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# SAMPLING IRON FOR RADIOCARBON DATING: INFLUENCE OF MODERN STEEL TOOLS ON $^{14}$C DATING OF ANCIENT IRON ARTIFACTS

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**ABSTRACT.** Before the 17th century, charcoal was regularly used in the production of iron (smelting and forging) and some of this charcoal carbon was incorporated into the iron. Depending on the age of the wood used to produce the charcoal, the age of the carbon incorporated in the iron lattice can reflect the age of manufacture of the iron artifacts. A reliable preparation method allowing for the routine dating of iron artifacts would permit the dating of numerous objects for which now the age can only be estimated. In an earlier work (Hüls et al. 2004), we tested the extraction of carbon from iron samples by closed-tube combustion. The samples were cut in small pieces to ease the release of the carbon from the lattice. During the tests, it became clear that the steel tools used to cut the samples can add contamination at the surface. As modern steel is made using coal, this leads to erroneously old ages. We have tested ways to reduce or eliminate this surface contamination from the sampling tools using iron artifacts of known ages. In order to quantify the contamination, we produced standard test materials from pure iron (99.998% Fe) melted with carbon of known $^{14}$C content and prepared samples using different cutting tools. The results of these tests indicate that the proper choice of cutting technique and tool, combined with an additional cleaning of the freshly cut surface, reduces sample contaminations to low levels; measured sample $^{14}$C concentrations are close to the $^{14}$C content of the charcoal used to produce these standard iron samples.

## INTRODUCTION

The dating of iron artifacts using radiocarbon has received considerable attention since accelerator mass spectrometry (AMS) reduced the required sample size to manageable proportions (Cresswell 1992; Harbottle et al. 1993; Nakamura et al. 1995; Beukens et al. 1999; Cook et al. 2001, 2003; Craddock et al. 2002; Enami et al. 2004; Scharf et al. 2004; Oinonen et al. 2009). In Hüls et al. (2004), we reported our ampoule combustion procedure to extract carbon from iron, based on the work of Cook et al. (2001), and our first successful dates on known-age iron artifacts. In a few cases, however, our measured $^{14}$C ages were significantly older than expected from the archaeological or historical context of the artifacts. In their review paper, Craddock et al. (2002) discussed the many intricacies of the production and processing of iron over the ages and their implications for the possible influence of old wood, fossil fuel, geological carbonate, or reworking of the iron on the measured $^{14}$C age of an iron object. Old carbon contamination may also be introduced into the sample by admixture of "modern" iron from the tools used for sampling (milling, drilling, sawing, etc.). As modern iron and steel is produced with $^{14}$C-free coal/coke, tool wear during sampling will lead to erroneously old ages (cf. Scharf et al. 2004). A prerequisite for the reliable $^{14}$C dating of iron is thus contamination-free sampling of the samples.

In this paper, we report $^{14}$C measurements on iron artifacts cut with different tools and methods. Broken pieces of the used milling tools were also measured. The results obtained for the archaeological artifacts provide an indication of the effect of sampling contamination on a selection of real archaeological materials. To avoid problems due to potential age inhomogeneity of our archaeological test samples, we also produced laboratory standards with known carbon contents and $^{14}$C concentrations to further test the various cutting techniques.

## MATERIALS AND METHODS

### Archaeological Iron Artifacts and Modern Iron Standards

We selected 5 iron artifacts (Table 1) with known archaeological ages: #1, an axe (0.5% C) from the 2nd to 3rd century AD; #2, an iron bloom (0.8% C) from the 3rd–2nd century BC; #3 and #4, two

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Table 1 $^{14}$C measurements of archaeological iron artifacts cut with different modern steel tools.

| | Tool I | | | Tool II | | | Metal saw | | | Cutting disc | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample<br>Archaeological age<br>$^{14}$C content (pMC)$^{a}$ | $^{14}$C content (pMC) | $^{14}$C age (yr BP) | $\delta^{13}$C (‰) | $^{14}$C content (pMC) | $^{14}$C age (yr BP) | $\delta^{13}$C (‰) | $^{14}$C content (pMC) | $^{14}$C age (yr BP) | $\delta^{13}$C (‰) | $^{14}$C content (pMC) | $^{14}$C age (yr BP) | $\delta^{13}$C (‰) |
| #1, Axe$^{b}$<br>(AD 200–300,<br>~1780 BP)<br>80.1 ± 0.8 pMC | 85.55 ± 0.39 | 1255 ± 35 | –24.0 ± 0.1 | 82.84 ± 0.22 | 1510 ± 20 | –23.3 ± 0.4 | | | | | | |
| | 86.05 ± 0.32 | 1205 ± 30 | –24.3 ± 0.1 | 82.01 ± 0.24 | 1595 ± 25 | –21.9 ± 0.1 | | | | | | |
| | | | | 82.04 ± 0.25 | 1590 ± 25 | –22.9 ± 0.2 | | | | | | |
| #2, iron luppe<br>(300–200 BC,<br>~2200 BP)<br>76.0 ± 0.5 pMC | 76.15 ± 0.24 | 2190 ± 25 | –20.3 ± 0.2 | 75.56 ± 0.18 | 2250 ± 20 | –18.7 ± 0.1 | | | | | | |
| | 76.53 ± 0.23 | 2150 ± 25 | –20.6 ± 0.2 | 75.42 ± 0.19 | 2265 ± 25 | –21.6 ± 0.1 | | | | | | |
| #3, sword$^{c}$<br>(AD 200–500,<br>~1700 BP)<br>80.9 ± 1.5 pMC | 80.14 ± 0.26 | 1780 ± 25 | –22.1 ± 0.1 | 78.87 ± 0.32 | 1905 ± 35 | –18.7 ± 0.2 | 79.21 ± 0.25 | 1870 ± 25 | –21.5 ± 0.1 | 80.79 ± 0.43$^{y}$ | 1715 ± 45$^{y}$ | –24.0 ± 0.4 |
| | | | | 79.95 ± 0.25 | 1795 ± 25 | –21.2 ± 0.1 | 79.70 ± 0.23 | 1825 ± 25 | –20.4 ± 0.2 | 80.49 ± 0.28$^{y}$ | 1745 ± 30$^{y}$ | –25.0 ± 0.1 |
| | | | | 76.45 ± 0.24 | 2175 ± 25 | –21.5 ± 0.1 | | | | 81.01 ± 0.31$^{x}$ | 1690 ± 30$^{x}$ | –27.3 ± 0.1 |
| | | | | 75.09 ± 0.25 | 2300 ± 25 | –22.5 ± 0.1 | | | | | | |
| #4, sword$^{c}$<br>(200–500 AD,<br>~1700 BP)<br>80.9 ± 1.5 pMC | 80.88 ± 0.38$^{x}$ | 1705 ± 40$^{x}$ | –26.6 ± 0.2$^{x}$ | | | | 80.36 ± 0.39$^{x}$ | 1730 ± 40$^{x}$ | –31.8 ± 0.1$^{x}$ | 80.05 ± 0.26$^{y}$ | 1785 ± 25$^{y}$ | –26.9 ± 0.1$^{y}$ |
| | 78.96 ± 0.27$^{x}$ | 1895 ± 25$^{x}$ | –23.5 ± 0.1$^{x}$ | | | | 78.96 ± 0.26$^{y}$ | 1900 ± 25$^{y}$ | –25.1 ± 0.1$^{y}$ | 79.89 ± 0.24$^{y}$ | 1805 ± 25$^{y}$ | –23.0 ± 0.1$^{y}$ |
| | 79.96 ± 0.27$^{x}$ | 1795 ± 25$^{x}$ | –25.5 ± 0.1$^{x}$ | | | | 78.22 ± 0.41$^{y}$ | 1975 ± 40$^{y}$ | –26.3 ± 0.1$^{y}$ | 79.90 ± 0.25$^{x}$ | 1800 ± 25$^{x}$ | –23.9 ± 0.1$^{x}$ |
| #5, ancient steel piece<br>(~2000 BC,<br>~3625 BP)<br>63.5 ± 0.6 pMC | 67.51 ± 0.28 | 3155 ± 35 | –20.3 ± 0.3 | 48.37 ± 0.18 | 5835 ± 30 | –24.8 ± 0.3 | 71.71 ± 0.28 | 2670 ± 30 | –26.3 ± 0.3 | | | |
| | 69.23 ± 0.29 | 2955 ± 30 | –19.5 ± 0.2 | 46.41 ± 0.18 | 6165 ± 30 | –24.0 ± 0.2 | 71.36 ± 0.27 | 2710 ± 30 | –19.9 ± 0.2 | | | |
| | 69.87 ± 0.24 | 2880 ± 30 | –18.3 ± 0.2 | | | | | | | | | |
| | 57.91 ± 0.29 | 4390 ± 40 | –23.4 ± 0.1 | | | | | | | | | |
| | 62.72 ± 0.22 | 3745 ± 30 | –21.1 ± 0.1 | | | | | | | | | |

[a] $^{14}$C content $A_t$ is inferred from the archaeological age and the corresponding $^{14}$C age.

[b] Archaeological age should be AD 200–300; however, all measured ages were much younger and thus the youngest $^{14}$C age of 1205 ± 30 BP (86.05 pMC) was chosen as a reference for contamination estimates.

[c] Sample cutting started from the outside of the sword: $^{x}$ material from the cutting edge; $^{y}$ material from the core.

swords with 0.4% C and 0.2% C from the 2nd–5th century AD; and #5, a steel sample (0.6% C) expected to date to the 20th century BC. Samples #1, #2, and #5 were provided by the German Mining Museum in Bochum; samples #3 and #4 are from different levels of the Nydam war booty offerings (Archäologisches Landesmuseum, Schleswig). Both swords have pattern-welded blades. Sample #4 has a hardness of ~120 HV (Vickers hardness test) at the edge and ~240 HV at the core (Buchwald 2005). No hardness measurement is available for sample #3; however, other swords from the same level have hardness values between 435 and 676 HV (Buchwald 2005), which also show the variability in mechanical properties.

We produced 3 large (~15 g; ST-1-4-1, ST-I-4-3, and ST-I-3-2) and 2 small (700 and 880 mg; ST-I-3-4 and ST-I-3-5) modern standard iron samples by melting pure iron powder (99.998% Fe) with varying amounts of modern wood charcoal ($^{14}$C: 116.61 ± 0.32 pMC, $\delta^{13}$C: –25.3 ± 0.5‰, $n = 2$ measurements) at ~1600 °C under an argon atmosphere. Two visible rings from a piece of charcoal were used, crunched to powder, and homogenized before usage. After melting, sample ST-I-3-2 was cooled down to ~1000 °C at a rate of 20 °C/min (~30 min) and then quenched to room temperature by cooling in water. Samples ST-I-4-1 and ST-I-4-3 were cooled down to 1000 °C likewise, kept at 1000 °C in an Ar atmosphere overnight, and then quenched to room temperature in water. This procedure should, depending on the C content, give hardened steel.

The 3 larger pieces with different carbon contents (see Table 2) were made to be cut and milled with different modern steel tools to evaluate the contribution of fossil carbon from the tools used. Of these, ST-I-4-1 has a low carbon content (~0.5 weight %), comparable to that of the archaeological iron samples used in this study. According to a preliminary hardness measurement (single Vickers hardness measurement: 329 HV), this sample is an unhardened steel. ST-I-4-3 contains about 1.8–2 weight % carbon and has a hardness of 605 HV, equivalent to the category of hardened steel, which should work as a worst-case sample for the sampling contamination tests. ST-I-3-2 contains a high carbon content, >4 weight %, which is characteristic of cast iron. However, the rather fast cooling from 1600 to 1000 °C in ~30 min may have prevented the formation of graphite layers between the iron crystals as is characteristic for cast iron.

Table 2 Modern steel samples.

| Sample | Fe weight (g) | Coal weight (mg) | Expected C content (%)[a] | Measured C content (%)[b] |
|---|---|---|---|---|
| ST-I-4-1[c] | 15.01 | 350 | ~0.2–0.7 | 0.5–0.6 |
| ST-I-4-3 | 15.04 | 600 | ~1.2 | 1.8–2.0 |
| ST-I-3-2 | 15.00 | 1230 | ~ >3.5 | 4–6 |
| ST-I-3-4 | 0.88 | 60 | ~ >3.5[d] | 0.4 |
| ST-I-3-5 | 0.70 | 50 | ~ >3.5[d] | 0.4 |

[a] Expected C content inferred from optical emission spectrometer measurements.

[b] Carbon estimated from $CO_2$ pressure in our reduction system.

[c] Sample names refer to the production batch, e.g. ST-I-4-1: Standard I, 4th batch, 1st sample.

[d] Expected carbon content based on a comparable iron/coal mixture as for ST-I-3-2.

Two small pieces (e.g. ~800 mg, Table 2; ST-1-3-4 and ST-1-3-5) were produced to measure the $^{14}$C concentration of the iron without the contamination during sampling. A significant fraction of volatiles in the charcoal used led initially to large mass losses during melting and low carbon contents in the iron. Increasing the amount of charcoal empirically produced desired carbon contents for the large samples but still low values in the 2 small test pieces. Preliminary estimates of the carbon content for the large pieces by optical emission spectrometry were confirmed by $CO_2$ measurements on combusted standards.

### Sampling Procedures

The archaeological iron samples were first mechanically cleaned from rust with a corundum ($Al_2O_3$) grinding tool until bright metal was exposed. The iron samples were then cut into smaller pieces, either by milling or sawing:

- Milling with a standard steel tool (tool I: Straight Shank End Mill, ~1% C, 1.65 ± 0.08 pMC, ~33 kyr);
- Milling with a steel tool coated with TiCN + TiN (tool II: Straight Shank End Mill, ~1% C, 1.13 ± 0.11 pMC, ~36 kyr);
- Milling with a shank end mill (solid carbide end mill, tool III) for hard steel (used only for modern standards);
- Sawing of thin sheets (~0.5 cm thickness), followed by cleaning of the cutting areas with a corundum grinding tool. Smaller pieces (~0.5–2 cm) were cut with a metal shear;
- Cutting of thin cross-sections (~0.3 cm thickness) with a cutting disc, a tool containing a composite of plastic fibers (usually a phenolic resin) with sintered corundum minerals, followed by cleaning of the cutting areas with a corundum grinding tool. Smaller pieces (~0.5–2 cm) were cut with a metal shear.

### Cleaning and Combustion

The iron pieces or chippings were cleaned with acetone to remove grease or fatty coatings. Samples #3 and #4, swords from the Nydam war booty offerings, were chemically cleaned with solvents in a Soxhlet-type extraction to remove conservation agents such as wax, which was put on the sample at the museum to prevent corrosion (Bruhn et al. 2001). Then, subsamples containing an inferred 1–2 mg C were weighed into 1/4″ quartz tubes, which were placed inside 3/8″ quartz tubes, together with CuO (CuO:Fe > 5) as an oxidant. The quartz tubes were cleaned by precombustion, along with 0.5 to 1 g of CuO in a muffle oven at 900 °C for 5 hr. The CuO oxidant used for combustion was likewise cleaned by precombustion. The 3/8″ quartz tubes, containing the 1/4″ tube with the iron aliquot together with the appropriate amount of CuO, were evacuated down to about $5 \times 10^{-4}$ mbar, then flame-sealed.

The carbon was extracted from the iron matrix by combustion at 1000 °C for 24 hr. The sample $CO_2$, resulting from the first combustion, was resealed in another quartz tube with CuO and cleaned silver wool (cleaned by combustion at 900 °C for 4 hr) and recombusted according to our standard combustion procedure (900 °C for 4 hr). This latter cleaning step proved necessary for samples with higher sulfur content as their sample $CO_2$ failed to reduce properly otherwise. The purified sample $CO_2$ was reduced to graphite and then measured according to our routine method (Nadeau et al. 1998).

Recombustion of some iron samples after a first thermal release of carbon indicates that the initial combustion recovers more than 95% of the available carbon and, for practical purposes, can be assumed to be complete (Table 3).

### Contamination by Sampling Tools

Carbon contamination originating from the sampling tools can be estimated from a simple $^{14}C$ mass balance calculation:

$$X\,(\%\ cont.) = (A_t - A_m)/(A_t - A_c) \times 100 \tag{1}$$

where $X$ (in % contamination) is the fraction of carbon derived from the sampling tool; $A$ represents the $^{14}$C concentration; and $t$, $m$, and $c$ indicate its "true" and measured value, and the measured activity for the contaminating tool steel, respectively. The "true" $^{14}$C concentration of an archaeological iron object is derived from its archaeological age estimate and the corresponding $^{14}$C age. Unfortunately, this introduces a considerable uncertainty, combining the uncertainty of the archaeological age attribution with that of the age of the carbon incorporated in the iron at the time of manufacture and the uncertainty of the reverse calibration. If the contamination is small, in the percent range, the uncertainty in $X$ may be relatively large and a quantitative estimation of the sampling contamination is difficult. An impression of the relative suitability of various tools for the sampling of archaeological iron samples may still be obtained from a comparison of the contaminant fractions, $X$, calculated for those tools for 1 iron sample as the uncertainty in $A_t$ affects each $X$ similarly.

Table 3 Efficiency of the carbon extraction for modern iron samples. The 2nd combustion was done on sample material from the 1st combustion.

| Sample | 1st combustion C extraction (mg) | 2nd combustion C extraction (mg) |
|---|---|---|
| ST-I-4-1 | 0.90 | <0.10 |
| | 1.45 | <0.10 |
| | 4.58 | <0.10 |
| ST-I-4-3 | 4.10 | <0.10 |
| | 3.98 | <0.10 |
| ST-I-3-2 | 7.64 | 0.60 |
| | 10.63 | 0.40 |
| | 4.27 | <0.10 |

## RESULTS

### Sampling Archaeological Iron Artifacts

We tested the effect of milling (using tools I and II) and sawing on the $^{14}$C age measured for a set of 5 archaeological samples (Table 1). The $^{14}$C content of the milling tools, tested on 2 samples of tool I (1.61 ± 0.11 and 1.70 ± 0.11 pMC) and 1 sample of tool II (1.13 ± 0.11 pMC), confirms the tools contain mostly fossil carbon (apparent age >33 kyr).

The results in Table 1 show discrepancies between expected and measured ages and also indicate some sample inhomogeneity and sampling contamination. Iron #1 clearly dates younger than the archaeologically expected 2nd–3rd century AD, samples #2–4 show ages closer to the archaeological expectation, and those obtained for iron #5 scatter widely. We made an inverse calibration using the estimated archaeological age of iron #2–5 to estimate the $^{14}$C concentration $A_T$ of the iron samples. Equation 1 provides with $A_T$ and the data of Table 1 the fraction $X$ (in % contamination) of sample carbon derived from the sampling tool. For iron #1, which is clearly younger than expected, we chose the age of the youngest measured sample as a baseline ("expected age") to provide $A_T$ and proceeded as for the others. The contaminating carbon fractions, $X$, are plotted for each tool and each iron sample in Figure 1. The differences in $X$ provide for each iron a comparison of the suitability of the different tools for sampling.

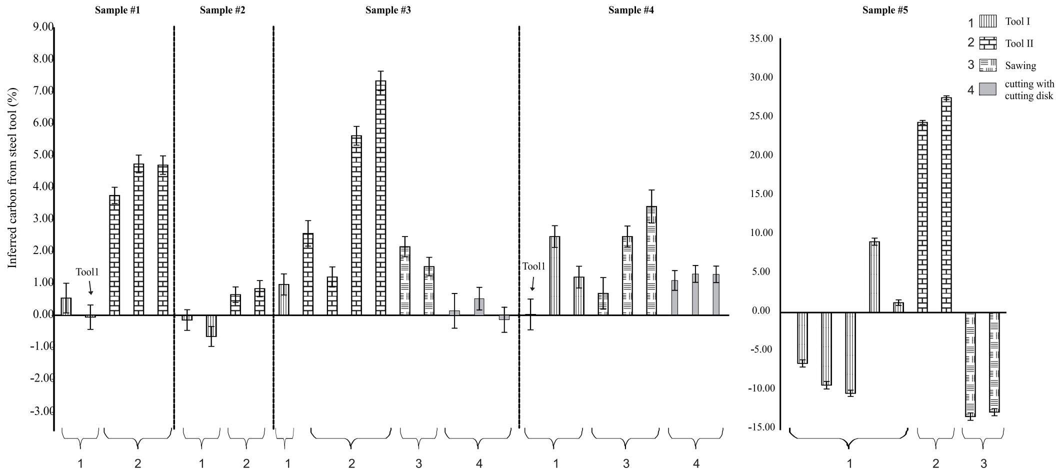

Figure 1 Calculated contamination of archaeological iron samples with carbon from modern steel tools using %cont. = $(^{14}C_{true}–^{14}C_{measured}) : (^{14}C_{true}–^{14}C_{tool}) \times 100$. For sawing, we assumed a comparable $^{14}C$ as measured for tool I since material should be comparable. Upper and lower contamination boundaries are calculated using the measurement uncertainties (sample and tool).

For iron #1 through #4, the youngest ages, indicating the least contamination, are measured on samples prepared with tool I. There is no statistically significant difference between the duplicates of iron #1 and iron #2, but for iron #4 the results indicate varying contamination of the order of 1–2% during the sampling with tool 1. Samples of iron #1–3 produced with tool II contain less $^{14}C$ than those milled with tool I, indicating a stronger and variable contamination by this tool. Sampling iron #3 and #4 by sawing produced slightly higher ages than tool I with a similar variability. However, sampling iron #3 and iron #4 with a cutting disc produced lower apparent ages than seen with samples cut by sawing, also with a smaller scatter. No age difference is seen between the core and the edge of the 2 swords. Iron #5 is an old steel that appeared quite hard during sampling. The sampling contamination for tool I and II is variable and large, with again tool II contaminating more. Sawing with subsequent cleaning of the saw cuts produced consistent younger ages and yielded an upper limit for the age of the carbon in iron #5.

Together, these results demonstrate that contamination by the sampling tool can be a serious problem. The degree of contamination clearly varies with the type of iron, from low for the iron bloom, which may be considered as being "soft," to high for the "hard" iron of the swords and the qualitative "hard" iron of the old steel. Evidently, the titanium-coated tool II causes serious contamination, perhaps due to abrasion of the TiCN component of this coating.

## Modern Laboratory Iron Standards

The $^{14}C$ measurements of archaeological iron show significant intrasample variability due to different cutting and milling techniques. However, the unknown sample ages make it difficult to quantify the degree of contamination and thus to test for the contamination-free sampling of iron artifacts. A set of (ideally hard) steel samples (e.g. C content >0.2%), with different carbon concentrations and a known modern $^{14}C$ signature, was produced to remedy this. The $^{14}C$ concentration $A_T$ (Equation 1) of the carbon remaining in the iron is assumed to be the same as the $^{14}C$ concentration of the charcoal.

### Small-Sized Iron Standards

Standards ST-1-3-4 and ST-I-3-5, with a charcoal/iron ratio similar to ST-I-3-2, were made small (~800 mg instead of ~15 g for the larger pieces) and intended for combustion in 1 piece to avoid sampling contamination due to cutting. The combustion of ST-1-3-4 yielded much less carbon than expected, which could indicate a lower carbon content than expected or an incomplete extraction of $CO_2$. In order to test this possibility, sample ST-I-3-5 was cut in halves with a metal shear, followed by a thorough cleaning of the cutting edge with a corundum grinding tool. Having only 1 cutting edge, which was carefully mechanically cleaned, we assume the effect of cutting to be negligible. Both samples gave much less carbon than expected, indicating a large carbon loss during melting. ST-I-3-4 and ST-I-3-5 show significantly lower $^{14}$C concentrations than the charcoal used (Table 4). Furthermore, both samples show a difference in $^{14}$C concentration of 1.1 ± 0.6 pMC (1.9 $\sigma$). Although this is not statistically significant at the 5% level, it may indicate a contamination with old carbon from the metal shear used to cut sample ST-I-3-5, contrary to our assumption. However, in comparison to the large iron samples and sample pieces with 6–8 cutting surfaces (cut, not milled), the apparent contamination seems disproportionately large.

At this stage, we believe that the observed isotopic differences are related to the manufacturing process, which seems to have been different for the smaller samples in comparison to the larger ones. The lower carbon and $^{14}$C content of the small standards may indicate problems during the melting and carbon uptake. Another cause for the lower carbon and $^{14}$C concentration of both small standards could be an incomplete combustion with isotope fractionation. However, a second combustion of sample ST-I-3-5 yielded no carbon and thus gave no indication of incomplete combustion. The results emphasize the need for more work with additional metallurgical analysis (i.e. microstructure analysis, physical properties such as hardness, etc.) to understand the carbon incorporation into the iron during melting to produce homogeneous iron standards with known $A_T$ for further tests.

### Larger Iron Standards

The 3 larger iron pieces (~15 g, Table 2) were used to test several sampling methods: milling with tool II and with a special high-speed tool for hard steel (tool III), sawing, and cutting using a cutting disc and metal shear. ST-I-4-1 and ST-I-4-3 turned out to be harder than expected regarding their behavior during cutting and milling, which is good as it provides harsher test conditions. For ST-1-4-1, a combination of sawing and cutting was used. ST-I-4-1 was first sawed into halves, then cut into slices with a corundum cutting disc as described above. Later, slices were sampled with a cutting disc only. ST-I-4-3 was cut into slices using the cutting disc only; ST-I-3-2 was cut into slices with a normal metal saw. The slices were later cut into smaller pieces of mm to cm size with a metal shear. This latter cutting step was necessary to get appropriate sample sizes to fit into our combustion tubes, which was not possible with a cutting disc due to the difficult handling of small irregular pieces.

No $^{14}$C measurements for the carbon of tool III, the saw blades, the metal shear, and the cutting disc are available yet. Being modern steel, we assume their $^{14}$C concentrations to be similar to that measured for milling tools I and II. The cutting disc has a supporting grid of plastic fibers with an assumed fossil carbon. To calculate the contribution of tool carbon from the measured $^{14}$C concentrations (Table 4) with Equation 1, we assume a $^{14}$C concentration similar to tool I for tool III, the saw blades, the metal shear, and the cutting disc.

The contribution $X$ (in %) of the different sampling (e.g. cutting) tools to the carbon measured for the iron sample, calculated from the $^{14}$C concentration of the measured test samples, is shown in Figure 2. Samples cut with a cutting disc only show no statistically significant contamination for ST-I-3-2 ($X$ = 0.3–0.9%) and ST-I-4-3 ($X$ = 0–0.9%) and $X$ values from 0.1 to 1.2%, which is significant, for ST-I-4-1. Saw cuts (ST-I-4-1 and ST-I-3-2) gave highly variable contamination. One cut of ST-I-4-1 and 2 cuts of ST-I-3-2 produced no significant apparent contamination, whereas 2 more cuts each of ST-I-3-2 and ST-I-4-1 indicate 2% and 7%, and 1.5% and 1.2% contamination, respectively. Samples milled with tool III show significant contamination (*X* = 1.5–2.1%) for ST-I-4-1 but no statistically significant contamination for ST-I-4-3 (*X* = 0.3–0.8%).

Table 4 $^{14}$C measurements of modern steel standards, made with charcoal of 116.61 ± 0.32 pMC ($\delta^{13}$C: –25.3 ± 0.5‰) cut with different modern steel tools.

| | Tool II | Tool III | Metal saw | Cutting disc | No cutting |
|---|---|---|---|---|---|
| Sample | $^{14}$C (pMC)<br>[*$\delta^{13}$C (‰)*] | $^{14}$C (pMC)<br>[*$\delta^{13}$C (‰)*] | $^{14}$C (pMC)<br>[*$\delta^{13}$C (‰)*] | $^{14}$C (pMC)<br>[*$\delta^{13}$C (‰)*] | $^{14}$C (pMC)<br>[*$\delta^{13}$C (‰)*] |
| ST-I-3–4 | | | | | 115.32 ± 0.29<br>[*–20.2 ± 0.1‰*] |
| ST-I-3–5[a] | | | | | 114.20 ± 0.49[a]<br>[*–1.6 ± 0.4‰*] |
| ST-I-4–1 | 96.96 ± 0.88<br>[*–24.7 ± 0.7‰*] | 114.96 ± 0.35<br>[*–17.3 ± 0.1‰*] | 116.57 ± 0.42<br>[*–18.5 ± 0.2‰*] | 115.84 ± 039[b]<br>[*–15.5 ± 0.1‰*] | |
| | | 114.10 ± 0.32<br>[*–15.8 ± 0.2‰*] | 114.84 ± 0.26<br>[*–15.0± 0.2‰*] | 116.53 ± 1.23<br>[*–7.1 ± 0.3‰*] | |
| | | 114.16 ± 0.38[b]<br>[*–17.0 ± 0.2‰*] | 115.21 ± 0.51[b]<br>[*–6.7 ± 0.2‰*] | 115.39 ± 0.32<br>[*–13.3 ± 0.2‰*] | |
| | | | | 115.27 ± 0.33<br>[*–15.5 ± 0.2‰*] | |
| ST-I-4–3 | | 116.29 ± 0.30<br>[*–21.5 ± 0.1‰*] | | 116.81 ± 0.34<br>[*–21.3 ± 0.3‰*] | |
| | | 115.87 ± 0.28<br>[*–22.2 ± 0.2‰*] | | 117.09 ± 0.26<br>[*–23.1 ±0.3‰*] | |
| | | 115.64 ± 0.37[b]<br>[*–23.3 ± 0.2‰*] | | 116.82 ± 0.44[b]<br>[*–16.7 ± 0.2‰*] | |
| | | | | 116.26 ± 0.36<br>[*–24.1 ± 0.2‰*] | |
| | | | | 115.66 ± 0.37<br>[*–21.5 ± 0.3‰*] | |
| | | | | 115.53 ± 0.3<br>[*–16.8 ± 0.2‰*] | |
| | | | | 116.79 ± 0.31<br>[*–23.9 ± 0.4‰*] | |
| ST-I-3–2 | 114.56 ± 0.48<br>[*–26.0 ± 0.1‰*] | | 116.29 ± 0.29<br>[*–27.6 ± 0.1‰*] | 116.28 ± 0.46<br>[*–29.3 ± 0.1‰*] | |
| | 114.93 ± 0.32<br>[*–25.3 ± 0.2‰*] | | 116.64 ± 0.39<br>[*–24.7 ± 0.2‰*] | 115.61 ± 0.29<br>[*–28.7 ± 0.1‰*] | |
| | | | 114.57 ± 0.32[c]<br>[*–26.1 ± 0.1‰*] | | |
| | | | 114.99 ± 0.33[d]<br>[*–26.9 ± 0.1‰*] | | |

[a] The piece was cut with a metal shear and cutting surfaces were cleaned by a grinding tool.

[b] 2nd combustion of combusted iron gave no carbon.

[c] 2nd combustion of combusted iron produced 0.6 mg C out of 8.2 mg C (~7%, Table 3), measured $^{14}$C = 114.25 ± 0.59 pMC, $\delta^{13}$C: –22.8 ± 0.1‰.

[d] 2nd combustion of combusted iron produced 0.4 mg C out of 11 mg C (~4%, Table 3), measured $^{14}$C = 108.06 ± 0.73 pMC, $\delta^{13}$C: –23.3 ± 0.2‰.

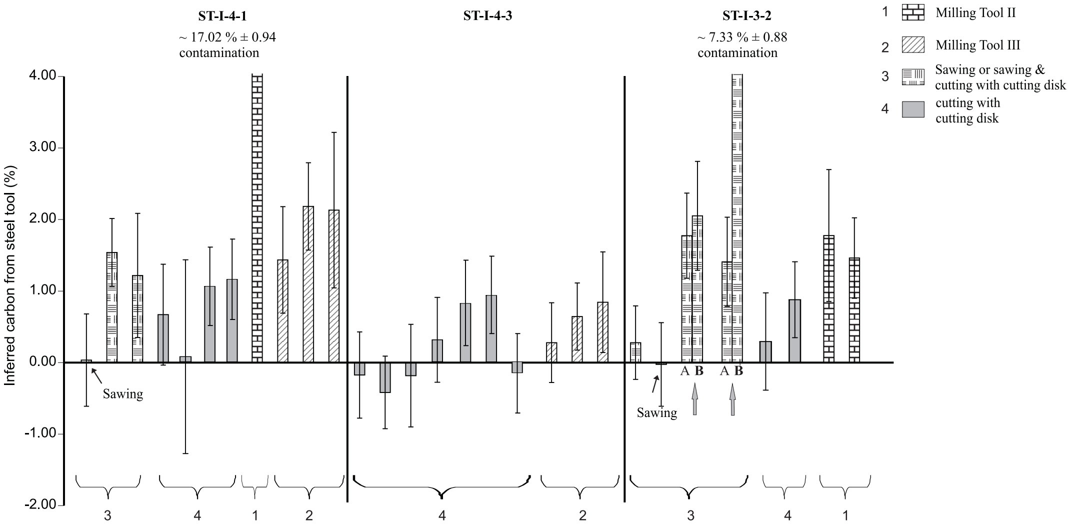

Figure 2 Calculated contamination of modern standard iron samples with carbon from modern steel tool using %cont. = ($^{14}C_{true}$–$^{14}C_{measured}$) : ($^{14}C_{true}$ –$^{14}C_{tool}$) × 100. Upper and lower contamination boundaries are calculated using the measurement uncertainties (coal, sample, and tool). For sawing and cutting with a cutting disc as well as for tool III, we assumed a comparable $^{14}C$ as measured for tool I. Gray arrows at ST-I-3-2 mark measurements done on A) 1st incomplete carbon extraction (7.6 and 10.3 mg C, respectively) and B) 2nd carbon extraction (0.6 and 0.4 mg C, respectively).

A strong contamination ($X = \sim 17\%$) is seen for 1 sample milled with tool II for ST-I-4-1. Its magnitude is comparable to that seen in the archaeological irons. The samples milled with tool II from standard ST-I-3-2 show, however, contaminations between 1–2%, not much larger than those milled, cut with tool III, and sawed. Whether this discrepancy is due to the hardness of the sampled iron, causing more tool wear for the comparably "harder" sample ST-I-4-1, or to its higher carbon content for ST-I-3-2—making a certain amount of wear relatively less important—is, as yet, unclear.

The results obtained for the modern steel test samples confirm and quantify the contamination originating from the tools used to sample iron for a carbon extraction and $^{14}C$ measurement. They also show that contamination can be minimized by using a cutting disc and cleaning the cut surfaces, e.g. cutting to larger pieces and thus decreasing the effective surface of iron samples (mean $X_{\text{cutting disc}} = 0.4 \pm 0.6\%$; $n = 23$).

## CONCLUSIONS

$^{14}C$ measurements on samples of archaeological iron artifacts, obtained with different milling tools or by sawing and cutting, show significant variability. The sampling of iron contaminates the sample with old carbon from the cutting tools, most likely due to abrasion and subsequent welding of chippings to the sample. The abrasion depends on the hardness of the tool and of the sample itself, but probably also on how the sampling is done. This results in a non-reproducible contamination that may be the cause of some of the erroneously old ages obtained in the $^{14}C$ dating of archaeological iron objects.

Sampling test irons of different modern carbon content and hardness with a cutting disc, and subsequent surface cleaning, gave $^{14}C$ concentrations close to that of the charcoal used to produce the test samples, indicating no statistically significant contamination. Samples obtained by sawing followed by cleaning of the cutting surfaces give inconsistent results; some are clean, some show old carbon contamination (1–2% in 4 out of 7 cases). Milled samples generally show significant contributions of old carbon from the milling tools. One tool (#II, a straight shank end mill coated with TiCN + TiN) proved particularly unsuitable with a maximum old carbon contamination of 17%. Sampling with a cutting disc followed by surface cleaning minimizes sampling contamination of iron artifacts to acceptable levels (~0.5% or less, equivalent to an age error <40 yr).

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