller, by pumping out the non-CO_2 gases, mainly O_2, with an oil rotary pump. A Pirani gauge showed *ca.* 1 Torr at the outlet of trap 4. In a few hours, after the combustion gas was completely processed, CO_2 collected in traps 3 and 4 was again separated from water vapor and SO_2 using a normal-pentane trap with a melting point of −131°C. The amount of CO_2 collected was determined from the pressure of CO_2 gas expanded in a calibrated volume, using a pressure transducer. The CO_2 sample was then sealed in a Pyrex tube of 6 mm diameter for further analyses.

The CO_2 from *ca.* 1 mg of carbon separated from the iron samples was made into a graphite target by reducing with hydrogen on iron powder at 650°C, as described by Kitagawa *et al.* (1993). The ^{14}C content of the graphite was then measured with a Tandetron spectrometer at Nagoya University (Nakamura *et al.* 1985, 1992).

RESULTS AND DISCUSSION

Carbon Collection Efficiency and ^{14}C Background

We tested the carbon collection efficiency and ^{14}C background of the carbon extraction system, using standard steel samples specially designed for carbon content analysis: 4.67%C steel supplied
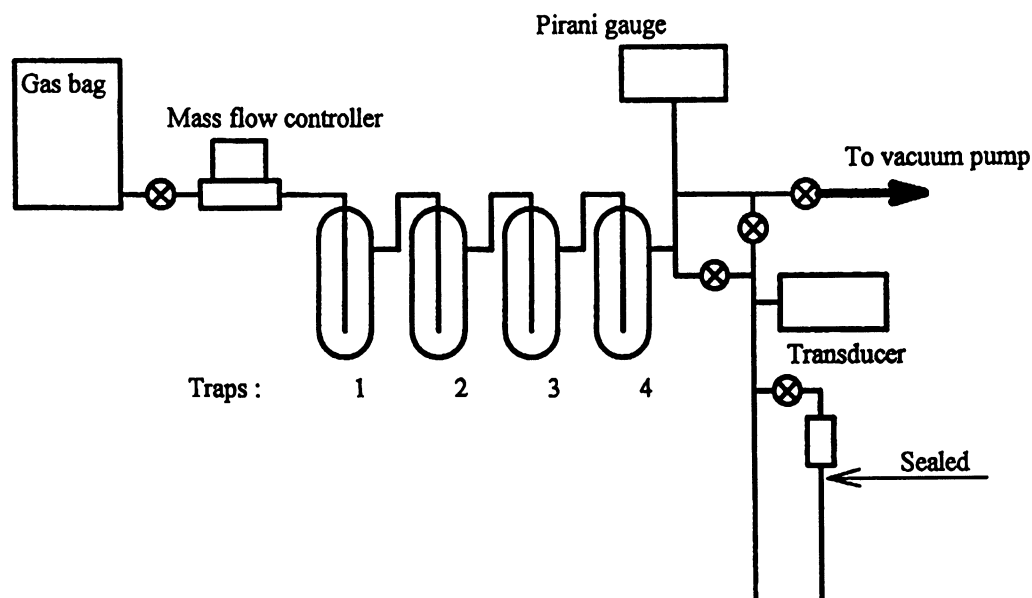
Fig. 2. Schematic diagram of the CO_2 separation system. See text for details. Traps 1, 2. Ethanol/liquid N_2 to trap H_2O at $-100\,°C$; Traps 3, 4. liquid N_2 to trap CO_2.

by LECO Corporation, 0.13%C (JSS-023-3), 0.05%C (JSS-201-10) and 0.0056%C (JSS-200-11) steels of Japanese iron and steel-certified reference materials supplied by the Iron and Steel Institute of Japan, and Sri Lanka ore graphite. Nearly equal amounts of combustion accelerant (Lecocel 2HP (W+Sn), LECO Corporation) were added to steel samples weighing >1 g, while *ca.* 1 g of accelerant was added to samples weighing <1 g.

As shown in Table 1, the carbon collection efficiency for steel samples weighing >1 g is >80%, except for runs 7 and 8. Carbon collection efficiency is 64–70% for 4.67%C steel, systematically lower than that for lower-carbon samples. The efficiency for graphite powder is much lower, 54–65%. We suspect that the combustion of carbon for high-carbon samples may not be complete, perhaps because the temperature was not high enough. Radio-frequency induction may not work well for small amounts of iron. Cresswell (personal communication, 1994) suggested another possibility. High-carbon samples would oxidize rapidly, and a surface skin of wustite/magnetite can form, hindering the diffusion of interior carbon to the surface for oxidation. He therefore suggests using an iron accelerant rather than a tungsten and tin mixture to prolong the melt at high temperature during the combustion. We need more tests to achieve higher collection efficiency for high-carbon samples.

Aliquots of CO_2 separated from the combustion gas from runs 3, 4 (4.67%C) and 11, 12 (0.13%C) were analyzed for $^{13}C/^{12}C$ ratios with a Finnigan Mat 252 mass spectrometer, giving $\delta^{13}C_{PDB}$ values of −25.9, −25.8, −23.4 and −23.3‰, respectively. The $\delta^{13}C_{PDB}$ values for the 4.67%C iron standard are lower by 2.5‰ than those for the 0.13%C standard. This indicates that the sources of carbon in the two standards are different, *i.e.*, they both derived from carbon in coal or oil, but were collected from different coal mines or oil wells.

Since standard steel samples are manufactured both in modern blast furnaces using iron ore and coke produced from coal, and in vacuum-induction furnaces using electrorite iron and oil-coke from oil as

TABLE 1. Extraction Efficiency of Carbon and ^{14}C Background for the Combustion and "Dry" CO_2 Separation System

Lab (NTUA-) / run nos.*	Sample	Fe sample (%C)	Sample amount (g)	Carbon content (mg)	Yield of CO_2 (mg C)	EE† (%)	^{14}C activity (pMC)	Apparent ^{14}C age (yr BP)	$\delta^{13}C_{PDB}$ (‰)	Modern carbon contamination (mg C)
3248/1‡	Graphite	100	0.0011	1.07	0.695	65	2.81 ± 0.34	28,700 ± 960	--	0.02
3254/2	Graphite	100	0.0020	1.97	1.056	54	3.11 ± 0.52	27,900 ± 1340	--	0.03
3255/3‡	Leco Fe	4.67	0.0969	4.52	3.18	70	1.32 ± 0.09	34,770 ± 560	−25.9	0.04
3256/4	Leco Fe	4.67	0.0537	2.51	1.616	64	5.01 ± 0.22	24,070 ± 350	−25.8	0.08
2959/5	JSS Fe	0.13	1.00	1.30	1.12	86	5.20 ± 0.18	23,760 ± 280	--	0.06
2961/6	JSS Fe	0.13	1.00	1.30	1.06	82	3.93 ± 0.26	26,000 ± 530	--	0.04
3206/7	JSS Fe	0.13	0.9683	1.32	0.932	71	6.43 ± 0.19	22,060 ± 240	--	0.05
3207/8‡	JSS Fe	0.13	1.0168	1.32	0.816	62	2.67 ± 0.11	29,120 ± 330	--	0.02
3224/9‡	JSS Fe	0.13	1.0075	1.31	1.151	88	3.45 ± 0.38	27,060 ± 890	--	0.04
3226/10‡	JSS Fe	0.13	0.9648	1.25	1.082	86	3.66 ± 0.12	26,580 ± 270	--	0.04
3214/11‡	JSS Fe	0.13	2.0048	2.61	2.302	88	3.08 ± 0.11	27,960 ± 300	−23.4	0.07
3227/12	JSS Fe	0.13	2.0363	2.65	2.351	89	2.33 ± 0.10	30,230 ± 350	−23.3	0.05
2960/13	JSS Fe	0.05	2.00	1.00	0.797	80	10.49 ± 0.33	18,120 ± 250	--	0.08
3225/14	JSS Fe	0.05	2.0078	1.00	0.972	97	9.33 ± 0.31	19,060 ± 270	--	0.09
/15	JSS Fe	0.0056	2.00	0.112	~0	~0	--	--	--	--
/16	Accelerant	~0	1.00	0	Not detected	--	--	--	--	--

*Run numbers are also indicated in Fig. 3.
†Extraction efficiency
‡CO_2 extraction was performed immediately following combustion of iron samples. For the other runs, the extraction was done 1–3 days after combustion.

raw materials, they should be completely ^{14}C-free. However, carbon extracted in our system contained an appreciable amount of ^{14}C, ranging from 1 to 10% modern carbon (pMC), giving apparent ages from 18 to 35 ka, as shown in Table 1. A steel sample with 4.67%C (run 3) showed the lowest ^{14}C activity. However, run 4 on the same steel showed higher ^{14}C activity. In the latter case, the CO_2 extraction was performed 3 days after the combustion. Thus, CO_2 in the combustion gas may have been contaminated by atmospheric CO_2 through the container bag. For runs 2, 5, 6, 7, 12, 13 and 14, CO_2 was extracted the day after the combustion. Some of them show high ^{14}C activities, perhaps because of similar contamination to run 4. ^{14}C activities for six samples in which CO_2 was extracted immediately following combustion ranged from 1.32 to 3.66 pMC, with an average of 2.8 ± 0.8 pMC.

We estimated the amount of modern carbon required to contaminate each ^{14}C-free sample by multiplying yield of CO_2 and ^{14}C activity. As shown in Table 1, for all samples (except for run 11) for which CO_2 was extracted from the combustion gas on the same day of the combustion, the contamination of modern carbon is <0.05 mg. For the other samples it is consistently above 0.05 mg, almost reaching 0.09 mg, suggesting a strong correlation between ^{14}C background and storage length of the combustion gas. Figure 3 shows the correlation between CO_2 yield and ^{14}C activity. Steel samples of 0.05%C show relatively high ^{14}C content compared to that of other standard materials. This high ^{14}C concentration possibly resulted from inherent ^{14}C contamination of the sample itself, though the ^{14}C contamination during the storage of the combustion gas may be the dominant source.

Cresswell (1992) suggested that normal steel whose carbon content is 0.65–0.96%C showed a ^{14}C background of 2.2–2.7 pMC when medical-grade oxygen was used for steel combustion. The use of
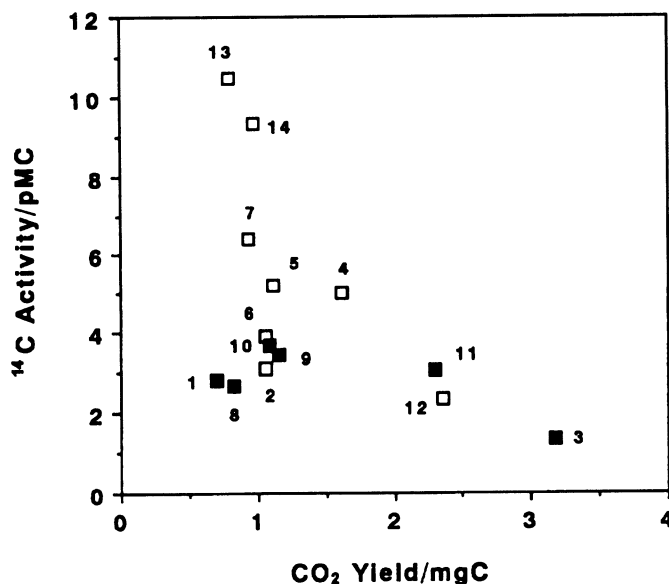
Fig. 3. Correlation between CO_2 yield and ^{14}C activity for standard iron materials. Numbers in the figure indicate run numbers given in Table 1: 1, 2 = graphite; 3, 4 = 4.67%C; 5–12 = 0.13%; 13, 14 = 0.05%C. Closed square indicates runs processed the same day, as described in the text.

high-purity oxygen markedly reduced the ^{14}C background to 0.47–0.82 pMC. We also tested the combustion system with both normal-grade oxygen (99.9%) and grade-A high-purity oxygen (99.99%), but could find no improvement in the ^{14}C background level. Commercial specifications indicate that the CH_4 content of both oxygens is <30 ppm, and concentrations of hydrocarbon, CO_2 and CO are <10 ppm for higher-grade oxygen. It seems reasonable that both oxygens show no difference, because they contain almost equal carbonaceous contaminants that may not be removed completely at the inlet trap of the combustion system. We recently discovered commercially available ultra-pure oxygen (99.9999%), whose CH_4 and CO_2 contents are <0.05 and 0.01 ppm, respectively. We hope the ^{14}C background will be reduced when the ultra-pure oxygen is used for combustion, as in the study by Cresswell (1992).

[14]C Dates of Oriental Iron Artifacts

We previously used the "wet" separation method (Igaki *et al.* 1994) to measure ^{14}C dates on carbon separated from three oriental artifacts: a Japanese sword; a planing adze; and an iron hook. Table 2 summarizes information on these dates. We used the CalibETH 1.5b program (Niklaus 1991; Niklaus *et al.* 1992) and dendro-calibration data of Stuiver and Pearson (1993) to calibrate the ^{14}C dates measured in this study.

The sword is believed to have been made by the "Maru-kitae" method, forging the original iron as a whole. This method was used before the appearance of the more elaborate composite forging method of covering a soft steel core with hard steel. The forging age of the sword was estimated historically to be from the late Kamakura (AD 1192–1333) to early Muromachi (AD 1336–1573) periods. The calibrated ^{14}C date, cal AD 1021–1263, although a bit older, is still consistent with the earlier historical estimate (Igaki *et al.* 1994).

TABLE 2. AMS ^{14}C Dates for Three Oriental Iron Artifacts

No.	Sample description	Sample weight (g)	Carbon content (%C)	Historical age	^{14}C dates (yr BP)	Cal range AD/ probability (%)	Lab no. (NUTA-)
1	Japanese sword	2.27	0.49	Heian-Kamakura	880 ± 150	1021–1263 (100)	2376
2	Planing adze (cast iron)	0.93	3.60	?	1720 ± 160	119–457 (94.8) 483–508 (5.2)	2407
3	Iron hook from Horyuji Temple	4.53	0.18	Late 7th to early 8th century	1330 ± 110	604–814 (97.3) 845–853 (2.7)	2773

The cast-iron adze is thought to have been originally unearthed in China. An X-ray picture of the sample revealed many internal pores, some of which contained fine iron oxide powder. As part of the tip of the adze is broken, we assume that it had been used. The calibrated range, cal AD 119–457, corresponds to the Late Han and Jin dynasties in China. This is also the period when cast-iron production was fully developed in China, and nowhere else in the world (Igaki *et al.* 1994).

The Horyuji Temple at Ikaruga, Nara Prefecture, Japan, is the oldest wooden building in the world. The temple was first constructed in AD 607; it burned down in AD 670, and was rebuilt by the early eighth century. The iron hook was found in the five-roofed pagoda. The calibrated range, cal AD 604–814, is consistent with the rebuilding date of the tower. Discussion of this iron artifact will be presented elsewhere in more detail.

CONCLUSION

We constructed a combustion and CO_2 separation system for AMS ^{14}C dating of iron artifacts. We summarize the performance of the system as follows:

1. CO_2 recovery efficiencies for 0.13%C and 0.05%C steel samples typically ranged from 80 to 90%. Pure graphite and 4.67%C iron samples showed lower efficiencies of 50 to 70%, perhaps because of the small size of the iron samples used for combustion. For small sample sizes, an induction furnace may not produce high enough temperatures to smelt iron. We must also test other possible ways of achieving higher collection efficiencies for high-carbon samples.

2. The ^{14}C background of the preparation system was tested using standard steel samples produced in blast furnaces using coke from coal and oil. The ^{14}C background showed a dependence on the storage history of the separated CO_2. When CO_2 was separated from the combustion gas immediately after combustion, the ^{14}C activity of the sample ranged from 1.32 to 3.66 pMC (avg. 2.8 ± 0.8 pMC). This range was systematically lower than for samples with CO_2 separation occurring on the following day or a few days after combustion.

3. Theoretically, ^{14}C contamination of 2.8 ± 0.8 pMC gives an apparent ^{14}C age 63 yr too young for a 2000-yr-old sample. This difference is almost equal to or slightly lower than the uncertainties of ^{14}C dates measured routinely by the Tandetron spectrometer at Nagoya University (Nakamura *et al.* 1985). We are continuing our attempt to reduce the ^{14}C background to the level of the IsoTrace Laboratory, Toronto, Canada, by using ultra-high-purity oxygen for the combustion of iron samples.

4. Three samples of oriental iron artifacts, weighing 2.27, 0.93 and 4.53 g, were prepared by the "wet" procedure and successfully AMS-dated. The calibrated ^{14}C dates are consistent with their historical age estimates, and provide constraints on their fabrication ages. We need, how-

ever, to test performances of ^{14}C trapping by the "wet" method to rely fully on the ^{14}C dates obtained in this study.

Further ^{14}C analyses of ancient iron artifacts are required, along with metallurgical analyses to help determine the source of the iron. As suggested by Cresswell (1992), chemical impurities in iron artifacts may help identify the origin of their raw materials.

ACKNOWLEDGMENTS

REFERENCES

Cresswell, R. G. 1991 The radiocarbon dating of iron artefacts using accelerator mass spectrometry. *Historical Metallurgy* 25: 78–85.

_____1992 Radiocarbon dating of iron artifacts. *In* Long, A. and Kra, R. S., eds., Proceedings of the 14th International ^{14}C Conference. *Radiocarbon* 34(3): 898–905.

Harbottle, G., Sayre, E. V. and Stoenner, R. W. 1979 Carbon-14 dating of small samples by proportional counters. *Science* 206: 683–685.

Igaki, K., Nakamura, T., Hirasawa, M., Kato, M., and Sano, M. 1994 Radiocarbon dating study of ancient artifacts with accelerator mass spectrometry. *Proceedings of the Japan Academy* 70(B1): 4–9.

Kitagawa, H., Masuzawa, T., Nakamura, T. and Matsumoto, E. 1993 A batch preparation method for graphite targets with low background for AMS ^{14}C measurements. *Radiocarbon* 35(2): 295–300.

Nakamura, T., Nakai, N., Sakase.,T. Kimura, M., Ohishi, S., Taniguchi, M., and Yoshioka, S. 1985 Direct detection of radiocarbon using accelerator techniques and its application to age measurement. *Japanese Journal of Applied Physics* 24: 1716–1723.

Nakamura, T., Nakazawa, T., Nakai, N., Kitagawa, H., Honda, H., Itoh, T., Machida, T. and Matsumoto, E. 1992 Measurement of ^{14}C concentrations of stratospheric CO_2 by accelerator mass spectrometry. *In*

Long, A. and Kra, R. S., eds., Proceedings of the 14th International ^{14}C Conference. *Radiocarbon* 34(3): 745–752.

Niklaus, T. R. 1991 CalibETH 1.5b, Program for calibration of radiocarbon dates. Institute for Intermediate Energy Physics, ETH, Zurich, Switzerland.

Niklaus, T. R., Bonani, G., Simonius, M., Suter, M. and Wolfli, W. 1992 CalibETH: An interactive computer program for the calibration of radiocarbon dates. *In* Long, A. and Kra, R. S., eds., Proceedings of the 14th International ^{14}C Conference. *Radiocarbon* 34(3): 483–492.

Sayre, E. V., Harbottle, G., Stoenner, R. W., Washburn, W., Olin, J. S. and Fitzhugh, W. W. 1982 The carbon-14 dating of an iron bloom associated with the voyages of Sir Martin Frobisher. *American Chemical Society Symposium Series* 176: 441–451.

Stuiver, M. and Pearson, G. W. 1993 High-precision bidecadal calibration of the radiocarbon time scale, AD 1950–500 BC and 2500–6000 BC. *In* Stuiver, M., Long, A. and Kra, R.S., eds., Calibration 1993. *Radiocarbon* 35(1): 1–23.

van der Merwe, N. J. and Stuiver, M. 1968 Dating iron by the carbon-14 method. *Current Anthropology* 9: 48–53.

Yoshida, K. 1992 Measurement of ^{14}C age by accelerator mass spectrometry. *Bulletin of the National Museum of Japanese History* 38: 171–198.