INTERPRETING $^{14}\text{C}$ MEASUREMENTS ON 3RD–4TH CENTURY AD IRON ARTIFACTS FROM NYDAM, DENMARK

C Matthias Hüls$^{1,*}$ · John Meadows$^{1,2}$ · Andreas Rau$^{2}$

$^{1}$Leibniz-Laboratory for Radiometric Dating and Isotope Research, Christian-Albrechts-Universitaet Kiel, Max-Eyth-Str.11-13, 24118 Kiel, Germany
$^{2}$Zentrum für Baltische und Skandinavische Archäologie, Stiftung Schleswig-Holsteinische Landesmuseen, Schloss Gottorf, Schleswig, Germany

ABSTRACT. Radiocarbon ($^{14}\text{C}$) ages were determined for 10 iron samples from the war booty offering site in the Nydam peat bog (SE Denmark), and compared to archaeologically inferred periods of deposition. Additional $^{14}\text{C}$ measurements were carried out for modern iron standards made with charcoal of known isotopic composition to evaluate possible effects of handling. Modern iron standards give depleted $^{14}\text{C}$ concentrations, compared to the initial charcoal $^{14}\text{C}$ composition, and may indicate carbon fractionation effects during carbon dissolution in the iron lattice. Further studies are needed to verify if this is a common effect during iron production. $^{14}\text{C}$ dating of two swords and one ax head are in comparatively good agreement with expected deposition times and indicate only small old-wood effects. In contrast, $^{14}\text{C}$ dating of iron rivets from the Nydam (B) oak boat proved difficult due to corrosion with siderite ($\text{FeCO}_3$) and conservation with wax. A step-combustion procedure was applied, using a low ($\sim 570$–$600^\circ\text{C}$) temperature prior to the high ($\sim 970$–$1000^\circ\text{C}$) combustion temperature for carbon extraction, aiming to remove siderite and wax before collecting the original carbon dissolved in the iron lattice. Nevertheless, measured $^{14}\text{C}$ ages of the iron rivets differ by about 200–300 years from the dendro-date of the Nydam (B) oak boat they belong to, indicating persisting aging effects (e.g. old-wood, contamination with fossil carbon added during iron making and/or handling prior $^{14}\text{C}$ dating). Also, a possible recycling of older iron cannot be excluded.

KEYWORDS: iron artifacts, radiocarbon dating, war booty offering.

INTRODUCTION

The Nydam peat bog in South Jutland, Denmark (see Figure 1), became internationally famous in the mid-19th century when two 20–25-m-long wooden boats from the early 4th century AD were discovered, i.e. the famous Nydam oak ship (Nydam B), which is still preserved and on display in Schleswig, and a fragmentary preserved pine boat (Nydam C). Together with these ships, masses of iron artifacts such as weapons (swords, lances, axes etc.) and personal items (buckles, fibulae, tweezers, etc.), attributed to the late Roman and Migration periods, were found (Bemmann and Bemmann 1998a, 1998b). Detailed archaeological analysis of the weapons indicates that sacrificial deposits of weapons were made at Nydam in several distinct phases, between AD 250 and AD 475 (Rau 2010).

Carbon is introduced into the iron lattice in variable quantities during the time of production (e.g. Buchwald 2005), and, provided that the carbon source used for smelting the iron ore is contemporaneous, iron objects can therefore be radiocarbon ($^{14}\text{C}$) dated, as has been successfully demonstrated (e.g. Van der Merwe and Stuiver 1968; Van der Merwe 1969; Cresswell 1992; Nakamura 1995; Possnert and Wetterholm 1995; Cook et al. 2001; Hüls et al. 2004; Scharf et al. 2004; Oinonen et al. 2009). Here we report on the $^{14}\text{C}$ dating of two swords, one ax head, an anchor, and several iron rivets from the famous Nydam oak boat (Nydam B). All these objects had been treated with a waxy conservation agent, and the unique depositional environment at Nydam led to the formation of a siderite corrosion layer on the iron artifacts (Matthiesen et al. 2003).

*Corresponding author. Email: mhuels@leibniz.uni-kiel.de.
To evaluate possible effects of sample handling before and during carbon extraction, modern control samples, i.e. iron with a known, modern $^{14}$C content, were produced (Hüls et al. 2011) and prepared for $^{14}$C measurements by the same methods as the archaeological samples.

**MATERIALS AND METHODS**

**Samples**

Ten archaeological iron objects and two modern iron standards were dated (see Table 1 and Figure 2). Both sword fragments represent so-called pattern-welded blades, i.e. different iron alloys with alternating high phosphorus content and medium carbon content (0.2–0.5 wt%$^\text{C}$) (Thomsen 1992; Buchwald 2005) are forged together. Based on typological features they are thought to have been deposited during the sacrifice 1 (FS4156, AD 250–AD 300) and sacrifice 3 (FS5409, AD 360–AD 400) (Rau 2010). The swords were conserved by a waxy coating (∼1 mm thick).

The ax head, from sacrifice 4 (AD 380–AD 420) (Rau 2010), was sampled by staff of the Archäologische Landesmuseum at Schloss Gottorf, Schleswig, Germany. A triangular section was cut from one face of the ax head, leaving a black, waxy surface coating on three sides of the sample and exposing fresh iron surfaces on the other sides.

The six iron rivets/nails were collected during the 1989–1997 excavation at Nydam by the National Museum of Denmark and are thought to be associated with the Nydam B oak boat, whose construction was dated dendrochronologically to AD 310–AD 320 (Bonde 1990). All rivets are heavily corroded and apparently soaked in wax.
Sample Nydam-3421 originates from a triangular metallurgical sample, set in a resin sample holder and polished from one side. This sample was taken from a large iron bar, a possible anchor shaft, collected during the Nydam excavation in 1993 (see Figure 2), and thought to be associated with either the Nydam (B) oak ship or the Nydam (C) pine boat (early 4th century AD; Rieck 2013). Metallographic examination show a ferritic/phosphor ferritic composition with a chemical signature of slag inclusions in accordance with an origin of iron made in western Jutland/Denmark at that time (Buchwald 2005). In contrast to the rivets and the sword samples, this sample appeared almost pure on the polished upper surface and was contaminated with resin on the sides and below.

Two iron samples with a modern $^{14}$C signature were produced using ultra pure iron powder (99.998%Fe) and powdered modern charcoal ($^{14}$C: 1.1667 $\pm$ 0.0017); $\delta^{13}$C$_{AMS}$: $-26.4$ $\pm$ 0.17‰ VBDB (Hüls et al. 2011), heated up to $\sim$1600°C in an argon-flushed muffle oven. Sampling, preparation and $^{14}$C measurement were done in parallel to the archaeological samples to check for effects occurring during the sample preparation.

| Sample name                  | Lab ID           | Description                        | Expected age                                  |
|------------------------------|------------------|------------------------------------|-----------------------------------------------|
| ST-I-3-1                     | KIA53025         | Pure Fe + charcoal                  | Modern $^{14}$C: 1.1667 $\pm$ 0.0017          |
| ST-I-4-2                     | KIA53026         |                                    | $\sim$AD 1988–1991                            |
| FS4156, Kat.Nr. 404          | KIA18268&32224   | Sword fragment                     | Sacrifice 1, AD 250–AD 300                    |
| FS 5409, Kat Nr. 431         | KIA18269&32223   | Sword fragment                     | Sacrifice 3, AD 360–AD 400                    |
| Nydam-Ax, Kat.Nr. 1865       | KIA19344         | Piece from ax                      | Sacrifice 4, AD 380–AD 420                    |
| Nydam-13705                  | KIA48372         | Iron rivet Nydam oak boat          | Nydam B oak boat: dendro age AD 310–AD 320    |
| Nydam-13707                  | KIA48373         | Iron rivet Nydam oak boat          |                                               |
| Nydam-12444                  | KIA48374         | Iron rivet Nydam oak boat          |                                               |
| Nydam-13944                  | KIA48375         | Iron rivet Nydam oak boat          |                                               |
| Nydam-6263                   | KIA48376         | Iron rivet Nydam oak boat          |                                               |
| Nydam-6279                   | KIA48377         | Iron rivet Nydam oak boat          |                                               |
| Nydam-3421                   | KIA48380         | Fragment of an anchor              | Sacrifice 2, associated with Nydam B or C, early 4th century AD |

$^{14}$C and Nydam Iron

Table 1  Iron samples for AMS-$^{14}$C measurements.
Sample Preparation

All iron samples were reduced in size by cutting and surface grinding prior to thermal carbon extraction in order to minimize possible contamination from modern tools used as was observed previously when using coring or milling (Scharf et al. 2004; Hüls et al. 2011).

- Swords, the ax head, and modern standards: cutting into sections using a cutting disk and subsequent thorough abrasion with a corundum grinding tool to remove a significant portion of the sample surfaces.
Iron rivets: surface cleaning with an iron wire metal brush until solid iron was exposed. Cleaned samples were cut into 3–4-mm sized pieces with a metal shear followed by grinding of cut edges with a corundum grinding tool.

Sample Nydam-3421 (triangular shaped ∼ 17 × 13 mm, 1.5 mm thick), after removal from the metallographic sample holder, was just abraded with a corundum grinding tool and further cut into smaller pieces.

In order to remove wax and/or unknown organic substances, either from conservation agents on the samples or from sample handling, the samples were then subjected to a Soxhlet type serial extraction with solvents. In sequence, they were extracted three times each with boiling tetrahydrofurane (THF), chloroform, petroleum-ether, acetone, and methanol and water, followed by drying ∼60°C in an oven.

**Carbon Extraction Method A**

Between 600 mg and 1600 mg of prepared sample material (see also Table 3) was sealed in prebaked quartz tubes together with CuO (5 times amount of sample material; Hüls et al. 2004) and combusted at 1000°C for 24 hr.

**Carbon Extraction Method B**

The severe contamination of Nydam rivets (corrosion with siderite, i.e. FeCO₃ [Matthiesen et al. 2003], soaking in PE wax as indicated by FTIR-ATR measurements) required additional cleaning efforts. To remove both contaminants, a step-combustion procedure with a low-temperature (LT, ∼570–600°C) step, followed by a high-temperature (HT, >970°C) step, was applied (due to crystal structure properties, carbon [dissolved in the iron lattice] diffusion is lower at temperatures <700°C in comparison to higher temperatures). For this purpose, precleaned sample material as outlined above was combusted:

- **(B1)** in a closed quartz tube together with CuO (500 mg) at 600°C for 4 hr (low-temperature CO₂ fraction LT); after collecting the LT-CO₂ fraction, the residue was combusted in closed quartz tubes together with CuO (5 times amount of sample material) at 1000°C for 24 hr (high-temperature CO₂ fraction HT).
- **(B2)** with high-purity O₂ (∼50 mL/min) in an electric resistivity oven, attached to a gas manifold for subsequent cryogenic CO₂ purification, at ∼570°C (LT-CO₂) for 4 hr, followed by a ∼980°C combustion (HT-CO₂) for 5 hr.

The resulting sample CO₂ was cryogenically cleaned using a dry-ice/ethanol and a n-Pentane cooling trap (freezing T ∼130°C) to remove and separate H₂O and possible SO₂ from sample CO₂ (e.g. Kusakabe 2005).

**AMS Measurements**

The sample CO₂ was graphitized by the Bosch reaction with an iron catalyst (Vogel et al. 1984; Nadeau et al. 1998). The resulting mixture of graphite and iron powder was pressed into aluminum target holders for accelerator mass spectrometry (AMS) ¹⁴C measurements with a 3MV HVEE Tandetron AMS system. ¹⁴C measurements are normalized to modern Oxalic Acid II standard (NBS SRM 4990C) and corrected for isotopic fractionation and
background effects (Nadeau and Grootes 2013). $^{14}$C ages are converted to calendar ages using the software package OxCal4 (Ramsey and Lee 2013) and the IntCal13 dataset (Reimer et al. 2013).

RESULTS AND DISCUSSION

Modern Iron Samples

The measurements of the two modern iron standards show depleted $^{14}$C concentrations compared to the charcoal and are in good agreement with previous measurements with comparable sample material (Hüls et al. 2011; see Table 2). In addition to the earlier study, detailed geometric information and mass-balancing during the grinding cleaning step were documented, revealing an overall material removal of 30–36% and, on average, a removal of $\geq 0.1$ mm from the sample surface. With this amount of material removed from the sample surface, the explanation of observed average $^{14}$C differences as proposed by Hüls et al. (2011) (i.e. surface contamination by cutting tools) may be questioned. Instead, we speculate that fractionation effects occurred during carbon dissolution into the metal. For example, the measurements of sample ST-I-4-2 (0.1 wt% C) with the lowest amount of charcoal used (see Table 2), show a rather low efficiency in carbon uptake (e.g. overall C-content in metal vs. charcoal carbon available), depleted $^{14}$C concentrations ($\Delta F^{14}$C $\sim 1.9\%$), and increased $\delta^{13}$C values ($\sim 5\‰$ VPDB) with respect to the carbon source. For the remaining 4 standards with a higher carbon incorporation efficiency, one standard (ST-I-4-3, 1.9wt% C) give a $^{14}$C concentration in agreement, the other standards give depleted $^{14}$C concentrations ($\Delta F^{14}$C $\sim 1\%$), compared to the charcoal source. Clearly, more experimental smelting studies would be needed to verify if a fractionation effect could occur during real iron production, e.g. smelting, which, consequently, would be needed to be considered in $^{14}$C dating of iron.

Nydam Swords and Ax Head

Multiple $^{14}$C AMS measurements of the three Nydam weapon samples gave internally consistent and reproducible $^{14}$C ages (Table 3, Figure 3). With one exception, all carbon extractions from the iron lattice were done by method A. For one sample of FS4156, carbon extraction was done by a step-combustion with a low and high temperature (570°C and 980°C, respectively, method B2). The measured $^{14}$C concentration is consistent to the measurements done with CO$_2$ extractions by method A, which seems to indicate that the mechanical surface and subsequent solvent cleaning is sufficient for this type of sample material.

Calculated weighted mean $^{14}$C ages of swords FS4156, FS5409, and the ax head of 1824 $\pm$ 9 BP, 1734 $\pm$ 13 BP, and 1791 $\pm$ 13 BP, respectively, are in reasonable agreement with the expected deposition time of sacrifices 1, 3, and 4 (Figure 3). Calibrated sample ages are older by about 0–60 years, which is within or slightly more than an expected old-wood effect (e.g., average wood-age used to make charcoal for iron ore smelting) of only a few decades, as indicated in the study of Leroy et al. (2015). For example, variable (average) wood ages up to several decades are estimated by anthracological analysis of sample material from a 3rd–5th century AD iron production site in Joldelund, northern Germany, not far from Nydam (Dörfler and Wiethold 2000). An additional reservoir effect, caused by fractionation during iron production as seen in modern test samples, cannot be rejected nor confirmed.
Table 2  Modern iron standards: carbon content and measured mean carbon isotope composition (charcoal F$^{14}$C: 1.1667 ± 0.0017; δ$^{13}$C$_{AMS}$: −26.4 ± 0.17‰VPDB). C-uptake efficiency is calculated by comparison of measured C-content with expected C-content, assuming a charcoal carbon yield of 80wt%.

| Sample  | Lab ID   | Fe weight (mg) | Charcoal weight (mg) | C uptake efficiency (%) | C-cont meas. (wt%) | Mean F$^{14}$C (%mC) / No. of measurements | Mean δ$^{13}$C$_{AMS}$ (% VPDB) | Apparent $^{14}$C difference (‰) charcoal – iron | Reference               |
|---------|----------|----------------|----------------------|------------------------|-------------------|-----------------------------------------------|---------------------------------|-----------------------------------------------|-------------------------|
| ST-I-3-1| KIA53025 | 14700          | 1310                 | 74                     | 5.3               | 1.1556 ± 0.0025/ 2                            | −26.1                           | 1.1 ± 0.30                                     | This study              |
| ST-I-3-2| KIA29350 | 15000          | 1230                 | 84                     | 5.5               | 1.1573 ± 0.0081/ 6                            | −27.2                           | 0.9 ± 0.83                                     | Hüls et al. 2011        |
| ST-I-4-1| KIA29348 | 15000          | 350                  | 28                     | 0.5               | 1.1552 ± 0.0055/ 6                            | −14.1                           | 1.1 ± 0.56                                     | Hüls et al. 2011        |
| ST-I-4-2| KIA53026 | 14950          | 260                  | 7                      | 0.1               | 1.1481 ± 0.0042/ 3                            | −5.0                            | 1.9 ± 0.46                                     | This study              |
| ST-I-4-3| KIA29349 | 15040          | 600                  | 60                     | 1.9               | 1.1662 ± 0.0057/ 10                            | −21.3                           | 0.05 ± 0.60                                     | Hüls et al. 2011        |

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

2 Carbon estimated from CO2-pressure in our graphitization system.
Table 3  Radiocarbon measurements on Nydam iron objects.

| Sample name       | Lab ID   | Treatment | Weight combusted (mg) | C-weight (mg) | C-content (wt%) | F$^{14}$C | $\delta^{13}$CAMS (‰ VPDB) | $^{14}$C age BP |
|-------------------|----------|-----------|-----------------------|---------------|----------------|---------|-----------------------------|-----------------|
| FS4156, Kat. Nr. 404, sword | 18268    | A         | 620.2                 | 2.05          | 0.33%          | 0.7921 ± 0.0024 | -21.49 ± 0.04 | 1872 ± 25          |
|                   | 18268    | A         | 546.0                 | 2.61          | 0.48%          | 0.7970 ± 0.0022 | -20.35 ± 0.17 | 1872 ± 25          |
|                   | 32224    | A         | 975.6                 | 3.14          | 0.32%          | 0.7917 ± 0.0022 | -20.91 ± 0.18 | 1876 ± 23          |
|                   | 32224    | A         | 1050.7                | 3.51          | 0.33%          | 0.8005 ± 0.0025 | -26.92 ± 0.14 | 1787 ± 26          |
|                   | 32224    | A         | 944.3                 | 3.36          | 0.36%          | 0.7989 ± 0.0023 | -23.06 ± 0.10 | 1803 ± 24          |
|                   | 32224    | B2_HT     | 1125.0                | 3.47          | 0.31%          | 0.7971 ± 0.0024 | -23.18 ± 0.36 | 1822 ± 25          |
|                   | 32224    | A         | 1237.0                | 4.53          | 0.37%          | 0.7990 ± 0.0022 | -22.49 ± 0.22 | 1802 ± 22          |
|                   |          |           |                       |               |               |         | Weighted mean age:          | 1824 ± 9        |
| FS5409, Kat Nr. 431, sword | 18269    | A         | 729.8                 | 0.85          | 0.12%          | 0.8063 ± 0.0029 | -31.79 ± 0.12 | 1730 ± 30          |
|                   | 32223    | A         | 950.6                 | 0.91          | 0.10%          | 0.8079 ± 0.0036 | -23.98 ± 0.44 | 1715 ± 40          |
|                   | 32223    | A         | 628.0                 | 1.54          | 0.24%          | 0.8049 ± 0.0024 | -25.03 ± 0.13 | 1744 ± 25          |
|                   | 32223    | A         | 576.9                 | 1.60          | 0.28%          | 0.8101 ± 0.0027 | -27.27 ± 0.12 | 1692 ± 28          |
|                   | 32223    | A         | 704.7                 | 1.38          | 0.20%          | 0.8021 ± 0.0026 | -26.57 ± 0.23 | 1771 ± 27          |
|                   | 32223    | A         | 1340.3                | 1.05          | 0.08%          | 0.8060 ± 0.0030 | -23.56 ± 0.25 | 1735 ± 35          |
|                   |          |           |                       |               |               |         | Weighted mean age:          | 1734 ± 13       |
| Kat. Nr. 1865; ax | 19344    | A         | 574.4                 | 1.68          | 0.29%          | 0.8044 ± 0.0020 | -27.54 ± 0.5  | 1748 ± 20          |
|                   | 19344    | A         | 718.0                 | 2.10          | 0.29%          | 0.7909 ± 0.0025 | -28.65 ± 0.11 | 1885 ± 26          |
|                   | 19344    | A         | 982.0                 | 2.05          | 0.21%          | 0.8020 ± 0.0022 | -32.16 ± 0.18 | 1773 ± 22          |
|                   |          |           |                       |               |               |         | Weighted mean age:          | 1791 ± 13       |
| Nydam-13705, rivet | 48372    | B2_LT     | 1663.7                | 2.42          | 0.15%          | 0.1932 ± 0.0012 | -25.06 ± 0.16 | 13,205 ± 50        |
|                   | 48372    | B2_HT     | 1663.7                | 1.18          | 0.07%          | 0.7769 ± 0.0019 | -28.85 ± 0.12 | 2028 ± 20          |
| Nydam-13707, rivet | 48373    | A         | 1131.1                | 5.58          | 0.49%          | 0.6891 ± 0.0026 | -11.53 ± 0.24 | 2990 ± 35          |
|                   | 48373    | B2_LT     | 710.3                 | 1.72          | 0.24%          | 0.6354 ± 0.0018 | -7.07 ± 0.22  | 3643 ± 24          |
|                   | 48373    | B2_HT     | 710.3                 | 0.30          | 0.04%          | 0.7832 ± 0.0027 | -31.18 ± 0.22 | 1963 ± 28          |

(Continued)
Table 3 (Continued)

| Sample name  | Lab ID (KIA . . .) | Treatment | Weight combusted (mg) | C-weight (mg) | C-content (wt%) | F\(^{14}\)C | \(\delta^{13}\)C\(_{AMS}\) (‰ VPDB) | \(^{14}\)C age BP |
|--------------|-------------------|-----------|-----------------------|---------------|----------------|--------|-----------------|-----------------|
| Nydam-12444, rivet | 48374 | A         | 1066.7    | 2.74          | 0.26%          | 0.5886 ± 0.0023 | –17.03 ± 0.23 | 4260 ± 35 |
|               |       | B1_LT     | 969.4     | 1.14          | 0.12%          | 0.6024 ± 0.0018 | –10.68 ± 0.28 | 4072 ± 25 |
|               |       | B1_HT     | 969.4     | 0.17          | 0.02%          | 0.7266 ± 0.0031 | –22.22 ± 0.17 | 2565 ± 35 |
|               |       | B1_HT     | 1064.9    | 0.91          | 0.08%          | 0.7598 ± 0.0020 | –24.99 ± 0.17 | 2207 ± 22 |
| Nydam-13944, rivet | 48375 | A         | 1007.7    | 0.97          | 0.10%          | 0.6023 ± 0.0024 | –21.46 ± 0.1  | 4070 ± 35 |
|               |       | B2_LT     | 1216.5    | 0.92          | 0.08%          | 0.4507 ± 0.0016 | –16.51 ± 0.45 | 6402 ± 29 |
|               |       | B2_LT     | 1411.4    | 1.68          | 0.12%          | 0.5213 ± 0.0016 | –14.38 ± 0.14 | 5232 ± 24 |
|               |       | B2_HT_2*LT| 1216.5    | 0.52          | 0.04%          | 0.7826 ± 0.0023 | –27.99 ± 0.41 | 1969 ± 24 |
|               |       | B2_HT     | 1411.4    | 0.55          | 0.04%          | 0.7812 ± 0.0022 | –26.45 ± 0.27 | 1984 ± 23 |
| Nydam-6263, rivet | 48376 | A         | 1047.2    | 1.58          | 0.15%          | 0.6523 ± 0.0025 | –25.53 ± 0.1  | 3430 ± 35 |
|               |       | B2_LT     | 1280.0    | 0.38          | 0.03%          | 0.3177 ± 0.0029 | –23.87 ± 0.82 | 9210 ± 75 |
|               |       | B2_HT     | 1280.0    | 1.79          | 0.14%          | 0.7874 ± 0.0023 | –22.77 ± 0.99 | 1920 ± 24 |
| Nydam-6279, rivet | 48377 | A         | 1067.8    | 5.15          | 0.48%          | 0.7440 ± 0.0028 | –28.12 ± 0.19 | 2375 ± 30 |
|               |       | B1_LT     | 2649.3    | 2.77          | 0.10%          | 0.4739 ± 0.0016 | –22.79 ± 0.27 | 5999 ± 27 |
|               |       | B1_HT     | 2649.3    | 16.90         | 0.64%          | 0.7820 ± 0.0022 | –27.57 ± 0.33 | 1976 ± 23 |
| Nydam-3421, anchor | 48380 | A         | 1092.1    | 1.67          | 0.15%          | 0.7256 ± 0.0028 | –28.69 ± 0.27 | 2575 ± 35 |
Nydam Iron Rivets

Carbon extracted by method A gave $^{14}$C ages varying from $\sim$2300 BP to 4300 BP, much older than expected and thus indicating incomplete removal of carbon-containing contaminants (see Table 3). In the course of sample preparation, we recognized two contamination sources. All analyzed iron objects from the Nydam peat bog are significantly corroded, and for the Nydam iron rivets this corrosion consists almost exclusively of iron carbonate (siderite, FeCO$_3$; Matthiesen et al. 2003). After recovery, these rivets were further contaminated by soaking in liquid wax.

Due to the high thermal stability of the carbon dissolved in the iron, a step-combustion procedure was applied to remove low-temperature volatile carbon sources such as siderite (Gallagher and Warne 1981) and wax before the final extraction of carbon from the iron lattice with higher combustion temperatures.

The LT-CO$_2$ fractions from the Nydam rivets give varying apparent $^{14}$C ages greater than 4000 BP, giving evidence of a remaining contamination in the precleaned iron sample, originating from a mixture of wax and siderite.

With the exception of Nydam-12444, the HT-CO$_2$ fractions give $^{14}$C ages ranging from 1920 to 2020 BP. A double low-temperature combustion and subsequent high-temperature CO$_2$ extraction by method B2 of one subsample of Nydam-13944 gave a $^{14}$C age in accordance to the measurement of the other subsample with only one low-temperature combustion, and in agreement to the results obtained for Nydam-13707, -6263, and 6279 (see Table 3). Apparently, the first low-temperature combustion was already sufficient for a removal of low-temperature stable carbon fractions, since the 2nd low-temperature combustion did not produce CO$_2$.

The HT-CO$_2$ fractions of Nydam-12444, extracted by method B1 (using closed-tube combustion), gave $^{14}$C ages of 2207 $\pm$ 22 BP and 2565 $\pm$ 35 BP (Figure 4), significantly older than the HT-CO$_2$ measurements of the other iron rivets. The sample material after surface and solvent cleaning of Nydam-12444 contained visibly more foreign substances in comparison to the other rivets, which, assuming incomplete removal of exogenous carbon by the low-temperature combustion using method B1, could explain the measured $^{14}$C differences of the HT-CO$_2$ fraction of this sample. Maybe a longer-lasting low-temperature combustion time (i.e. $>$4 hr) is needed to completely remove the low-temperature carbon fraction.

Nevertheless, the overall close agreement between the HT-CO$_2$ $^{14}$C measurements between the rivets Nydam-13705, -13707, -13944, -6263, and Nydam-6279, and the result of the double

![Graph showing calibrated sample ages for swords FS4156, FS5409 and ax Kat_Nr 1865. Black bar below probability curves give the time span of sacrifices 1, 3, and 4, respectively.](image-url)
precombusted (at 570°C) subsample of Nydam-13944, indicate sufficient removal of siderite and wax contamination for these samples.

Calibrated sample ages of Nydam-13705, -13707, -13944, -6263, and Nydam-6279 lie between to 90 BC–AD130 (see Figure 3), which is at least 200 years older than the dendro-date for the construction of the large Nydam oak boat (i.e. AD 310–AD 320; Bonde 1990).

Assuming a complete removal of siderite and wax contamination by combustion below 600°C, additional contaminating carbon sources need to be considered. Possible preaged carbon sources could be the use of older trees for charcoal production, and/or fossil carbon added during the iron making (e.g., carbonates in ore or flux, geogenic material of smelting oven wall lining). None of the mentioned causes can be rejected nor confirmed without further metallographic analysis. Likewise, the possibility of an aging effect, caused during iron making as seen in modern test samples, cannot be excluded.

In contrast to the precleaning of the swords and ax head samples, contamination during the mechanical removal of corrosion and conservation coating of the rivets also remains possible. As outlined above, corrosion and wax was removed using a metal (iron) brush. While the mineral corrosion product and wax seem softer compared to the iron brush, the brush show a considerable wear after usage. A tiny amount of metal from the metal brush, containing fossil carbon as shown in previous studies for modern iron (a.o. Cook et al. 2001; Hüls et al. 2004; Scharf et al. 2004, etc.), could be responsible for an additional observed age difference, since the irregular shaped sample surface prevent additional cleaning by surface grinding using a corundum grinding tool.

Finally, one need to mention the possibility of a reuse of older iron, as was indicated by Disser et al. (2016) in their study of Carolingian architectural iron fastenings.

**Anchor Nydam-3421**

The metallurgical sample of an iron bar from a ship anchor gave a $^{14}$C age 2575 ± 35 BP, which is obviously too old with respect to its expected archaeological age (4th century AD). Although this sample appeared comparably well preserved, similar to the sword and ax head samples, the apparent age difference indicates the abundance of a significant amount of exogenous carbon, which likely comes from the embedding resin.
CONCLUSIONS

In this study we present the results of 14C measurements for 10 archaeological iron objects from the war booty offering site at Nydam, SE Denmark. Additionally, we measured the 14C composition of iron samples made with modern charcoal to evaluate possible contamination effects during handling of iron samples.

Measured 14C concentration of modern iron samples are depleted with respect to the original 14C composition of the charcoal used for the making of the standards. Due to the large amount of surface material removed during sample preparation, the measured isotopic differences may indicate isotope fractionation effects, requiring further studies to verify if this is a common effect occurring during iron making.

Multiple 14C measurements of sample material from two swords and one ax head give consistent age estimates. Corrected and calibrated sample ages are in good agreement with expected ages and indicate small old-wood effects.

A step-combustion carbon extraction procedure was applied for the 14C dating of 6 iron rivets to remove low-temperature volatile contamination before extraction of assumed original carbon dissolved in the iron. Measured 14C ages of HT-CO2 fractions of 5 rivets gave consistent 14C ages of 1920–2020 BP, about 200–300 years older compared to the dendro-age of the Nydam B oak boat (AD 310–AD 320, equivalent to ca. 1760 BP). Single or multiple aging effects such as the use of old wood during iron production and/or contamination with fossil C (during iron production or precleaning) might be responsible for the observed age difference. The reuse of older iron may also be a possible explanation.

The 14C age of an iron anchor fragment, associated to the Nydam ships (early 4th century AD), is significantly older than the inferred archaeological age, probably due to inefficient cleaning of sample material prior carbon extraction for 14C measurements.

ACKNOWLEDGMENTS

For valuable information on conservation methods of the Nydam artifacts, comments and assistance with the choice of potential samples: Jan Bruun Jensen, Curation and Cultural Heritage Conservation, National Museum of Denmark, Eva Salomonsen, Curation and Cultural Heritage Conservation, National Museum of Denmark, Henning Matthiesen, Environmental Archaeology and Materials Science, National Museum of Denmark. For the allowances to sample the Nydam iron material: Michael Gebühr, Archaeological Museum Schleswig-Holstein, Poul Otto Nielsen, Keeper of the Danish Prehistoric Collections and Environmental Archaeology at the National Museum of Denmark. The comments of two reviewers are appreciated.

REFERENCES

Bemmann G, Bemmann J. 1998a. Der Opferplatz von Nydam. Die Funde aus den älteren Grabungen: Nydam-I und Nydam-II. Band 1. Neumünster: Wachholtz Verlag.
Bemmann G, Bemmann J. 1998b. Der Opferplatz von Nydam - Die Funde aus den älteren Grabungen: Nydam I und Nydam II. Band 2. Neumünster: Wachholtz Verlag.
Bonde N. 1990. Dendrochronologische Altersbestimmung des Schiffes von Nydam. OFFA 47:157–168.
Buchwald VF. 2005. Iron and steel in ancient times. Copenhagen: The Royal Danish Academy of Sciences and Letters.
Cook AC, Wadsworth J, Southon JR. 2001. AMS radiocarbon dating of ancient iron artifacts: a
new carbon extraction method in use at LLNL. Radiocarbon 43(2A):221–227.
Cresswell RG. 1992. Radiocarbon dating of iron artifacts. Radiocarbon 34(3):898–905.
Disser A, Dillmann P, Leroy M, Merluzzo P, Leroy S. 2016. The bridge of Dieulouard (Meurthe-et-Moselle, France): a fresh perspective on metal supply strategies in Carolingian economy. ArcheoSciences 40:149–161.
Dörfler W, Wiethold J. 2000. Holzkohlen aus den Herdgruben von Rennfeueröfen und Siedlungsbe funden des spätkaiserzeitlichen Eisengewinnungs- und Siedlungsplatzes am Kam mberg bei Jodelund, Kr. Nordfriesland. In: Hoffner A, Jöns H, Reichenstein J, editors. Frühe Eisengewinnung in Jodelund, Kreis Nordfriesland: ein Beitrag zur Siedlungs- und Technikgeschichte Schleswig-Holsteins [aus dem Institut für Ur- und Frühgeschichte der Universität Kiel] (Universität). Bonn: Dr. Rudolf Habelt GmbH. p. 217–262.
Gallagher PK, Warne SSJ. 1981. Thermomagnetometry and thermal decomposition of siderite. Thermochimica Acta 43(3):253–267.
Hüls CM, Groottes PM, Nadeau M-J. 2011. Sampling iron for radiocarbon dating: influence of modern steel tools on δ14C dating of ancient iron artifacts. Radiocarbon 53(1):151–160.
Kusakabe M. 2005. A closed pentane trap for separation of SO2 from CO2 for precise δ18O and δ34S measurements. Geochemical Journal 39:285–287.
Leroy S, L’Héritier M, Delqué-Kolic E, Dumoulin J-P, Moreau C, Dillmann P. 2015. Consolidation or initial design? Radiocarbon dating of ancient iron alloys sheds light on the reinforcements of French Gothic cathedrals. Journal of Archaeological Science 53: 190–201.
Matthiesen H, Hilbert LR, Gregory DJ. 2003. Siderite as a corrosion product on archaeological iron from a waterlogged environment. Studies in Conservation 48(3):183–194.
Nadeau M-J, Groottes PM. 2013. Calculation of the compounded uncertainty of 14C AMS measurements. Nuclear Instruments and Methods in Physics Research 294:420–425.
Rau A. 2010. Nydam Mose 1–2. Die personen-gebundenen Gegenstände. Aarhus: Aarhus University Press.
Reimer PJ, Bard E, Bayliss A, Beck JW, Blackwell PG, Bronk Ramsey C, Buck C, Cheng H, Edwards RL, Friedrich M, Grootes PM, Guilderson TP, Haf lidason H, Hajdas I, Hatté C, Heaton TJ, Hoffman DL, Hogg AG, Hughen KA, Kaiser KF, Kromer B, Manning SW, Niu M, Reimer RW, Richards DA, Scott EM, Southon JR, Staff RA, Turney CSM, van der Plicht J. 2013. IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. Radiocarbon 55(4):1869–1887.
Rieck F. 2013. Funde von Schiffen und Schiffsteilen aus dem Nydam Moor 1859-2011. In: Rau A, editor. Nydam Mose Band 4: Die Schiffe. Aarhus: Aarhus University Press. p. 1–147.
Scharf A, Kretschmer W, Morgenroth G, Uhl T, Kritzler K, Hunger K, Pernicka E. 2004. Radiocarbon dating of iron artifacts at the Erlangen AMS facility. Radiocarbon 46(1):175–180.
Thomsen R. 1992. Metallografiske undersøgelser af sværd og spidsviser fra mosefundene i Illerup og Nydam. Aarbøger for Nordisk Oldkyndighed og Historie 1992, p. 281–310.
Van der Merwe NJ. 1969. The carbon-14 dating of iron. Chicago: The University of Chicago Press.
Van der Merwe N, Stuiver M. 1968. I. Dating iron by the carbon-14 method. Current Anthropology 9(1):48–53.
Vogel JS, Southon JR, Nelson DE, Brown TA. 1984. Performance of catalytically condensed carbon for use in accelerator mass spectrometry. Nuclear Instruments and Methods in Physics Research 5:289–293.