AMS RADIOCARBON DATING OF ANCIENT IRON ARTIFACTS: A NEW CARBON EXTRACTION METHOD IN USE AT LLNL

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ABSTRACT. A new sealed double tube combustion method was developed at Lawrence Livermore National Laboratory (LLNL) to extract carbon from modern steels and ancient iron artifacts. Iron samples were chemically pretreated with 10% nitric acid, vacuum sealed in 6 mm quartz tubes with CuO, vacuum sealed again inside 9 mm quartz tubes, and combusted at 1000 °C for a minimum of 10 hr. The resulting CO_2 was graphitized routinely using hydrogen reduction (Vogel et al. 1989). After the initial phase of development, carbon yields of 100% were consistently obtained. The activities of two modern high carbon steels (treated as process blanks, manufactured using only coal as the carbon source) were determined to be 0.0077 ± 0.0009 (n = 12, $\pm 1 \sigma$) for a 1.3% C steel and 0.0090 ± 0.0038 (n = 12, $\pm 1 \sigma$) for a 1.9% C steel, indicating that very little contamination is introduced during the sample preparation process. Since the Iron Age began less than 5000 years ago, these background uncertainties should introduce errors of no more than ±30 years to the radiocarbon ages of actual artifacts. Two ancient iron artifacts of known date were analyzed and demonstrate that the new methodology can be used to obtain the correct date of manufacture for iron objects, provided that they are made exclusively using charcoal that was contemporaneous with the manufacture of the artifact. Since only 1 mg of carbon is required for accelerator mass spectrometry (AMS), very small iron samples can now be analyzed (50 mg of a 2.0% C iron or 1 g of a 0.1% C iron). We anticipate that this methodology will be particularly useful to archeologists who currently have to rely on context to date iron artifacts.

INTRODUCTION

Carbon can be extracted from the various alloys of iron (wrought iron, steel, and cast iron) and radiocarbon dated. Van der Merwe and Stuiver (1968) were the first to demonstrate the feasibility of this technique. Because beta counting was the only ^{14}C dating method available at that time, up to 1 kg of wrought iron was required (500 mg of C). This meant that an artifact needed to be both large and sacrificed to be radiocarbon dated. The applicability of the iron dating technique was severely limited by this large sample size requirement. Van der Merwe (1969) was able to date a total of 11 iron artifacts. In the years that followed, developments in proportional counters reduced the required sample size to tens of grams of wrought iron, but only one new iron artifact was dated (Sayre et al. 1982).

With the advent of accelerator mass spectrometry (AMS), the sample size requirement was reduced to 1mg of carbon. Cresswell (1987, 1991, 1992) built a carbon extraction system at Isotrace (Toronto, Canada) that was a smaller version of van der Merwe's apparatus at Yale, consisting of flowing oxygen, a furnace, and a series of steps to purify and trap the CO_2. Using this methodology, Cresswell (1992, 1997) and collaborators (Kusimba et al. 1994) dated 12 iron artifacts by AMS, including 3.4 g of a medium carbon (0.4%) wrought iron bloom and 274 mg of a high carbon (1.79%) wootz steel fragment, demonstrating the feasibility of the technique on very small samples.

Others have since dated iron and experimented with different procedures for carbon extraction. Yoshida (1992) acid treated iron samples and dated the solid residues, but found that he could analyze only high carbon cast iron samples. Igaki et al. (1994) and Nakamura et al. (1995) modified van der Merwe's gas trapping method and came up with two alternatives, a "wet" chemical version and a "dry" cryogenic version. Nakamura et al. (1995) used AMS and these new gas trapping methodologies to successfully date three additional iron artifacts, bring the total to 27.

Clearly, it is possible to radiocarbon date iron. Why is more iron not being dated? We believe that it is a combination of at least the following two factors: 1) few archeologists are aware of the technique so the demand is low, and 2) the carbon extraction methodology for iron is so equipment intensive that it has not become a routine procedure at any radiocarbon dating laboratory. The labs that have dated iron have had students dedicated to developing and maintaining the extraction apparatus. After the students depart, the capability has not been maintained.

In this paper, we describe a new carbon extraction procedure for iron that is within easy reach for the typical graphite preparation laboratory. The new method relies on materials that are readily available in the lab: quartz tubes, CuO, vacuum lines, and a standard electric furnace capable of reaching 1000 °C. No exotic gas trapping equipment is required. This simplification of the carbon extraction methodology should allow iron to become a material that can be routinely dated at AMS ^{14}C facilities.

SAMPLE DESCRIPTIONS

Sample acquisition began by obtaining specialty steels that were made exclusively using coal in the smelting process. Since most coal today is derived from either Carboniferous (360–285 Ma) or Cretaceous (145–65 Ma) deposits, samples of this type should yield activities which reflect typical laboratory blanks (0.0025 ± 0.0008 or approximately 50,000 BP). Any deviation from this minimum radiocarbon activity reflects contamination during preprocessing, making it easy to detect. Because the carbon content in specialty steels is precisely known, such samples can also be used to test combustion yields.

Initial methodological development was undertaken using only modern steels made exclusively with coal. These modern steel samples were treated as process blanks. Actual artifacts were not analyzed until contamination levels were determined to be very low, the sample preparation process was well characterized, and the carbon yields were consistently near 100%.

Modern High-Carbon Steels

Two high-carbon specialty steels produced in modern times were obtained from a collection of steels belonging to one of the authors (JW). These steels were manufactured in small experimental batches by United States Steel (Pittsburgh, Pennsylvania) for an evaluation of mechanical properties. The steels differed primarily in carbon content, with one being 1.3% carbon and the other being 1.9% carbon (by weight). Steel 76-USS-8003-1.3C contained (by weight) 1.26% C, 0.78% Mn, 0.015% P, 0.024% S, and 0.25% Si while 76-USS-8005-1.9C contained 1.90% C, 0.79% Mn, 0.017% P, 0.027% S, and 0.25% Si.

Ancient Iron Artifacts of Known Date

Himeji Castle Nail

A small nail from the Himeji Castle was provided by Yoshindo Yoshihara, a tenth generation sword maker from Japan. The steel was given to swordsmiths like Yoshindo about 35 years ago when the Himeji Castle was undergoing restoration. Most of the steel was old and thin, but could be reworked into traditional guards (tsuba) for Japanese swords, or traditional Japanese paperweights or other traditional small steel items. The nail was thought to be unaltered and original to the castle. Its carbon content was estimated to be low, 0.1–0.2% or less.

The Himeji Castle is unanimously acclaimed as the most magnificent of the handful of Japanese castles still standing in original (non-concrete) form. It is known as Shirasagi, the White Egret, a title

that derives from its stately white form. While there have been fortifications in Himeji since AD 1333, today's castle was built in AD 1580 by Toyotomi Hideyoshi and enlarged some years later (AD 1600–1609) by Ikeda Terumasa for the Tokugawa Shogunate. The five-story castle is surrounded by moats and defensive walls and has been home to 48 successive lords.

According to Leon Kapp (University of California, San Francisco, personal communication 2000), the castle was built between AD 1600 and 1609 at a location where an earlier castle stood. Over a period of nine years, the steel for the castle was manufactured nearby, or on site, as it was needed for construction. The steel was made in the traditional manner, likely in small batches using fresh, locally made, charcoal. Most of the steel would have been made new, and not recycled. The possibility exists, however, that some older pieces of steel were recycled from either the earlier structure built in the mid- to late-1500s, or even possibly from mass produced swords made in the mid- to late-1500s and confiscated from the local people by the Toyotomi, who ruled the area up to AD 1600. Even if some of the steel was recycled, the radiocarbon date obtained for the nail should be close to AD 1600.

Damascus Knife

Damascus steel swords and knives have been in existence since the time of Alexander the Great and reviews exist of their history and manufacture (Sherby and Wadsworth 1985; Figiel 1991). They are characterized by very high carbon content (typically 1.3–1.9% C), unusual surface patterns, and extreme sharpness and toughness. Although named after Damascus, they were usually made in the form of small castings (called "wootz") made in India and exported to Damascus where Europeans first encountered them and traded for them. The sample in this study was provided from a private collection and believed to be of Indian origin and to date from about AD 1650. Metallographic studies were carried out and the microstructure was found to be typical of Damascus steels.

METHOD

Both the modern steels and the ancient iron artifacts were evaluated at Lawrence Livermore National Laboratory (LLNL). All visible surface rust was removed mechanically using a combination of abrasive sanding techniques until a shiny piece of solid metal was obtained. The metal was then reduced to small pieces of various sizes, using either a drill or a diamond saw. The iron was chemically etched in 10% nitric acid (in the hood), washed three times in de-ionized water, and dried in alcohol.

Immediately after drying, the iron samples were weighed to yield 1 mg of C (e.g. 50 mg of a 2.0% C steel or 200 mg of a 0.5% C steel). Samples were then placed into 6 mm quartz tubes (pretreated at 900 °C for three hours to remove any carbonaceous contaminants on the quartz) with sufficient CuO (three times the weight of the Fe) to oxidize all the iron to Fe_2O_3 and all the carbon to CO_2. Each 6-mm tube was then sealed under vacuum.

After the sealed 6mm tubes were cleaned with acetone, they were placed inside larger 9 mm quartz tubes (also pretreated at 900 °C for 3 hr). The double tube arrangements were baked for one hour at 400 °C to remove any contaminates still adhering to the quartz tubes. While still warm from the oven, a small amount of additional CuO was added between the two quartz tubes, and the 6 mm tube was sealed under vacuum inside the 9 mm tube. The entire sealed double tube arrangement was then combusted for a minimum of 10 hr at 1000 °C.

The outer quartz tube prevented sample loss in the cases where the iron ate through the inner quartz tube during combustion. Ultimately, a minimum of 10 hr of combustion time was used to ensure that all the carbon had enough time to diffuse out of the iron matrix. The additional CuO between the

tubes was added to insure that there was enough oxygen present to oxidize any carbon in this volume, regardless of whether the inner tube broke, thus ensuring consistent blanks.

The resulting CO_2 was graphitized routinely using hydrogen reduction (Vogel et al. 1989). [14]C was measured by AMS at LLNL (Southon et al. 1990). Data are expressed as activity (fraction modern) and radiocarbon years before present (Stuiver and Polach 1977). Calibrated ages are given (OxCal v3.0, using INTCAL98) whenever radiocarbon dates for actual iron artifacts are reported.

RESULTS

During the first iron trials, only the two modern high-carbon steels (76-USS-8003-1.3C, 76-USS-8005-1.9C) were investigated. Initial yields were highly variable, ranging from 5% to 95% (Table 1, Part A). The ^{14}C activities were very promising, however, ranging from 0.0301 ± 0.0009 to 0.0060 ± 0.0001. Particle size class (small drill shavings <1 mm, medium drill shavings >1 mm, and large pieces >3 mm cut with a diamond saw) showed no obvious trend with ^{14}C activity or apparent ^{14}C age. These initial results indicated that very little modern C was being introduced during the sample preparation procedure, but that full yields were not achieved (Table 1, Part A).

Table 1, Part A Initial results from modern steel blanks

Modern steel	Size class[a]	Fraction modern	Age (BP)	Yield (%)
1.3% carbon	Small	0.0085 ± 0.0001	38,290 ± 140	48
1.9% carbon	Small	0.0074 ± 0.0003	39,420 ± 300	58
1.3% carbon	Medium	0.0077 ± 0.0002	39,120 ± 180	46
1.9% carbon	Medium	0.0301 ± 0.0009	28,130 ± 250	5
1.3% carbon	Large	0.0113 ± 0.0003	36,010 ± 190	8
1.9% carbon	Large	0.0060 ± 0.0001	41,150 ± 200	95

[a]The size classes are defined as follows: small = drill shavings <1 mm, medium = drill shavings >1 mm, large = pieces > 3 mm cut with a diamond saw.

In an attempt to increase yields, the minimum combustion time was increased from 8 to 10 hr to allow more time for the carbon to diffuse out of the iron matrix. In addition, the amount of CuO added to the 6 mm tube was also increased to three times the weight of the iron sample, ensuring that there would be enough oxygen present to turn all the Fe into Fe_2O_3 and all the carbon into CO_2.

After these changes in the initial methodology, carbon yields of 100% were consistently obtained from the modern high carbon steels (Table 1, Part B). The apparent ^{14}C ages were determined to be nearly 40,000 BP (Table 1, Part B) for these steels which had been manufactured using exclusively coal. Since any non-coal carbon extracted from iron will be relatively young, these process blank corrections are extremely small. The associated uncertainties, propagated through ^{14}C age calculations, will add a contribution of no more than ±30 yr to the uncertainty in the age of a typical artifact 5000 years old. Only 53 mg of the 1.9% C steel and 78 mg of the 1.3% C steel were required to produce the 1 mg of carbon necessary for each of the background analyses.

Table 1, Part B Results from modern steel blanks

Modern steel	Fraction modern	Age (BP)[a]	n	Yield (%)
1.3% carbon	0.0077 ± 0.0009*	39,140 ± 970*	12	105 ± 9*
1.9% carbon	0.0090 ± 0.0038*	38,330 ± 2,870*	12	102 ± 13*

[a]All errors are ± 1 σ

To determine the amount of contamination that might be introduced by the presence of corrosion products, three samples that had been cleaned in nitric acid were allowed to rust in the open atmosphere of the laboratory for approximately three months prior to analysis. The results show that a significant amount of foreign carbon can be present in corrosion products, changing the activity of the process blanks to 0.1195 ± 0.0005–0.0230 ± 0.0003 (Table 1, Part C). The amount of foreign carbon present seems to depend at least in part on the surface area to volume ratio of the sample, with the largest size class having the least foreign carbon contamination. We assume conservatively that blanks can vary by $\pm 30\%$, and propagate this uncertainty through to the final age uncertainty for a 5000-year-old sample. We find that process blanks for rusty samples in the large size class will result in ^{14}C age uncertainties of no more than ± 70 yr, while blanks for rusty samples in the medium size class will result in ^{14}C age uncertainties of up to ± 350 yr for the same 5000-year-old artifact. As a result, only the large size class of metal was used for all of the subsequent analyses, including the process blanks in Table 1 Part B and the artifacts of known date discussed below.

Table 1, Part C Results from rusty modern steel blanks

Modern steel	Size, class	Fraction modern	Age (BP)	Yield (%)
1.9% carbon	Small, rusty	0.0800 ± 0.0007	$20,290 \pm 70$	100
1.3% carbon	Medium, rusty	0.1195 ± 0.0005	$17,060 \pm 40$	100
1.9% carbon	Large, rusty	0.0230 ± 0.0003	$30,290 \pm 100$	105

Two iron artifacts of known date were analyzed to demonstrate that the new methodology is robust and can be used to obtain accurate ages for objects of known origin and manufacturing process. To minimize any pretreatment contamination, all rust was removed prior to analysis and samples were cut into the large size class (>3 mm) using a diamond saw. Since the Himeji Castle nail was 0.28% carbon, 357 mg of iron was need per analysis. For the Damascus knife which contained 2.13% carbon, only 47 mg of iron was needed per analysis. Since plenty of iron was available, replicate analyses were made on both artifacts.

For both the Himeji Castle nail and the Damascus knife, dates were obtained using the new methodology that were consistent with the dates of known manufacture. The Himeji Castle nail was thought to be manufactured in approximately AD 1600, and our results show with 39.7% confidence that it was made between AD 1550 and AD 1640 (Table 2). In the case of the Damascus knife which was thought to be manufactured in AD 1650, our results show with 71.0% confidence that is was made between AD 1640 and AD 1670 (Table 2). Clearly, the new methodology was able to arrive at accurate dates for both of these objects.

Table 2 Results from iron artifacts of known date analyzed in this study

Artifact	Date of manufacture	Fraction modern	Age (BP)	n	Carbon (%)	Calibrated age[a]
Himeji Castle Nail	AD 1600	0.9645 ± 0.013	373 ± 31	2	0.28 ± 0.005	95% confidence limit 1440AD (55.7%) 1530AD 1550AD (39.7%) 1640AD
Damascus Knife	AD 1650	0.9710 ± 0.004	240 ± 19	5	2.13 ± 0.068	95% confidence limit 1640AD (71.0%) 1670AD 1780AD (24.4%) 1800AD

[a]Ages were calibrated at the 95% confidence limit by the program OxCal v3.0 using the decadal smoothed data set of INTCAL98 (Stuiver et al. 1998).

DISCUSSION

Van der Merve (1969) and Cresswell (1991) have already published good summaries of the history, issues, and limitations surrounding the carbon dating of iron and steel artifacts. For ^{14}C dating on iron to be meaningful, the source of carbon in the steel making process must be charcoal from young freshly cut wood. Other carbon sources such as coal, coke, or old wood are depleted in ^{14}C and will cause artifacts to appear too old. Coke became a universal fuel in the industrial world only in the 19th century, but the Romans and Chinese did use coal from the 4th century AD. The recycling of artifacts and the possible use of geological carbonate in smelting (to produce lime—a fluxing agent) must also be considered.

Meteoric iron, or even terrestrial iron, may have also been used in ancient steel making. Both forms can have high carbon content (up to 2.5% in both carbon-iron compounds and graphitic forms). Although these contributions confuse the dating of ancient artifacts, the presence of meteorite iron can be identified by its high nickel content (4.7%), whereas terrestrial iron is rare and is sufficiently well documented to not be problematical. Other complications arising from the use of coal can usually be determined indirectly by the presence of sulfur in the iron or by radiocarbon dates which are obviously too old (e.g. 25,000 BP).

Our primary goal was to improve upon and simplify the carbon extraction procedures developed by others for iron, not to solve the dating complications that can arise when iron incorporates old carbon. If an ancient iron artifact has been made with coal, coke, old wood, lime, meteoric iron, terrestrial iron, or recycled objects, it will be difficult, if not impossible, to date accurately, regardless of how well the new extraction technique works. The occurrence of these constraining factors is thought to be rare in ancient steel making, but until more iron artifacts are radiocarbon dated, this will be difficult to determine with certainty.

We have developed a new, sealed, double-tube, carbon extraction methodology that is 100% efficient in extracting carbon from iron. The process blanks yielded apparent radiocarbon ages near 40,000 BP and introduced less than ±30 yr of uncertainty into the radiocarbon ages for actual artifacts. The new methodology yielded accurate dates for two ancient artifacts of known origin, an AD 1600 nail from the Himeji Castle in Japan and an AD 1650 Damascus knife from India. The nail contained a relatively small amount of carbon (0.28%) while the Damascus knife contained a relatively large amount of carbon (2.13%), demonstrating that the new methodology works on steels over a wide range of carbon contents.

Unlike previous methodologies, all of the materials required for this new carbon extraction procedure are standard to graphite laboratories. The equipment intensive, carbon extraction methodologies of the past can now be avoided. This fact alone should enable more AMS ^{14}C laboratories to make analyses on iron, and we encourage such efforts. We look forward to exploring the limits of the new methodology—can it be used to obtain accurate dates for very old, extremely corroded, low carbon wrought irons, for example? Since demonstrating this range of ability to date objects of known origin may require access to highly prized iron artifacts, how quickly we reach this goal will depend in part on the interest shown by the archeological community.

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REFERENCES

Cresswell RG. 1987. Radio-carbon dating of iron using accelerator mass spectrometry [MSc dissertation]. University of Toronto. 158 p.

Cresswell RG. 1991. The radiocarbon dating of iron artifacts using accelerator mass spectrometry. *Historical Metallurgy* 25:76–85.

Cresswell RG. 1992. Radiocarbon dating of iron artifacts. *Radiocarbon* 34(3):898–905.

Cresswell R. 1997. Radiocarbon dating of iron artifacts. Extended abstract (paper #41). 6th Australasian Archaeometry Conference, Sidney Australia, 10–13 February.

Figiel LS. 1991. *On Damascus steel*. Atlantis: Atlantis Arts Press. 145 p.

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

Kusimba CM, Killick DJ, Cresswell RG. 1994. Indigenous and imported metals at Swahili sites on the coast of Kenya. *Society, Culture, and Technology in Africa* 11 (supplement):63–77.

Nakamura T, Hirasawa M, Igaki K. 1995. AMS radiocarbon dating of ancient oriental iron artifacts at Nagoya University. *Radiocarbon* 37(2):629–36.

Sayre EV, Harbottle G, Stoenner RW, Washburn W, Olin JS, Fitzhugh WW. 1982. The carbon-14 dating of an iron bloom associated with the voyages of Sir Martin Frobisher. *American Chemical Society Symposium Series* 176:441–51.

Sherby OD, Wadsworth J. 1985. Damascus steels. *Scientific American* 252(2):112–20.

Southon JR, Caffee MW, Davis JC, Moore TL, Proctor ID, Schumacher B, Vogel JS. 1990. The new LLNL AMS spectrometer. *Nuclear Instruments and Methods in Physics Research* 52:301–5.

Stuiver M, Polach HA. 1977 Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Stuiver M, Reimer PJ, Bard E, Beck JW, Burr GS, Hughen KA, Kromer B, McCormac G, van der Plicht J, Spurk M. 1998. INTCAL98 radiocarbon age calibration, 24,000–0 cal BP. *Radiocarbon* 40(3):1041–83.

van der Merwe NJ. 1969. *The Carbon-14 dating of iron*. Chicago: University of Chicago Press. 137 p.

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

Vogel JS, Nelson DE, Southon JR. 1989. Accuracy and precision in dating microgram carbon samples. *Radiocarbon* 31(1):145–9.

Yoshida K. 1992. Measurement of ^{14}C age by accelerator mass spectrometry. *Bulletin of the National Museum of Japanese History* 38:171–98. In Japanese.