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

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ABSTRACT. Radiocarbon (^{14}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}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}C concentrations, compared to the initial charcoal ^{14}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}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}C dating of iron rivets from the Nydam (B) oak boat proved difficult due to corrosion with siderite (FeCO_3) and conservation with wax. A step-combustion procedure was applied, using a low ($\sim 570\text{--}600^\circ\text{C}$) temperature prior to the high ($\sim 970\text{--}1000^\circ\text{C}$) combustion temperature for carbon extraction, aiming to remove siderite and wax before collecting the original carbon dissolved in the iron lattice. Nevertheless, measured ^{14}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}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}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}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).

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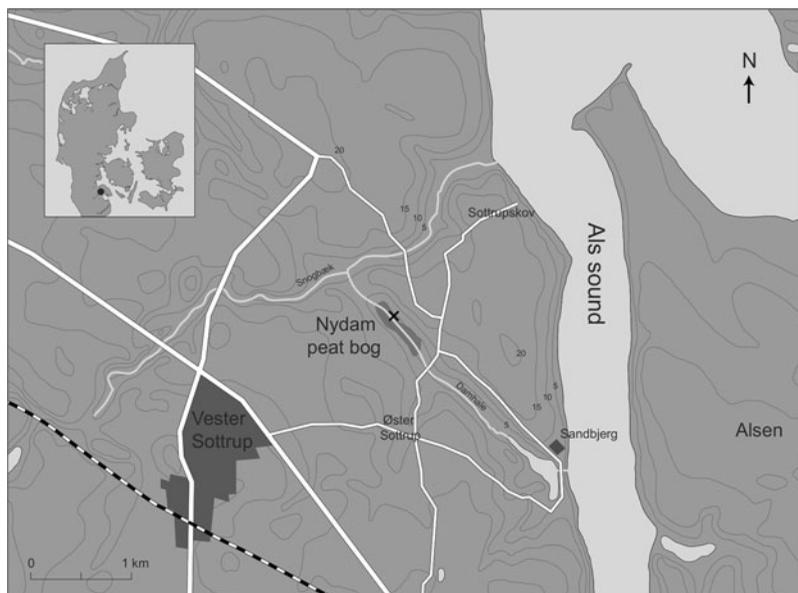


Figure 1 Location of the Nydam peat bog and the location of the Nydam B oak boat in particular (x).

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% 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.

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

Sample name	Lab ID	Description	Expected age
ST-I-3-1	KIA53025	Pure Fe + charcoal	Modern
ST-I-4-2	KIA53026	F^{14}C : 1.1667	F^{14}C : 1.1667 ± 0.0017 ~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

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 (F^{14}C : 1.1667 ± 0.0017 ; $\delta^{13}\text{C}_{\text{AMS}}$: $-26.4 \pm 0.17\%$ VBDB) ([Hüls et al. 2011](#)), heated up to $\sim 1600^\circ\text{C}$ 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.

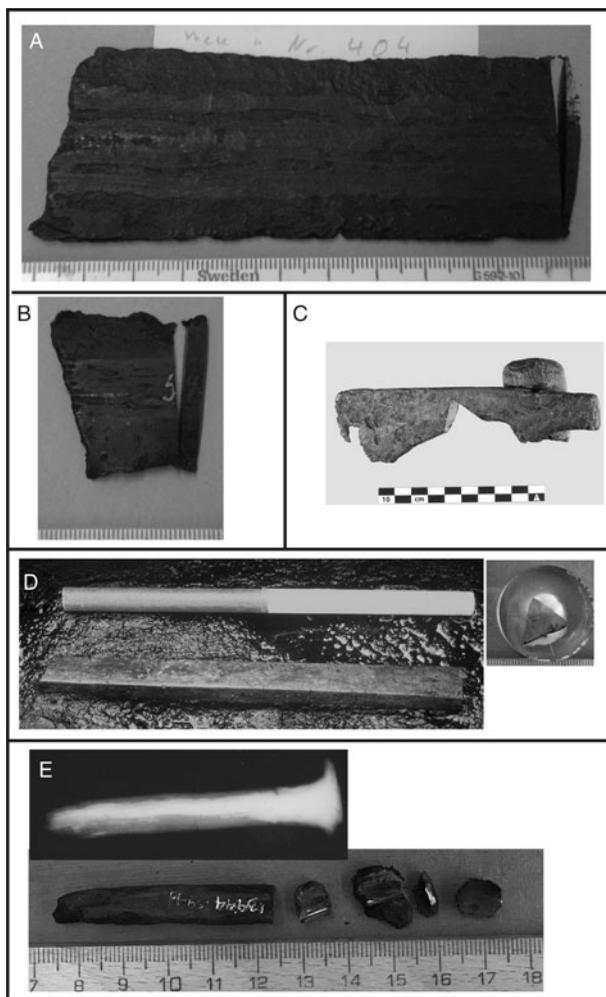


Figure 2 Iron samples from the Nydam peat bog. A: sword fragment FS4156, B: sword fragment FS5409, C: ax Kat.Nr.1865 (© Museum für Archäologie Schloss Gottorf, Landesmuseen Schleswig-Holstein), D: iron bar (find situation, upper scale is 40 cm) and metallographic object carrier of this sample used for C measurements, and E: one example of Nydam rivets (Nydam-13944; upper figure: X-ray image [© Roland Aniol, Museum für Archäologie Schloss Gottorf, Landesmuseen Schleswig-Holstein], lower figure: situation during sample preparation).

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 tetrahydrofuran (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 Tandem 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 ≥ 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 ($\Delta F^{14}\text{C} \sim 1.9\%$), and increased $\delta^{13}\text{C}$ values (-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, 1.9 wt% C) give a ^{14}C concentration in agreement, the other standards give depleted ^{14}C concentrations ($\Delta F^{14}\text{C} \sim 1\%$), 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 ± 9 BP, 1734 ± 13 BP, and 1791 ± 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 ; $\delta^{13}C_{AMS}$: -26.4 ± 0.17 ‰VDB). C-uptake efficiency is calculated by comparison of measured C-content with expected C-content, assuming a charcoal carbon yield of 80wt%.

Sample ¹	Lab ID	Fe weight (mg)	Charcoal weight (mg)	C uptake efficiency (%)	C-cont meas. (wt%) ²	Mean $F^{14}C$ (%mC) / No. of measurements	Mean $\delta^{13}C_{AMS}$ (‰ 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 (KIA ...)	Treatment	Weight combusted (mg)	C-weight (mg)	C-content (wt%)	F ¹⁴ C	δ ¹³ C _{AMS} (‰ 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	1823 ± 22
	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 ± 0.09	1803 ± 24
	32224	A	591.3	4.26	0.72%	0.7990 ± 0.0025	-23.85 ± 0.08	1802 ± 25
	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
		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
		B2_LT	710.3	1.72	0.24%	0.6354 ± 0.0018	-7.07 ± 0.22	3643 ± 24
		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	δ 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
Nydam-6263, rivet	48376	B2_HT	1411.4	0.55	0.04%	0.7812 ± 0.0022	-26.45 ± 0.27	1984 ± 23
		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
Nydam-6279, rivet	48377	B2_HT	1280.0	1.79	0.14%	0.7874 ± 0.0023	-22.77 ± 0.99	1920 ± 24
		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
Nydam-3421, anchor	48380	B1_HT	2649.3	16.90	0.64%	0.7820 ± 0.0022	-27.57 ± 0.33	1976 ± 23
		A	1092.1	1.67	0.15%	0.7256 ± 0.0028	-28.69 ± 0.27	2575 ± 35

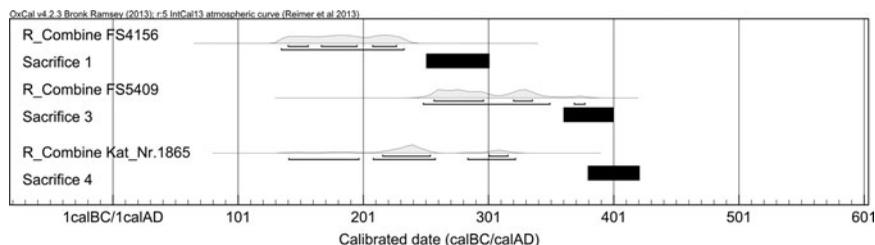


Figure 3 Calibrated sample ages for swords FS4156, FS5409 and ax Kat_Nr 1865. Black bar below probability curves give the time span of sacrifices 1, 3, and 4, respectively.

Nydam Iron Rivets

Carbon extracted by method A gave ^{14}C ages varying from ~ 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 ± 22 BP and 2565 ± 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

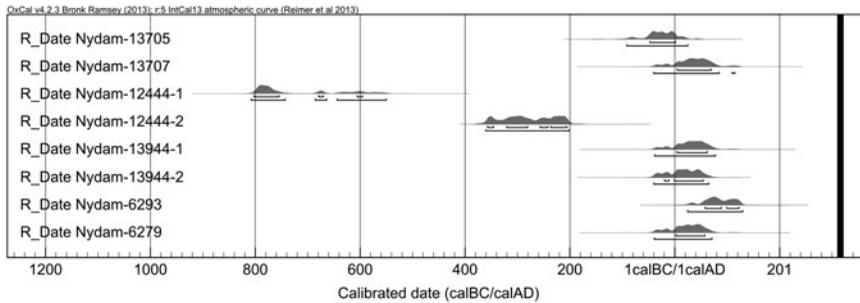


Figure 4 Calibrated sample ages Nydam iron rivets (pale gray area). Dendro-age for Nydam B is indicated.

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

Measured ^{14}C concentration of modern iron samples are depleted with respect to the original ^{14}C 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 ^{14}C 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 ^{14}C dating of 6 iron rivets to remove low-temperature volatile contamination before extraction of assumed original carbon dissolved in the iron. Measured ^{14}C ages of HT- CO_2 fractions of 5 rivets gave consistent ^{14}C 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 ^{14}C 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 ^{14}C measurements.

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