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journal homepage: www.elsevier.com/locate/nimb The hardwater effect in AMS ^{14}C dating of food crusts on potteryBente Philippsen^{a,*}, Henrik Kjeldsen^a, Sönke Hartz^b, Harm Paulsen^b, Ingo Clausen^c, Jan Heinemeier^a^aAMS ^{14}C Dating Center, Department of Physics and Astronomy, University of Aarhus, Ny Munkegade, Bygn. 1520, 8000 Århus C, Denmark^bArchäologisches Landesmuseum, Stiftung Schleswig-Holsteinische Landesmuseen, Schloss Gottorf, 24837 Schleswig, Germany^cDezernat 5 (Süd) Außenstelle Neumünster, Archäologisches Landesamt Schleswig-Holstein, Gartenstraße 10, 24534 Neumünster, Germany

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ABSTRACT

The pottery investigated in this study comes from late mesolithic inland sites next to rivers in Northern Germany. The first AMS ^{14}C datings of food crusts from these sites showed surprisingly high ages, which could be caused by the hardwater effect.

Modern samples from the rivers have ages of several hundred ^{14}C years, and a modern food crust prepared from fish with a certain reservoir age shows the same age as the fish. Surprisingly, there was a large age difference between water samples and fish/mollusc shell from the same river. Associated archaeological samples of terrestrial and fluvial origin show age differences of several hundred and up to 3000 years. These high age differences are only to a limited extent transferred to the archaeological food crusts.

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1. Introduction

Pottery is one of the most important materials for prehistoric archaeology and often used to define cultures and to study cultural contacts and developments. For relating the archaeological sequences to a calendar time scale, an accurate scientific dating of the pottery is essential. Radiocarbon dating of pottery is often possible when charred organic remains ("food crusts") are preserved on the pots, as these can be regarded contemporaneous to the usage of the pottery. Problems arise when the food crusts are affected by reservoir effects.

In the case of a reservoir with a different radiocarbon activity than the atmosphere, corrections of the initial radiocarbon activity have to be applied. Otherwise, spurious ages would be obtained. The effect the radiocarbon activity of a certain reservoir has on the radiocarbon age of a sample is called reservoir effect. There are different sources of ^{14}C depleted carbon in freshwater environments. The most important is the dissolution of geologic carbonates. In this case, the freshwater reservoir effect is called hardwater effect. The water hardness is defined as the concentration of the alkaline earth metal ions, predominantly calcium and magnesium. They originate often from carbonates. The water hardness is therefore an indicator of the carbonate concentration and thus of the amount of ^{14}C -dead material in the water. The hardwater effect is expected to be greater in running water (riv-

ers), than in stagnant water (lakes). If there is not a noticeable meltwater component, river water consists largely of groundwater [8].

The effect of dissolved bicarbonates on the radiocarbon age has been anticipated very early, when Godwin [4] examined dates from British lake deposits. The occurrence of the hardwater effect on food crusts on pottery was first proposed in 2003 [5].

The mechanisms leading to the hardwater effect are explained in [3] and [6]. Dissolved inorganic carbon (DIC) is a mixture of active carbon from soil gas CO_2 and old carbon from carbonate in the subsurface. The definition of DIC comprises four species: (1) Carbon dioxide CO_2 , (2) Carbonic acid H_2CO_3 , (3) Hydrogencarbonate HCO_3^- , (4) Carbonate CO_3^{2-} . In the soil, root respiration and the decay of organic material release CO_2 . In contact with water, a small amount of this CO_2 forms carbonic acid (H_2CO_3) which can dissolve lime from the surrounding rock. The dissolved lime hardly contains any ^{14}C because of the high age of the lime stone. When an extensive amount of the CO_2 in the water has a high age, then plants that incorporate this CO_2 via photosynthesis will accordingly show high radiocarbon ages. Correspondingly, fish that feed on these plants, will also have too high radiocarbon ages. This effect could also be transferred to food crusts on pottery in which a considerable amount of aquatic food was cooked.

2. Measurements and results

The sites analysed in this work are shortly occupied hunting stations from the Ertebølle culture. The archaeological period of

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Table 1

^{14}C datings and stable isotope values of modern samples. Note that the water samples are much older than the fishbones from the same rivers, and that even the snail-shell is younger than the water-DIC. DI (“dual inlet”) denotes mass spectrometric measurements on CO_2 , yielding $\delta^{13}\text{C}$. EA (“elemental analyzer”) denotes measurements directly on the pretreated sample, using continuous flow (EA–CF), yielding both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. For the calculation of the reservoir age in years, the physical mean life of ^{14}C , 8267 a, was used.

Lab no. AAR	Sample material	pmC	^{14}C age (year BP)	Reservoir age (year)	$\delta^{13}\text{C}$ ‰w.r.t. PDB	$\delta^{15}\text{N}$ ‰w.r.t. AIR
<i>Alster</i>						
11779	Water	78.28 ± 0.32	1966 ± 33	2449 ± 45	–14.96 (DI)	
11461	Snail-shell	94.75 ± 0.37	433 ± 32	868 ± 47	–15.36 (DI)	
11462	Fishbone	97.27 ± 0.35	222 ± 29	653 ± 46	–25.29 (EA) –25.46 (DI)	12.24
<i>Trave</i>						
11780	Water	86.54 ± 0.57	1170 ± 55	1631 ± 63	–13.59 (DI)	
11394	Fishbone (fresh)	96.51 ± 0.38	284 ± 32	722 ± 47	–26.00 (EA) –25.91 (DI)	15.02
11396	Fishbone (cooked)	97.00 ± 0.34	244 ± 28	679 ± 41	–24.30 (EA) –24.24 (DI)	15.66
11414	Food crust (fish)	96.11 ± 0.31	371 ± 23	756 ± 41	–28.14 (EA) –30.47 (DI)	18.08
11411	Food crust (boar meat)	106.87 ± 0.45	-537 ± 34		–17.84 (EA) –18.03 (DI)	7.91

the Ertebølle culture is called Nordic Terminal Mesolithic. It is the transition from the hunter–gatherer society to a farming society. Although the economy of the Ertebølle culture is Mesolithic (hunting, gathering and fishing), some aspects of a Neolithic way of life had been adopted. This includes the use of pottery, a tendency towards sedentariness and possibly the first domesticated animals. The pottery examined in this study is believed to be the first pottery that was made in Northern Germany. The rivers in the study area contain hard (carbonate-rich) water, so that a hardwater effect is expected.

Modern water samples, fish, and food crusts on pottery have been radiocarbon dated to determine the possibility and order of magnitude of the freshwater effect. Water dating was done on the DIC. Fish dates were obtained from the bone collagen. Archaeological food crusts as well as associated samples of terrestrial and

fluvial origin have been dated. If applicable, the same sample preparation methods were used for both sample categories, modern and archaeological. The results of the radiocarbon datings are presented in Tables 1 and 2.

With F being the fraction modern carbon of the riverine sample and F_0 the corresponding value of the terrestrial sample, the reservoir age Δt can be calculated as

$$\Delta t = \tau(\ln F_0 - \ln F) = \tau \ln \frac{F_0}{F}. \quad (1)$$

If the reservoir age is to be expressed in radiocarbon years, the conventional mean life 8033 a belonging to Libby's radiocarbon half-life has to be taken. For an estimation of the reservoir effect in calendar years, the mean life of 8267 a belonging to the physical half-life of radiocarbon, 5730 a, is used.

Table 2

Kayhude, Alster and Schlammersdorf, Trave – archaeological samples. The fishbones from both sites are much older than the other samples, and none of the food crusts is as old as the fishbone. The food crust samples have about the same or higher ages than the terrestrial samples. The ages of terrestrial samples from Schlammersdorf are widely spread, but still the fishbones are significantly older. See Table 1 for an explanation of “EA”/“DI”.

Lab no. AAR	Sample material	^{14}C age	Date calendar BC (95.4%)	$\delta^{13}\text{C}$ ‰w.r.t. VPDB	$\delta^{15}\text{N}$ ‰w.r.t. AIR
<i>Alster</i>					
11403	Food crust	5692 ± 54	4690 – 4374	–29.80 (EA) –28.63 (DI)	6.51
11403	Food crust (humic)	6740 ± 160	5984 – 5379		
11404	Food crust	6088 ± 56	5209 – 4849	–28.74 (EA) –28.90 (DI)	11.28
11479	Food crust	5349 ± 106	4443 – 3960	–26.53 (EA)	1.78
11480	Charcoal	5437 ± 41	4359 – 4178	–24.83 (DI)	
11695	Fishbone (pike)	8514 ± 83	7734 – 7369	–22.41 (DI)	
<i>Trave</i>					
11398	Wildcat	5685 ± 60	4687 – 4371	–19.16 (EA) –19.27 (DI)	6.60
11399	Beaver	6480 ± 90	5618 – 5303	–22.54 (EA) –22.42 (DI)	4.68
11400	Wild boar	6035 ± 60	5206 – 4780	–21.20 (EA) –21.39 (DI)	5.01
11407	Burnt wood	5750 ± 90	4796 – 4371	–27.03 (DI)	
11476	Red deer	6275 ± 65	5461 – 5047	–23.63 (DI)	
11476	Red deer	6370 ± 65	5475 – 5223	–23.54 (DI)	
11481	Food crust	6850 ± 120	5987 – 5559	–27.23 (EA)	–9.44
	Outer crust	5190 ± 110	4321 – 3715	–28.01 (EA)	–6.36
11482	Food crust	5590 ± 110	4707 – 4237	–27.03 (EA)	–9.39
11483	Plant rest from sherd	5985 ± 50	4999 – 4729	–27.36 (EA) –27.62 (DI)	–5.12
11484	Food crust	5830 ± 180	5207 – 4344	–27.46 (EA)	–19.49
11842	Fishbone	7640 ± 65	6631 – 6398	–26.78 (DI)	
11844	Fishbone	7620 ± 110	6679 – 6237

Fig. 1. Calibrated ages of samples from Kayhude, Alster and Schlammersdorf, Trave. The age ranges of terrestrial and fluvial samples are marked with shading, and food crust dates are marked with pictures of Ertebølle pottery. (a) Kayhude, (b) Schlammersdorf.

2.1. Modern samples

In the case of recent samples, F_0 is the fraction modern carbon of the atmosphere at the moment of collecting the samples from the river (Summer 2007). The relevant atmospheric radiocarbon concentration, measured in southern Germany and Switzerland, was between 105 and 105.5 pmC (pers. comment Bernd Kromer). Modern reservoir ages are only estimates because of the unknown influence the bomb pulse had on the carbon entering the river. Table 1 shows the dating results and reservoir ages for both rivers. The DIC of the river water has a radiocarbon age of 1966 (Alster) and 1170 (Trave) radiocarbon years, which results in estimated reservoir ages of about 2450 and 1630 calendar years, respectively.

In contrast to that, fishbones from recent fish have radiocarbon ages of 220 (Alster) and 280 (Trave) radiocarbon years and estimated reservoir ages of 650 (Alster) and 720 (Trave) calendar years. There are several possible explanations for the age differences between water and fish. Firstly, the fish we caught for our studies, the common roach/*Rutilus rutilus*, could partly feed on terrestrial food sources (surface insects or terrestrial material that is washed into the river?), and not only on water animals and water plants. Secondly, the water dating only represents a snap-shot of the water's radiocarbon age at the moment of sampling, while the fishbone radiocarbon age is integrated over the time of bone formation. It is possible that the reservoir age of the water varies with season or weather conditions like amount of rainfall. Thirdly, we only measured DIC, and not the reservoir age of the total carbon available to the fish.

As the main study material are archaeological food crusts on pottery, not only water and fish have been analysed, but also recent food crusts. For this purpose, two food crusts have been prepared: One from the roach, and one from wild boar as a terrestrial control material. The wild boar food crust had a radiocarbon age of –540 radiocarbon years BP (see Table 1), out of the range of the used calibration curve “Kueppers et al.” [7]. The curve was extended to present using an exponential decay curve. The calibrated age of the wild boar food crust is 3 ± 2 years. An age like this was expected, since the incorporation of atmospheric CO_2 takes about one year, and as the meat which was bought frozen in July most likely came from a wild boar that was killed in the autumn before. The wild boar's $\delta^{13}\text{C}$ value shows that it was fed with C4-plants (probably maize), which did not play a role in the nutrition of archaeological wild boars from that area. The fish food crust has a radiocarbon age of 370 ^{14}C years BP and its reservoir age is estimated to 760 calendar years. It has thus the same age as the bones of the fish from which the crust has been made.

2.2. Archaeological samples

Table 2 shows the radiocarbon determinations on archaeological material. They were calibrated with OxCal [1,2] using the ter-

restrial calibration curve IntCal04 [9]. In Fig. 1, the calibrated ages of the samples can be seen. The age ranges of terrestrial and fluvial samples are marked with shading, and food crust dates are marked with pictures of Ertebølle pottery.

There is a remarkable age difference between fishbone samples and terrestrial samples for both sites. In Schlammersdorf, there is a big variability of terrestrial ages, which might be caused by the unsure stratigraphy. Being situated close to rivers, both sites were repeatedly inundated, and no clear stratigraphy could be seen. However, the fishbone dates are significantly older than the terrestrial samples. At both sites, the food crust samples have the same or higher ages than the terrestrial samples. None of the food crusts is as old as the fishbones. If one assumes that the food crusts and fishbones were contemporary, it would mean, that the food crusts are not exclusively made from fish but from a mixture of freshwater fish and terrestrial ingredients. The $\delta^{13}\text{C}$ values indicate a significant freshwater component, but terrestrial plants cannot be ruled out either. $\delta^{15}\text{N}$ values can apparently not be used for the identification of the ingredients, as some food crusts even had negative $\delta^{15}\text{N}$ values. It is not yet clear which mechanism causes these unusual $\delta^{15}\text{N}$ values.

3. Future plans

The hardwater effect in the rivers Alster and Trave will be monitored by analysing water samples that will regularly be taken throughout the next year. This will show if the very high reservoir ages were exceptional, or if the reservoir ages generally are high in these rivers. Additionally, DOC and more organic samples from the rivers like plants, fish and molluscs will be collected. The water plants should show reservoir ages that are integrated over the whole growth period of the plants, whereas fish show integrated reservoir ages of all their food sources. This will hopefully explain the age difference we measured between the roach and the water. ^{14}C and stable isotopes will be measured on food crusts produced from plants and from different mixtures of fish, terrestrial meat and plants. Other analysis methods will also be tested. The aim is to find a method that can be applied to the archaeological food crusts for identifying the former ingredients of the meals cooked in the stone age vessels.

References

- [1] C. Bronk Ramsey, Radiocarbon 37 (2) (1995) 425–430.
- [2] C. Bronk Ramsey, Radiocarbon 43 (2A) (2001) 355–363.
- [3] I.D. Clark, P. Fritz, Environmental Isotopes in Hydrogeology, Lewis Publishers, CRC Press LLC, New York, Boca Raton, 1997.
- [4] H. Godwin, Am. J. Sci. 249 (1951) 301–307.
- [5] A. Fischer, J. Heinemeier, Radiocarbon 45 (2003) 449–466.
- [6] J.-C. Fontes, J.-M. Garnier, Water Resour. Res. 15 (1979) 399–413.
- [7] L.M. Kueppers, J. Southon, P. Baer, J. Harte, Oecologia 141 (4) (2004) 641–651.
- [8] J.N. Lanting, J. Van der Plicht, Palaeohistoria 37/38 (1995/1996) 491–519.
- [9] P.J. Reimer et al., Radiocarbon 46 (3) (2004) 1029–1058.