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FRESHWATER RESERVOIR EFFECT IN ^{14}C DATES OF FOOD RESIDUE ON POTTERY

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ABSTRACT. Radiocarbon dates of food residue on pottery from northern European inland areas seem to be influenced significantly by the freshwater reservoir effect ("hardwater" effect) stemming from fish and mollusks cooked in the pots. Bones of freshwater fish from Stone Age Åmose, Denmark, are demonstrated to be 100 to 500 ^{14}C yr older than their archaeological context. Likewise, food residues on cooking pots, seemingly used for the preparation of freshwater fish, are shown to have ^{14}C age excesses of up to 300 yr. It is probable that age excesses of similar or even larger magnitude are involved in food residue dates from other periods and regions. Since this effect cannot, so far, be quantified and corrected for, ^{14}C dating of food residue, which may potentially include material from freshwater ecosystems, should be treated with reserve.

BACKGROUND AND HYPOTHESIS

Radiocarbon dates of charred food remains on pottery have become very popular among archaeologists. In principle, this kind of material has the obvious advantage of indisputable chronological association with the very usage of the pottery, a category of artifacts of fundamental importance for the study of prehistoric cultural processes. In practice, however, it has recently become apparent that many ^{14}C dates of food residue from northern Europe are up to several centuries older than expected from other kinds of evidence (Fischer 2002; cf. Koch 1998:96, 98, 101, 107; Persson 1999:86).

Some of these surprisingly old food residue dates are probably due to the marine reservoir effect, which applies to cases where the $\delta^{13}C$ values are greater (less negative) than about –26‰ (see below). This paper discusses the hypothesis that dates of food residue which do not contain material of marine origin may also have significant reservoir effects, in this case stemming from freshwater organisms such as fish and mollusks cooked in the pots. This hypothesis was formulated on the basis of the following observations and inferences:

- Many of the surprisingly old food residue dates from northern Europe derive from Stone Age pots which are found in inland regions, including the Åmose bog in eastern Denmark. Some of the most striking examples are marked in Figure 1.
- Examinations of Stone Age food residue on pottery found in the inland have revealed remains of bones and scales of freshwater fish, which apparently have been cooked in the vessels (Koch 1998:151).
- In the Åmose, which is a bog with very fine preservation conditions for food remains, bones and scales from freshwater fish and shells from freshwater mollusks (*Anodonta*) often constitute a major part of Stone Age culture layers. Consequently, freshwater food is expected to have been a frequent ingredient in the food prepared in the cooking vessels found in this bog and probably in cooking pots found in other wetlands as well, where faunal remains were not so well preserved.
- Present-day river water and freshwater fish and mollusks from other parts of northern Europe are reported to have reservoir ages in the order of several hundred to a few thousand yr (Lanting and van der Plicht 1996, 1998; Heinemeier et al. 1997; Heinemeier and Rud 1998; Cook et al. 2001). Similarly, several studies have reconstructed past reservoir ages, based on pre-bomb samples in freshwater systems (e.g. Heier-Nielsen et al. 1995; Geyh et al. 1998). Thus, it can be expected that freshwater organisms prepared in the cooking pots from Stone Age Åmose have

significant apparent ages. This age offset can result from the hardwater effect and other varieties of reservoir effect.

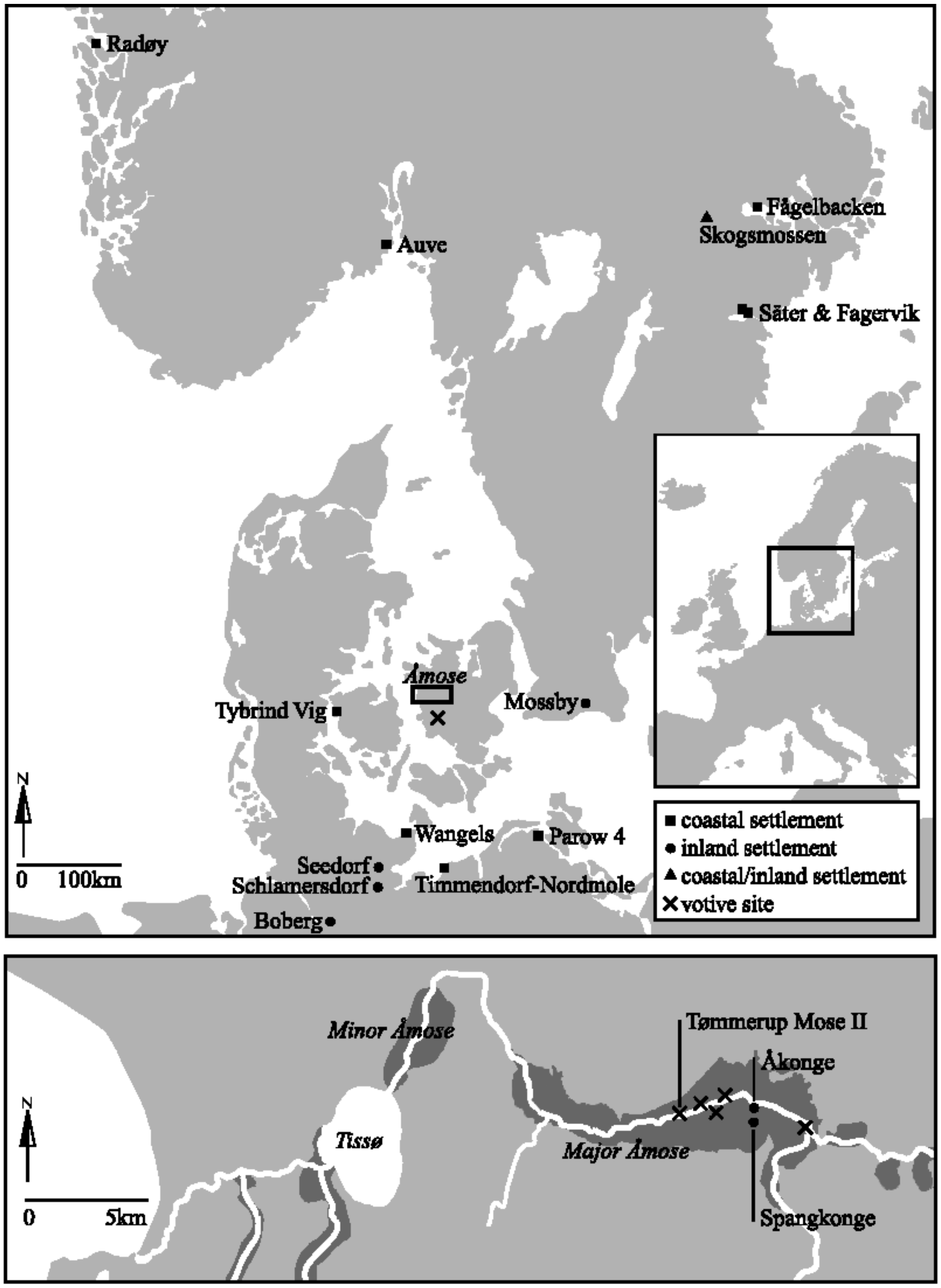

Figure 1 Northern European Stone Age sites with ^{14}C-dated food residue on pottery, some of which has produced surprisingly old dates. In the case of the coastal settlements (rectangular signatures), the age offsets probably derive primarily from hitherto unrecognized marine reservoir effect. The apparent age of food residues from inland settlements (round signatures) and votive pots (x signatures) can in most cases be explained by hitherto unrecognized freshwater reservoir effect.

FOOD RESIDUE

In this paper, the term "food residue" refers to charred, usually dark residues up to several mm thick, which adhere to the inner surface of cooking pottery (Figure 2). The color of this material varies from pot to pot from black to dark brown to brownish gray—probably reflecting differences in the original composition, as well as in the secondary decomposition of the residue. It is generally considered to be the remains of food, fixed to the vessels during the cooking process (e.g. Andersen and Malmros 1985; Koch 1987, 1998; Isaksson 1997; Persson 1997, 1999; Nakamura et al. 2001).

Figure 2 Food residue on the inner surface of a sherd of a cooking pot from the Åkonge site. On this sherd, major parts of the approximately 1-mm-thick layer have peeled off (scale in cm). Photo courtesy of John Lee, The National Museum of Denmark.

The same kind of residue is regularly seen on the upper parts of the outer surface of many cooking vessels, where it probably ended up as a result of boiling over (cf. Andersen and Malmros 1985; Koch 1987, 1998:117). On the upper parts of the outer surface of such pots, another, generally thinner and more glossy coating is often seen, too (Figure 3). The latter seems (primarily) to be deposits of soot from the cooking fire (cf. Koch 1998:117).

A study of hundreds of Neolithic wetland votive pots with well-preserved traces of use concludes that the vessels in question were used for boiling food (Koch 1998:117). The blistery inner structure, which is often seen in the organic residues on the inner surface of the vessels, has been interpreted

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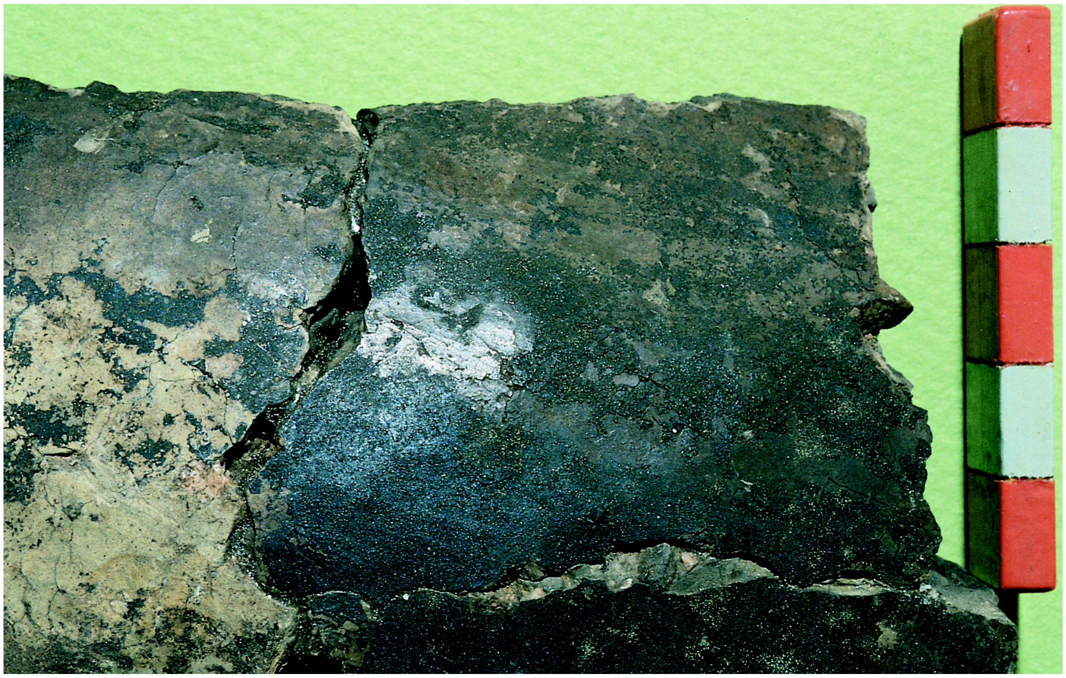

Figure 3 Potsherd with a thin layer of glossy, dark coating on its outer surface, probably mainly consisting of soot from the cooking fire (scale in cm). Photo courtesy of Geert Brovad, The Zoological Museum, Copenhagen.

as a result of intentional fermentation (Arrhenius 1984; Arrhenius and Lidén 1989; Isaksson 1997), but might also have resulted from boiling food. Observation of microscopic fragments of pottery, which apparently have entered such food residue as a result of stirring, may indicate that the food was soup or porridge (Isaksson 1997).

Chemical analyses have revealed a diversity of fats, proteins, and trace elements in food residue on northern European pottery (Arrhenius 1984; Arrhenius and Lidén 1989; Lidén 1990; Isaksson 1997; cf. Malainey et al. 1999). Microscopic examination has, furthermore, demonstrated stray fragments of plant material in a matrix lacking cellular structure (Arrhenius 1984; Andersen and Malmros 1985; Arrhenius and Lidén 1989; Isaksson 1997).

From the coastal Mesolithic site *Tybrind Vig*, food residues with clearly visible remains of vegetable matter as well as bones and scales of marine fish are reported (Andersen and Malmros 1985; cf. Koch 1998:305). Likewise, organic residues adhering to the inner surfaces of Stone Age cooking pots from inland bogs have been demonstrated to include scales and bones of freshwater fish (Koch 1998:151, 307, 320; cf. Koch 1998:321, 323, 339). An apple seed embedded in the food residue is also reported (Koch 1998:119).

Most of the dates of food residue presented in Table 3 and 4 were made at the AMS laboratory at the University of Aarhus, Denmark (labeled "AAR"). The samples were given a standard AAA treatment (1M HCl and NaOH at 80 °C for several hr prior to combustion and graphitization for dating). The ^{14}C dates are reported in accordance with international convention (Stuiver and Polach 1977) and normalized to a δ^{13}C of –25‰ VPDB as described in Andersen et al. 1989. Table 3 also includes some dates produced by the AMS laboratory in Uppsala, Sweden (samples labeled "Ua"). To this are added a number of context dates produced by the former ^{14}C laboratory in Copenhagen (labeled "K").

TEST DESIGN

The Åmose in eastern Denmark (Figure 1) stands out as a suitable case for testing the hypothesis on freshwater reservoir effect in food residue on pottery from inland areas. Among the numerous Stone Age sites from this bog, the kitchen midden at the Åkonge site (Fischer 1985, 1999, 2002) was selected as the primary source of data. It consists of 2 stratigraphic units, termed layer 3a (upper part of the midden) and layer 3b (lower part of the midden). Both of these layers include pottery with food residue, and both are rich in organic cultural remains of direct relevance, such as bones of freshwater fish and marrow-split bones of terrestrial mammals (Figure 4).

Figure 4 A 0.5 × 0.5 m square of the Åkonge inland kitchen midden during excavation, seen obliquely from above. The site belongs to the time immediately after the introduction of farming, when hunting and fishing still formed the primary subsistence base. Fragments of cooking pots are scattered in between food remains of terrestrial and freshwater origin. Bones of terrestrial mammals are the most conspicuous, but a closer view reveals numerous fragments of cracked hazelnut shells and scales and bones of freshwater fish. Due to leaching, the carbonate of the mollusk shells has disappeared in the upper part of the deposit. Photo courtesy of Peer Rievers.

A program for testing the hypothesis of freshwater reservoir effect in food residue dates was outlined in 1998. It included 4 experiments, which should provide the following kind of data:

1. A series of ^{14}C dates of present-day fish and mollusks from the Åmose freshwater system.
2. Series of ^{14}C dates from chronologically and stratigraphically well-defined Stone Age culture layers. These series should include samples of bones of freshwater fish as well as samples of terrestrial material of negligible lifespan, which could neither be suspected to be redeposited nor influenced by marine or freshwater reservoir effects.

3. Series of ^{14}C dates from stratigraphically and chronologically well-defined sediments including samples of food residue as well as samples of terrestrial material with negligible lifespan, which could neither be suspected of having been redeposited nor influenced by reservoir effects.
4. Combinations of food residue dates and dates on less problematic material (preferably terrestrial plant material of negligible lifespan) from individual potsherds.

Experiment 1

Live samples of relevant species of fish and mollusks were taken from present-day Lake Tissø in the Åmose river valley (Figure 1). Hydrologically and geologically, this lake is related to the former lakes in the Åmose basin in many ways, including its mix of groundwater and precipitation water (Høy and Dahl 1993; Noe-Nygaard 1995; Hedeselskabet 2000:13).

It was expected that any reservoir effect in prehistoric fish bones from the Åmose would primarily be the result of dissolved fossil carbonate in the groundwater. It would have seeped into the former lake from the surrounding hills with their calcareous underground, which is characteristic of most of north and east Denmark. Alternative—but in the specific case less probable—causes of a potential age offset could be water-absorbed CO_2 resulting from decay of old organic material in the lake and CO_2 with a high residence time in truly old groundwater seeping into the lake (cf. Tauber 1983).

In principle, the potential apparent age of the groundwater could be up to about 1 ^{14}C half-life (about 5700 yr) due to a 50% dilution with CO_2 from fossil carbonate (Heier-Nielsen et al. 1995). It was uncertain, however, if the hardwater effect in the groundwater could be detected in present-day fish in Tissø, which are also influenced by the atomic bomb pulse.

Experiment 2

The Åkonge kitchen midden is very rich in bones and scales of freshwater fish (Figure 4). Of the larger fish bones, 5404 had already been determined to species (Enghoff 1995). The dominant categories were cyprinids (*Cyprinidae*) and pike (*Exox lucius*), with a relative representation of 49% and 35%, respectively. Among the cyprinids, tench (*Tinca tinca*) was most numerously represented.

A collection of tench and pike bones from the Åkonge kitchen midden was selected for ^{14}C dating. It was decided to study these particular species for 2 reasons. First of all, because they apparently were the species most frequently consumed on this site, and secondly, because they represent different trophic levels. Tench feed on insect larvae (primarily mosquito), bivalves, snails, and slugs (Muus 1998). Pike of the size represented in the Åkonge sample almost exclusively feed on fish such as cyprinids, but may also occasionally eat ducklings and frogs (Muus 1998). If the hardwater effect was influencing the dates of these bones, it should be most pronounced in the tench samples since its food is generally more aquatic than that of the pike.

From the Åkonge kitchen midden, 6 ^{14}C dates of red deer bone were already available and these were subsequently supplemented with dates on terrestrial plant and bone material. The same series of dates was used also in Experiment 3.

Experiment 3

The large collection of potsherds with well-preserved food residue from the Åkonge midden had been excavated and curated in such way that post-excavation pollution from dust, finger-grease, car combustion particles, etc. could be excluded.

Experiment 4

A detailed inspection of pottery from the Åkonge site had revealed a number of sherds from which could be taken a sample of food residue, as well as a sample of other material of a less problematic nature. These potential combinations of samples included terrestrial material of negligible lifespan that had been incorporated in the clay when the pottery was produced.

In the following, the complete set of dates from the test program is presented, with the exception of 1 fishbone sample which yielded too little collagen carbon (<0.2 mg) for a precise date.

Apparent Age in Present-Day Freshwater Fish

In Table 1, we list the result of dating a series of freshwater species caught live in Lake Tissø in May 2001 (mollusks) and February 2002 (fish). As can be seen, all individuals have unrealistic, positive ^{14}C ages of, on average, about 300 BP. Due to the remains of the atmospheric ^{14}C bomb pulse caused by nuclear bomb tests since the late 1950s, negative ^{14}C ages of around –700 yr BP are expected for contemporaneous terrestrial samples (see e.g., Goodsite et al. 2001). By extrapolation of the dataset presented in this reference, the atmospheric ^{14}C level around the time of collection is estimated at 109.4 percent modern carbon (pMC) and from the pMC ratio fish/atmosphere, estimated equivalent reservoir ages of the fish samples have been calculated in the last column of Table 1, averaging about 1000 yr. Since the atmospheric ^{14}C level has been even higher in the preceding years (1963–2000), this value is probably underestimated, but it may be taken as indicative of local freshwater reservoir ages in the past having been considerably higher than the typical marine reservoir age of 400 yr.

Table 1 ^{14}C dates on flesh from present-day fish and mollusks (*Anodonta*) from Lake Tissø in the Åmose Valley. From the ratio of the measured ^{14}C level in the fish to the expected atmospheric ^{14}C level of 109.4 pMC (percent modern carbon) around the time of collection (2001/2002), the apparent reservoir ages have been calculated in the last column. The average observed reservoir age is 1034 yr.

Sample species	Lab nr AAR-	^{14}C age BP	$\delta^{13}C$ ‰ VPDB	Measured ^{14}C level (pMC)	pMC ratio fish/ atmosphere	Reservoir age (yr)
Pike	8369-1	209 ± 44	–26.4	97.4	0.891	931
Bream	8370-1	185 ± 55	–29.0	97.7	0.893	907
Pike-perch	8371-1	505 ± 36	–26.2	93.9	0.858	1226
Roach	8372-1	325 ± 60	–28.0	96.0	0.878	1049
Perch	8373-1	225 ± 80	–27.9	97.3	0.889	945
Freshwater mussel	8374	281 ± 43	–29.8	96.6	0.883	1003
Freshwater mussel	8375	315 ± 41	–32.0	96.2	0.879	1037
Freshwater mussel	8376	283 ± 36	–31.6	96.5	0.882	1005
Freshwater mussel	8377	417 ± 39	–31.2	94.9	0.868	1139
Freshwater mussel	8378	375 ± 34	–30.4	95.4	0.872	1097

A considerable part of the water in Tissø stems from groundwater. Some of it comes directly into the lake through its bottom. During the summers of 1998–2002, for instance, the average inflow of groundwater through the lake bottom was about 14% of the total inflow to the lake (Vestsjællands Amt 1999, 2000, 2001, 2002, 2003). A probably larger supply of groundwater arrives through the Åmose River and smaller streams from the hills surrounding the Åmose Valley (personal communication 2003 with Claus Koch, County Administration of West Zealand; cf. Hedeselskabet 2000:13).

The moraine hills bordering the Åmose Valley are rich in grains of fossil carbonate, which is gradually dissolved in the groundwater and transported into the lakes. Here, its ^{14}C-dead fossil carbon enters the aquatic food chain through photosynthesis.

Dates on Stone Age Fish Bones Versus Dates on Their Context

Table 2 presents the result of dating extracted collagen from 6 samples of freshwater fish bones from the Åkonge site in the Åmose. In one of these cases, the residual material—after extraction of collagen—has also been dated (AAR-4573), yielding the same age and δ^{13}C value within the measuring uncertainty. In the table the weighted average age of the collagen and of the residue from this sample is presented.

The context samples from the 2 layers of the Åkonge kitchen midden all represent cultural debris with well-documented find circumstances, which makes it reasonable to exclude the possibility that they were brought into the culture layer as a result of erosion or bioturbation. The zoological samples come from large, horizontally positioned bones of terrestrial mammals, the lifespan of which is of the order of 1–10 yr. The charred rootlet has a lifespan of less than 1 yr, and derives from a terrestrial tree.

The observed scatter in the ages of the terrestrial context samples is so small (70% of the statistically expected scatter) that all samples within each stratigraphic unit can be considered of the same ^{14}C age. In Table 2, this is expressed by the value *S*, the observed scatter (relative to the measuring uncertainty), which should be around 1 for a large number of samples assumed to be contemporaneous.

Table 2 Dates of bone of freshwater fish versus dates of context samples from 2 culture layers at the Åkonge site, Denmark. The dates of the contexts are based on terrestrial samples that have negligible lifespan and are not influenced by reservoir effects. It transpires that the ^{14}C age of the fish bones are systematically older than the context samples. * = standard value assumed. S = observed scatter.

Stratigraphic unit	Sample category	Material dated	Nr of bones in the sample	^{14}C age BP	δ^{13}C ‰	Lab nr	Weighted average ^{14}C age BP	Reservoir ^{14}C age
Layer 3b	Fish bone	Tench	2	5565 ± 40	–26.7	AAR-4576	5347 ± 19	480 ± 46
		Tench	2	5395 ± 40	–25.0	AAR-4574	(S = 3.0)	310 ± 46
		Pike	3	5245 ± 40	–23.1	AAR-4575		160 ± 46
		Pike	2	5238 ± 32	–21.2	AAR-4573		153 ± 39
	Context	Domestic ox bone	1	5120 ± 40	–21.8	AAR-4452	5085 ± 23	
		Charred rootlet	0	5095 ± 45	–26.6	AAR-5363	(S = 0.75)	
		Red deer bone	1	5070 ± 65	–20.9	K-4882		
		Red deer bone	1	5060 ± 65	–20.8	K-4881		
		Red deer bone	1	5010 ± 65	–21.4	K-4883		
Layer 3a	Fish bone	Tench	1	5315 ± 55	–20.9	AAR-4580	5229 ± 43	340 ± 66
		Pike	1	5090 ± 70	–24.6	AAR-4577	(S = 2.5)	115 ± 79
	Context	Red deer bone	1	4990 ± 65	–21.9	K-4886	4975 ± 36	
		Red deer bone	1	4990 ± 65	–21.6	K-4884	(S = 0.37)	
		Red deer bone	1	4950 ± 60	–22.6	K-4885		

The weighted average context ages of the 2 layers are used for calculating the reservoir age of each fish sample. All tench samples show highly significant reservoir ages of 310–480 ^{14}C yr. The pike samples show much smaller reservoir ages, although significant for both layers, at about 115–160 ^{14}C yr.

Present-day Åmose has a significant inflow of lime-rich groundwater from the surrounding hills (Hedeselskabet 2000:13). Due to differences in topography and water permeability of the under-

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ground, some places in the basin now have a much higher influx of groundwater than others. Since the same general hydrological situation existed in the Stone Age, some branches of this former lake system probably had relatively high concentrations of groundwater, too. This may be the cause of the considerable variation in reservoir age within each of the 2 species of fish.

The results of experiments 1 and 2 are compatible and allow a clear conclusion: if the food residues in the pots from Åkonge are exclusively derived from the cooking of freshwater fish or mollusks, these residues would theoretically have apparent ages in the order of 100–500 ^{14}C yr.

Dates of Food Residues Versus Dates of Their Context

In Table 3, we present results from the analysis of 3 small, chronologically and stratigraphically well-defined Stone Age inland sites: the Åkonge and Spangkonge sites in the Åmose, Denmark (Fischer 2002), and feature 8 from the Mossby site, Sweden (Larsson 1992), from each of which dates of food residue, as well as a number of dates on terrestrial context samples are available. All 3 sites belong to the initial part of the Neolithic, which in Denmark and southern Sweden began around 5150 BP (Fischer 2002).

Table 3 Examples of discrepancy between dates of food residue on the inner surface of pottery and their chronologically well-defined contexts. The dates of the contexts are based on samples of terrestrial material with a negligible lifespan. * = standard value assumed; S = observed scatter.

							Reservoir ^{14}C age of food residue	
Site	Provenance	Material	^{14}C age BP	δ^{13}C ‰	Lab nr	Weighted average BP	Individual pot-sherds	Average
Åkonge, Layer 3b	Pottery	Food residue	5385 ± 40	–28.8	AAR-5108	5228 ± 21 (S = 2.5)	300 ± 46	143 ± 31
		"Food" residue	5260 ± 70	–32.5	AAR-2678		175 ± 74	
		Food residue	5185 ± 40	–28.0	AAR-5112		100 ± 46	
		Food residue	5150 ± 100	–27.0*	AAR-5110		65 ± 103	
		Food residue	5115 ± 40	–30.6	AAR-5107		30 ± 46	
	Context	Domestic ox bone	5120 ± 40	–21.8	AAR-4452	5085 ± 23 (S = 0.75)		
		Charred rootlet	5095 ± 45	–26.6	AAR-5363			
		Red deer bone	5070 ± 65	–20.9	K-4882			
		Red deer bone	5060 ± 65	–20.8	K-4881			
		Red deer bone	5010 ± 65	–21.4	K-4883			
Spangkonge	Pottery	Food residue	5180 ± 40	–26.7	AAR-4818	5180 ± 40	72 ± 52	72 ± 52
	Context	Bone, red deer	5140 ± 65	–21.9	K-5044	5108 ± 33 (S = 0.62)		
		Antler, red deer	5130 ± 65	–22.9	K-5043			
		Bone, red deer	5110 ± 65	–22.6	K-5041			
		Bone, red deer	5050 ± 65	–20.7	K-5042			
Mossby Feature 8	Pottery	Food residue	5215 ± 120	–27.0*	Ua-429	5128 ± 60 (S = 1.05)	295 ± 144	
		Food residue	5170 ± 90	–27.0*	Ua-754		250 ± 120	
		Food residue	4995 ± 110	–27.0*	Ua-430		75 ± 135	
	Context	Charred cereal grain	4925 ± 115	–25.0*	Ua-755	4920 ± 79 (S = 0.06)		
		Charred hazelnut shell	4915 ± 110	–25.0*	Ua-753			

In the table, we only include dates of food residue from the inner surface of pottery. It shall, furthermore, be noticed that 1 of these dates (AAR-2678) is from a so-called blubber lamp. The others are from larger, round-belly vessels of the cooking-pot type.

The $\delta^{13}C$ value of the 3 food residue samples from the Mossby site is assumed to be –27.0‰. The choice of this value is based on the trend in the measured $\delta^{13}C$ values of northern European food residues on Stone Age cooking vessels from inland areas (Tables 3 and 4; Hallgren and Possnert 1997; Koch 1998; Persson 1999; Fischer 2002). We have applied a minor correction to the food residue dates from this site by subtraction of 15 yr from their originally published ages (Larsson 1992), which had been calculated on the basis of an estimated $\delta^{13}C$ value of –25.0‰.

The contextual dates from each of the 3 assemblages agree so closely ($S \leq 1$) that their weighted average values can be used as a base for comparison with the respective food residue dates.

The food residues in the individual cooking pots are most likely the remains of a somewhat different material. Some may primarily be sintered organic material from the cooking of freshwater fish or mollusks, others may derive mainly from the cooking of terrestrial plants or animals. Therefore, we cannot expect the food remains in different pots from one and the same site to have identical apparent age. This assumption agrees with the data in Table 3, which imply that the individual residues have significantly different age offsets, ranging between 30 and 300 yr.

Combinations of Dates from Individual Pot Sherds

Four cross-dates of cooking pots from the Åkonge site have been produced (Table 4). They consist of dates based on 3 different kinds of material:

1. Food residue from the inner surface of the vessels;
2. Or coating from the outer surface of the vessels; Based on visual inspection, these coatings primarily consist of soot deposited during cooking on fire. In the case of AAR-5109 and AAR-5113, it cannot be excluded, though, that the samples include a minor proportion of the material which was cooked in the pots;
3. Or botanical material that was incorporated in the clay during the production of the vessels.

The latter group (3) of material includes the following 2 samples:

- *AAR-5363* is a charred rootlet of lime tree. Determined on the basis of its shape and preservation, the rootlet had its full strength and was probably alive when the clay was dug up. The absence of year-rings in the rootlet implies that its lifespan was less than 1 yr (report from Claus Malmros, The Danish National Museum). It, therefore, forms a solid basis for determination of the true age of the vessel from which it derives.
- *AAR-4817* is a small piece of charcoal of a deciduous tree of undeterminable species and lifespan, of which oak cannot be excluded (report from Kjeld Christensen, The Danish National Museum). The lifespan of the sample is estimated to about 20 yr or more, and potentially, up to several hundreds of yr.

Apparently, the dates of the coating of the outer sides of the vessels agree better with the actual time of production than those based on food residue from the inner surfaces.

The dates on food residue are consistently older than the dates on other types of material from the respective vessels. In 3 cases, this age excess is significant, being close to 2 σ or more (Table 4). The 3 dates from the sherd Åkonge 49,5/77,0:26 (Figure 5) are especially informative, indicating (in agreement with Table 3) that the food residue in question has an apparent age of about 300 yr.

On the basis of the data in Table 4, we conclude that food residue, even of non-marine origin, can have a significant apparent age.

Table 4 Combinations of AMS dates from sherds of 4 cooking pots from the Åkonge site, Denmark. The age excess of the food residues is calculated in relation to the reference material from the respective sherds (rootlet, charcoal, coating on outer surface). These cross-dates indicate that the food remains dealt with have apparent ages of up to about 300 yr. * = standard value assumed.

Pot sherd identification nr	Material dated	^{14}C age BP	^{14}C age excess	δ^{13}C ‰	Lab nr
49,5/77,0:26	Food residue, inner surface	5385 ± 45	290 ± 64	–28.8	AAR-5108
	Coating, outer surface	5195 ± 45	100 ± 64	–27.1	AAR-5109
	Charred rootlet, lifespan 0 yr	5095 ± 45	0	–26.6	AAR-5363
49,5/77,0:18	Coating, outer surface	5195 ± 40	> 40 ± 57	–27.0	AAR-4816
	Charcoal, lifespan ≥ about 20 yr	5155 ± 40	> 0	–24.3	AAR-4817
50,0/75,5:18	Food residue, inner surface	5185 ± 40	≥ 115 ± 60	–28.0	AAR-5112
	Coating, outer surface	5070 ± 45	≥ 0	–26.5	AAR-5113
49,5/77,5:10	Food residue, inner surface	5150 ± 100	≥ 10 ± 108	–27.0*	AAR-5110
	Coating, outer surface	5140 ± 40	≥ 0	–26.8	AAR-5111

We suggest that the age discrepancies observed in food residue from the Åkonge site are (primarily) the result of hardwater effect in freshwater organisms that were cooked in the pots. We base this suggestion on the facts referred to above regarding: i) the remains of freshwater fish observed in Åmose food residues, ii) the high density of freshwater fish and mollusks observed in the Åmose kitchen middens, and iii) the groundwater chemistry and hydrology of this area.

We furthermore suggest that freshwater reservoir effect of the same or even greater scale applies to ^{14}C dates of food residue on Stone Age pottery from many other northern European inland freshwater systems that appear to have had similar groundwater chemistry, hydrology, and food habits.

DISCUSSION

Considering the composition of food remains in the Early Neolithic Åkonge kitchen midden (Figure 4; cf. Enghoff 1995; Gotfredsen 1998), the food residue on cooking pots from this site must represent a diversity of ingredients, including terrestrial plants and animals as well as freshwater fish and mollusks. It is, therefore, no surprise that the δ^{13}C value and apparent age of food residue from different pots vary to some degree (Tables 3 and 4). We have the impression that very negative δ^{13}C values may in some cases be taken as a warning that the food residue in question may have a particularly high age offset (cf. Fischer et al., forthcoming *b*). There is, however, no clear correlation between the δ^{13}C values and the apparent ages presented in this paper. Consequently, we cannot presently point out a method for detecting and possibly correcting for freshwater reservoir effect in food residue dates.

The measurement of δ^{13}C in food residue has been one of the most popular ways of exploring what kind of food was prepared in Stone Age pottery. Knowledge about δ^{13}C values in human bone collagen has formed the basis for the interpretations in many such studies of German, Danish, Swedish, and Norwegian Stone Age food residues. It is typically assumed that humans who consume a 100%

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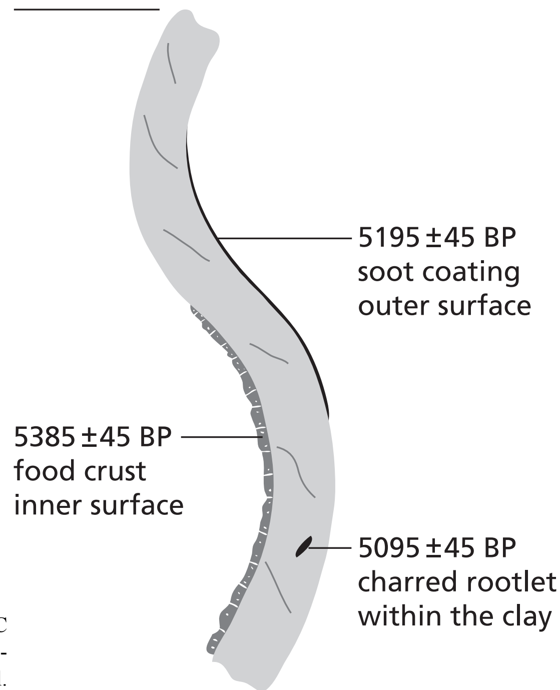

Figure 5 Schematic diagram of a potsherd from which 3 ^{14}C dates have been produced. The date on food residue is significantly older than the dates on the other types of material.

terrestrial northern European diet have δ^{13}C values in the order of –21‰. Less negative values imply that a proportion of the person's diet came from the sea, while values more negative than –21‰ are indicative of a proportion of freshwater food (cf. Fischer et al., forthcoming *a*,*b*).

The δ^{13}C values measured in northern European food residue on Stone Age pottery are generally more negative than –22‰ (Figure 6; cf. Persson 1997, 1999:Tables 24, 36; Fischer 2002:Table 22.3). On this basis it has frequently been assumed that these food remains do not include marine ingredients, even if most of them derive from archaeological cultures believed to have subsisted primarily on marine resources (Segerberg et al. 1991; Glørstad 1996; Østmo et al. 1996; Thomsen 1997; Hallgren and Possnert 1997; Edenmo et al. 1997; cf. Andersen and Malmros 1985). Results from the analysis of potsherds from the coastal Mesolithic site Tybrind Vig exemplify this paradox. In the food residue on these sherds, many indisputable remains of marine fish are recorded (Andersen and Malmros 1985) and yet they have ^{13}C values of –22.1 to –26.6‰.

As far as we can see, this paradox-debate is a result of misinterpretation of the existing data. It is a generally accepted and a solidly tested model that δ^{13}C values of bone collagen are in the order of 5‰ less negative than the δ^{13}C values of the food from which it derives (van der Merwe and Vogel 1978; van der Merwe 1982; Chisholm 1989; Ambrose 1993; Ambrose and Norr 1993; Schwarcz 2000). In northern Europe, where all indigenous terrestrial plants have a normal Calvin (C_3) photosynthesis, flesh of plant-eating mammals has δ^{13}C values in the order of –26‰, and when consumed by carnivores, turns into bone collagen with a δ^{13}C value around –21‰. Flesh from marine species has less negative δ^{13}C values.

The organic material on the inner surface of Stone Age pottery represents food, not bone collagen. Consequently, food remains having δ^{13}C values less negative than about –26‰ must include a proportion of marine food. This assumption is strongly supported by the many δ^{13}C values of food res-

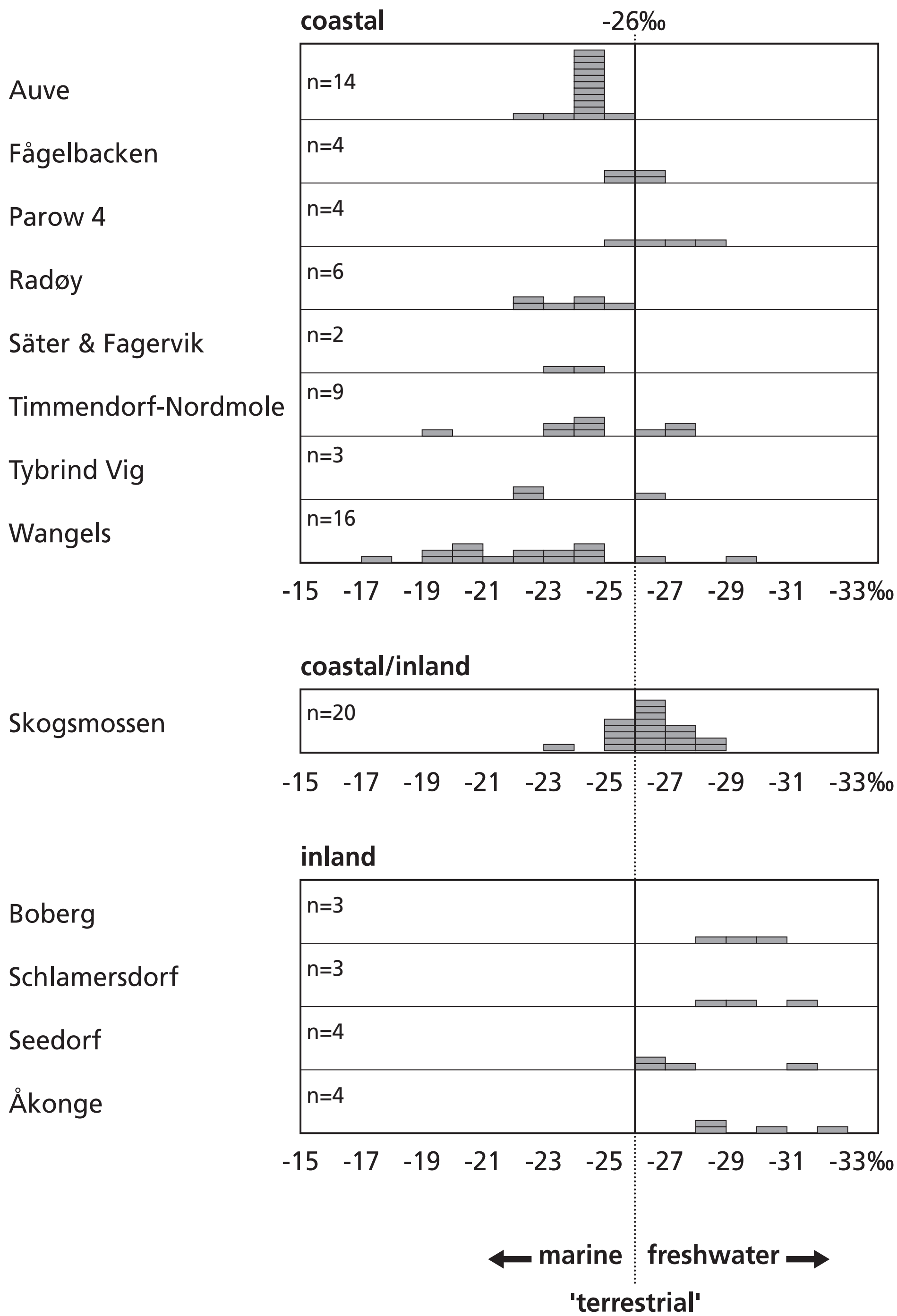

Figure 6 The distribution of $\delta^{13}C$ values in food residue from coastal and inland sites from Stone Age northern Europe. $\delta^{13}C$ = –26‰ VPDB is the approximate value of terrestrial food, and some mixtures of marine and freshwater components. The $\delta^{13}C$ values from the coastal sites are generally less negative than those from the inland sites; this implies that marine species formed a substantial part of the food cooked in the pots at the coastal sites.

idue available. The greatest value reported from Denmark so far is –17.2‰, which has been found in a Neolithic pot from Tømmerup Mose (Rahbek and Lund Rasmussen 1996:313). If it derives from a mixture of marine and terrestrial material, approximately 80% of the food remains in this funnel beaker must thus have been of marine origin and the ^{14}C date of the pot thus needs correction for a marine reservoir effect of about 320 yr. If it also includes freshwater substance, the marine content and the age offset may potentially be even greater.

In Figure 6, we present the scatter of $\delta^{13}C$ values of organic residues on pottery from a number of northern European Stone Age sites. The diagram includes settlements from where 2 or more $\delta^{13}C$ measurements of food residue are available (Andersen and Malmros 1985; Segerberg et al. 1991; Hallgren and Possnert 1997; Persson 1999:Tables 24, 36; Åstveit 1999; Lübke et al. 2000; Hartz et al. 2002; Lübke 2002, 2003; Østmo, personal communication 2003). Some of these sites we classify as "coastal" on the basis that they were originally located in a marine environment, close to the shoreline of their time. In those cases where faunal remains are preserved, these finds furthermore indicate a subsistence dependent on marine fish and mammals. Another group of sites we classify as "inland." They were originally located along freshwater systems several km from the seashore of their period. The fauna remains from these sites indicate a heavy reliance on terrestrial and/or freshwater food. The Neolithic settlement *Skogsmossen* in eastern Sweden we classify as intermediate ("coastal/inland") since it was originally located approximately 1 km from the coast and has a faunal assemblage with more than 10% seal bones (Halgreen et al. 1997). The illustration indicates that $\delta^{13}C$ values of food residue from the coastal sites are normally within the interval –19 to –28‰ (range –17.7 to –29.5). Values from the inland sites are within the range of –26.1 to –32.5‰. Thus, contrary to what has been reported in many recent publications, marine organisms seem to have been prominent constituents of the food cooked in pots in northern European Stone Age coastal sites.

^{14}C dates of food residue, which includes organic material of marine origin, will be influenced by a reservoir effect of up to about 400 yr. In principle, this effect can be detected and corrected for by means of $\delta^{13}C$ measurements. Based on the considerations above, we conclude that dates of samples with $\delta^{13}C$ values less negative than about –26‰ need to be corrected. Failure to apply such corrections has caused confusion among archaeologists and publication of a number of false chronological "sensations."

So far, we do not have a method which allows us to detect if a sample is influenced by freshwater reservoir effect. We are, thus, facing a major problem since the error may, in some regions, potentially be much larger that the marine reservoir effect. In the case of the Åmose bog, the organisms in question represent freshwater reservoir effect of a magnitude up to 500 yr. ^{14}C dates of present-day river water and of freshwater species elsewhere in Europe have demonstrated even higher apparent ages (Lanting and van der Plicht 1996, 1998; Heinemeier and Rud 1998; cf. Cook et al. 2001). Consequently, food residues deriving from freshwater organisms from these waters may have apparent ages in the order of many hundred yr.

A number of ^{14}C dates made on food residue on pottery have recently been presented as remarkably or inconceivably early appearances of various cultural phenomena in northern Germany (Hartz et al. 2000), Denmark (Koch 1998:96, 98, 101, 107, 321, 324, 331), Sweden (Segerberg et al. 1991; Hallgren and Possnert 1997; Persson 1997, 1999), and Norway (Østmo 1993; Glørstad 1996; Persson 1997, 1999). Based on the information presented above, these aberrant dates can now be explained as a result of marine or freshwater reservoir effect or a combination of both. It can, furthermore, be added that several other food residue dates from Danish votive pottery (Koch 1998), which have not hitherto been considered dubious, are probably also influenced significantly by the freshwater reservoir effect.

Freshwater fish and mollusks usually have relatively negative $\delta^{13}C$ values. Furthermore, fish from lakes and rivers, as in the case of marine species, are characterized by relatively high $\delta^{15}N$ values due to the long food chains found in aquatic environments in general. Therefore, measuring both of these isotopes in food residues may be potentially indicative of samples which are to a high degree of freshwater origin and may, therefore, have significant excess ages.

CONCLUSION

Much is still to be found out about the materials and processes involved in the formation of food residues on northern European Stone Age pottery. It is, however, most likely that some of this organic material derives from preparation of aquatic organisms, such as freshwater fish and mollusks. This is very likely the case with the food residues seen in numerous Neolithic cooking pots found in the Danish bogs, where the well-preserved, contemporary food remains clearly point to the dietary importance of freshwater fish and mollusks. This paper demonstrates that ^{14}C dates of fish bones from the Åmose have apparent ages in the order of 100–500 ^{14}C yr.

The food residues seen in the pots from the Åmose are expected to derive from a combination of sources, including terrestrial plants, terrestrial mammals, and—not least—freshwater fish and mollusks. In accordance with this expectation, food residues from the Åmose are demonstrated to have apparent ages of varying magnitude up to about 300 ^{14}C yr. So far, there is no method available either for detecting or correcting this error in ^{14}C dates.

Although a larger volume of data would be desirable, the present study seems to justify a call for caution in the uncritical use of food residue as a dating material. Future measurements of stable isotopes, such as ^{15}N and ^{34}S in charred food remains, may provide information of relevance for detecting which dates are significantly influenced by freshwater reservoir effect, and hopefully lead to a means of correcting these dates.

The apparent ages dealt with in this paper undoubtedly stem from fossil carbonate which is dissolved in groundwater and subsequently ends up as ^{14}C-dead carbon in the aquatic food chain (hardwater effect). In areas other than dealt with here, freshwater reservoir effect in food residue dates may also, to some degree, originate from CO_2 absorbed in groundwater with residence times of thousands of yr before it ended up in the lake or river in question.

An apparent age of modern river water in the scale of up to 4000 yr indicates that even larger discrepancies than the 100–300 ^{14}C yr seen in the Åmose material may be present in food residue dates from other inland regions around the world.

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