Radiocarbon, Vol 56, Nr 1, 2014, p 341–353 DOI: 10.2458/56.16898

A RE-EVALUATION OF THE RELIABILITY OF AMS DATES ON POTTERY FOOD RESIDUES FROM THE LATE PREHISTORIC CENTRAL PLAINS OF NORTH AMERICA: COMMENT ON ROPER (2013)

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ABSTRACT. Ancient carbon reservoirs in freshwater bodies have the potential to introduce ancient carbon into charred cooking residues adhering to pottery wall interiors when aquatic organisms are parts of cooked resource mixes. This ancient carbon results in old apparent ages when these cooking residues are subjected to accelerator mass spectrometry dating, the so-called freshwater reservoir effect (FRE). Roper's (2013) assessment of the FRE on ^{14}C ages from cooking residue in the Central Plains is only the second such peer-reviewed regional assessment in eastern North America. Roper suggests that 13 of 23 ^{14}C ages on residue are too old as a result of ancient carbon from fish or leached from shell temper or old carbon introduced via maize nixtamalization. Herein, we re-assess Roper's data set of ^{14}C ages on cooking residues and annual plants and argue that she is mistaken in her assessment of the accuracies of ^{14}C ages from residues. This outcome is placed in the context of the larger FRE literature.

INTRODUCTION

In a recent article in this journal, Roper (2013) seeks to explain what she believes are old apparent ages produced through accelerator mass spectrometry (AMS) assays on charred cooking residues (hereafter, residues) from the Central Plains of North America. Her explanation is that the old apparent ages are the result of the freshwater reservoir effect (FRE), as initially hypothesized by Fischer and Heinemeier (2003). FRE produces offsets between contextual radiocarbon ages on terrestrial resources and residues containing ancient carbon derived from aquatic organisms, referred to as freshwater reservoir offsets (FRO; Keaveney and Reimer 2012).

BACKGROUND

Reservoirs of ancient (dead) carbon in freshwater bodies result from the weathering of calcareous bedrock and soil substrates and other carbon-rich rocks. This phenomenon has been known since the early 1950s (e.g. Broecker and Walton 1959; Deevey et al. 1954; Godwin 1951) and is currently under investigation in a variety of disciplines (e.g. Yu et al. 2007; Keaveney and Reimer 2012; Zigah et al. 2012; Ishikawa et al. 2013). The FRE occurs when ancient carbon is metabolized by aquatic organisms and then is deposited in residues formed on pottery vessel interior walls when the aquatic resources are cooked in a liquid medium. When these residues are subjected to AMS assays, the resulting ^{14}C ages can produce FROs of decades to millennia.

The foundational article on the potential archaeological impact of FRE is by Fischer and Heinemeier (2003) in which they compare ages on residues with those on terrestrial resources from the same contexts at three inland Danish sites. They suggest that there is a systematic offset between ^{14}C ages on residues and contextual dates, with the assays on residues producing old apparent ^{14}C ages of 30 to 300 ^{14}C yr. This publication has generated a large number of articles in the archaeological literature that attribute apparent old ^{14}C ages on AMS-assayed residues to the FRE (e.g. Boudin et al. 2010; Philippsen et al. 2010; Miyata et al. 2011). Other articles explore the FRE and its impact on ^{14}C ages on contemporary aquatic organisms (e.g. Keaveney and Reimer 2012). While recognizing the existence of freshwater ancient carbon reservoirs, we questioned Fischer and Heinemeier's

(2003) results (Hart and Lovis 2007a). Through statistical analyses, we showed that rather than systematic offsets between ^{14}C ages on residues and terrestrial organisms at the three sites, there is a single outlying ^{14}C age from layer 3b at the Åkonge site. We concluded that "a single outlier is not sufficient evidence on which to build a case for the freshwater reservoir effect" at the sites in question (Hart and Lovis 2007a:1409).

We subsequently surveyed ^{14}C ages on residues from New York and the Great Lakes region of North America (Hart and Lovis 2007b). We found that a maximum of 5.7% of the 70 ^{14}C ages on residues from 25 site components statistically evaluated against contextual dates are potentially too old. Until Roper's (2013) publication, this has been the only peer-reviewed systematic assessment of ^{14}C ages on residues in eastern North America. This places Roper's analysis at a key position in the developing archaeological literature on FRE, which has focused primarily on northern Europe.

Roper's assessment is on a suite of 23 ^{14}C ages on residues from 14 sites belonging to the southern distribution of the North American Central Plains Tradition. Prior to development of a large set of AMS dates on annual plant remains and residues (Roper 2012; Roper and Adair 2011, 2012), this tradition was thought to range in age from AD 900/1000 to 1400/1500 based primarily on ^{14}C ages obtained from charred wood. Roper now believes the tradition dates between AD 1150 and 1350/1400 based on the recently accumulated suite of ^{14}C ages obtained on annual plant remains (Roper 2013:153). In the article in question, Roper (2013) compares eight residue ^{14}C ages against ^{14}C ages on annual plants at five sites, four residue ^{14}C ages against ^{14}C ages on wood charcoal from three sites, and 11 ^{14}C ages on residues from six sites for consistency with her current hypothesis for regional culture history chronology. Roper concludes that 13 of the 23 ^{14}C ages on residues are incongruent with the contextual dates or their cultural context: "significant questions can be raised about more than half of the dates, leading to the conclusion that the consistent accuracy of age determinations on residue in this region is suspect" (Roper 2013:158).

One of Roper's (2013:152) stated assumptions is that the earth lodges characterizing the Central Plains Tradition were each occupied for approximately a decade before being abandoned. This is an assumption that cannot be confirmed or refuted using various forms of ^{14}C dating because the statistical errors exceed the range of the assumed lodge occupations. An unstated assumption is that there was neither prior nor subsequent use of the lodge locations. In other words, Roper assumes that ^{14}C ages from contexts within a given lodge should not vary significantly from one another.

VARIANCES IN SOUTHERN CENTRAL PLAINS ^{14}C AGES ON ANNUAL PLANTS

Roper limits her analysis to ^{14}C ages from sites, or contexts within sites, from which ^{14}C ages were obtained on residues. However, because of the emphasis Roper places on annual plant AMS assays, it is important explore the full data set of ^{14}C ages when assessing her suggestion of a potential FRE in this region. The ^{14}C ages used by Roper (2013) are a subset of 91 ^{14}C ages from sites assigned to the southern portions of the Central Plains Tradition obtained on residues (n = 23) and annual plant remains (n = 68) reported in Roper and Adair (2011, 2012) and Roper (2012) (see Table S1, online Supplementary file). Roper (2013) suggests that AMS assays on annual plant remains are more accurate than assays on wood charcoal because they are not subject to the old-wood effect.

Roper (2013) has already statistically compared ^{14}C ages on residues to those on terrestrial plant remains from specific contexts, where available. However, because her emphasis is building a regional chronology, a broader perspective is required. Given the importance that Roper places on annual plant ^{14}C ages, we assess whether variances (age ranges) between ^{14}C ages on residues and annual plants from same-lodge contexts exceed those established for variances between ^{14}C ages on annual plants from same-lodge contexts for the southern Central Plains Tradition as a whole. If two or more ^{14}C ages on annual plants from same-lodge contexts vary significantly and yet are considered acceptable, then a ^{14}C age on a residue with a similar variance from a ^{14}C age on an annual plant in same-lodge contexts should not be rejected out-of-hand. Multiple ^{14}C ages on a single specimen can vary substantially (e.g. Scott 2003) as can specimens from different organisms that were deposited during a particular site occupation (e.g. Shott 1992). Site formation processes almost guarantee that objects of different age will occur within the same archaeological context (e.g. Lovis et al. 2012).

We also assess whether the oldest ^{14}C ages on residues are significantly different from the oldest age on an annual plant remain from the southern Central Plains Tradition using Ward and Wilson's (1978) technique. If a ^{14}C age on a residue is not significantly different from the oldest ^{14}C age on an annual plant from the Central Plains Tradition, then it should not be rejected out-of-hand. The oldest ^{14}C age for an annual plant is 926 ± 33 BP on maize (*Zea mays* ssp. *mays*) from site 14SA414 (Roper and Adair 2011:13).

As shown in Table 1, ^{14}C ages on annual plants from single-lodge contexts vary widely. For example, ^{14}C ages on bean (*Phaseolus vulgaris*) from Lodge 1 features 1 and 1A at site 23PL16 vary by 202 ^{14}C yr. Four ^{14}C ages obtained on crop remains recovered from a single feature at site 14GE127 vary by 109 ^{14}C yr. Two ^{14}C ages on maize from Feature 3 at 23PL80 vary by 85 ^{14}C yr. Other such matches produce identical ^{14}C ages or vary by decades, establishing a range of 0 to 202 ^{14}C yr. Given that there is statistical variation in ^{14}C ages, such ranges are to a degree expected, even when dating the same event (Scott 2003). Whether the ^{14}C ages resulting in the largest range for each context are

Table 1 Variances between ^{14}C ages on annual plants from same-site contexts (see Table S1 in the online Supplementary material for a complete list of dates).

Site	Context	Nr of ages	Largest ^{14}C yr variance	Significantly different?[a]
23PL16	Lodge 1, F1, F1A	2	202	Yes
14CY17	Lodge floor	3	175	Yes
14LV1071	149N, 57E; 160N, 57E	2	130	No
14GE600	Lodge floor, F2, 3	4	117	Yes
14GE127	Lodge 1, F144	4	109	Yes
23CL115	Feature 3	2	75	Yes
14OT5	Lodge 23, F136, 155	3	66	No
14SD305	Lodge hearth and postmolds	3	50	Yes
14MP407	Lodge 1, F74	2	45	No
14CY1	Lodge floor	3	43	No
14RY401	Lodge	2	36	No
14CY4	Lodge 2	3[b]	22	No
14WH319	Lodge	3	15	No
14CY102	Lodge	2	0	No
25FT56	Feature 1	2	0	No
23PL4	Lodge 1 floor, F17	2	0	No

[a]Between ^{14}C ages resulting in the largest variance using Ward and Wilson's (1978) technique.
[b]Includes assay on outer rings of a lodge timber.

significantly different from one another depends on the size of the range and each ^{14}C age's standard deviation (see Table S1). There is also considerable variation in ^{14}C ages from different lodges at single sites. For example, ^{14}C ages on maize from what are inferred to be two different lodges at 14LV1071 (Logan 1998) vary by 130 ^{14}C yr.

Roper (2013) does not explore the variances of ^{14}C ages on annual plants. Rather, she focuses only on offsets between ^{14}C ages on residues and annuals or charcoal and those that do not meet her current hypothesis of culture-history chronology when context ^{14}C ages are not listed.

RE-ASSESSING THE SOUTHERN CENTRAL PLAINS RESIDUE ^{14}C AGES

Roper (2013:158) claims that 13 of 23 ^{14}C ages on residues are questionable. Seven of these she claims are incongruent with context dates or with the currently accepted culture-historic chronology. These ^{14}C ages are from five sites, 23PL4, 14WB322, 14LC301, 14OT5, and 25FR6.

At 23PL4, there is a difference of 109 ^{14}C yr between two identical ^{14}C ages on beans, 685 ± 20 BP, and one on residue, 790 ± 20 BP. This range is well within that of ^{14}C ages obtained on annual plant remains from single-lodge contexts on southern Central Plains Tradition sites. Roper and Adair (2011:7) list two previous ^{14}C ages on wood charcoal from this site of 880 ± 100 and 660 ± 100 BP, one older and one younger than the residue age, which Roper (2013) does not include in her current re-assessment of the ^{14}C age estimate on residue.

At 14WB322, a ^{14}C age on a residue (1110 ± 25 BP) is 412 ^{14}C yr older than a ^{14}C age on hackberry (*Celtis occidentalis*) seeds (698 ± 35 BP). This exceeds the range for ^{14}C ages on annual plants from single-lodge contexts at southern Central Plains Tradition sites, although there is no evidence that a lodge was present at this site (Roper 2005). The residue is from a shell-tempered vessel. Roper (2013:159) reports that no evidence for fish was found in the pot using Fourier transform infrared spectrometry. Rather, oil from an unidentified source was detected. Roper suggests that the cooking of fish and mussels in the area may have resulted in fish oils becoming impregnated in the residue even if not cooked in the specific pot. Alternatively, she suggests that ancient carbon leached from the shell temper may have been absorbed into the residue. In either case, there is no direct evidence that cooking aquatic organisms in this pot introduced ancient carbon. Of note is that the age in question is only 40 ^{14}C yr older than an age on a residue from 14OT5 and 95 ^{14}C yr older than an age on residue from 25FR6. Of further note is that Roper (2005:98) previously concluded the residue is not derived from cooking food, but rather that it is the residue of fuel from the fire that damaged the exterior of the vessel. Moreover, she attributes the abundant hackberry seeds to natural seed rain or deposition by animals rather than to the human occupants of the site (2005:107, 116). There seems, then, no necessary chronological association between the residue and the hackberry seeds. Further, if Roper's interpretation of the residue is correct, it seems she would attribute it to the old-wood effect to which she attributes ^{14}C ages on charcoal of similar time depths from the region (Roper and Adair 2011; Roper 2013).

At 14LC301 there are two ^{14}C ages on residue, one of which, 935 ± 15 BP, is 28 ^{14}C yr younger and the other, 990 ± 15 BP, is 27 ^{14}C yr older than an age estimate on charcoal of 963 ± 100 BP. Roper argues all of these dates are 150 to 200 ^{14}C yr too old for the context. However, the ^{14}C ages on residues are only 9 and 64 ^{14}C yr older than, and neither is significantly different from, the oldest age on an annual plant in the region.

For 14OT5, Roper (2013) treats lodges 1 and 2 as separate sites with no contextual ^{14}C ages. However, there are four ^{14}C ages on annual plants and two on wood charcoal from two other lodges at this site (Roper and Adair 2011:6, 11). Three ^{14}C ages on maize from Lodge 23 range from 700 ± 40 to 766 ± 41 BP. A single ^{14}C age on maize from Lodge 8 is 758 ± 41 BP, while two ^{14}C ages on wood charcoal from this lodge are 680 ± 70 and 730 ± 70 BP. The ^{14}C age from Lodge 1 on residue is 675 ± 15 BP, while the ^{14}C age from Lodge 2 on residue is 1070 ± 15 BP. The first of these ages is 91 ^{14}C yr younger than the oldest date on an annual plant from the site. Roper claims the age on residue from Lodge 2 is 2 to 3 centuries too old for its context. This age is 144 ^{14}C yr older than, and significantly different from, the oldest ^{14}C age on maize from the region. In her analysis of pottery from this site, Beck (1998) found that the assemblage from Lodge 2 is substantially different from those of lodges 1 and 3 and suggests that one explanation for the difference is chronological. While Roper (2013) claims that the age from Lodge 2 reflects the FRE, Roper and Adair (2011:22) were willing to accept the possibility of it being accurate, indicating that they will "reserve judgment until we can find a way to obtain at least one, and preferably two more dates from this lodge, and/or replicate a date this early on appropriate contexts elsewhere." There does appear to be a complementary age on residue at site 25FR6.

At 25FR6, the two ^{14}C ages on residues of 910 ± 15 and 1015 ± 20 BP differ by 105 ^{14}C yr, well within the range established for annual plants in the region. Roper argues that these ages are 200 to 300 ^{14}C yr too old for their cultural context. However, the first is 16 ^{14}C yr younger and the second only 89 ^{14}C yr older than the oldest annual plant age for the region. The older of the two ^{14}C ages is 55 ^{14}C yr younger than the older of the two ages from residues at 14OT5.

The remaining six ^{14}C ages Roper questions are from three sites, 23PL13, 23BN2, and 14CY2, from which she reports no contextual ^{14}C ages. Roper (2013:158) asserts that the ^{14}C ages from these sites "are credible for their cultural context, but fall toward the early end of the time range for that context, or even provide the earliest dates for their locality. In one instance (23BN2), multiple residue dates are not congruent with one another."

At 23PL13, ^{14}C ages on two residues from shell-tempered sherds are 885 ± 20 and 900 ± 20 BP. These are well within the range of ^{14}C ages on annual plants for the southern Central Plains Tradition. Roper and Adair (2011:7) listed five ^{14}C ages on wood charcoal from this site that range from 720 ± 110 to 1090 ± 110 BP. Roper (2013) does not compare the ^{14}C ages on the residues to these ages, perhaps because of their large standard deviations and the potential for an old-wood effect.

At 23BN2, the three ^{14}C ages on residues of 905 ± 15, 860 ± 20, and 850 ± 20 BP vary by 55 ^{14}C yr, well within the range established for ^{14}C ages on annual plants from same-lodge contexts in the southern Central Plains Tradition. The ages are also well within the range of ages established with ^{14}C ages on annual plants for the tradition.

For 14CY2, Roper suggests the single ^{14}C age on residue of 725 ± 20 BP is acceptable, but that it is early for this locality referencing her Figure 2, which groups ^{14}C ages by county. It is only 11 ^{14}C yr older than an age estimate on maize from site 14CY14. Thus, of the 13 ^{14}C ages Roper questions, only one from 14WB322 at 1110 ^{14}C yr stands out as potentially exceptionally at odds with its context and the available dates on annual plants from the southern Great Plains Tradition (Table 2). However, there are ambiguities about the residue's origin and its chronological association with the ^{14}C-assayed hackberry seeds.

RESIDUE FORMATION AND AGE OFFSETS

Of importance to the FRE is the manner in which cooking residues form (Hart et al. 2007a, 2009; Lovis et al. 2011). Ancient carbon from aquatic organisms must contribute enough dead carbon to

Table 2 Summary of residue ^{14}C age variance evaluations.

Site	Residue ^{14}C age BP	Variance	>202 ^{14}C yr variance?[a]	>926 ^{14}C yr BP
Sites with ^{14}C ages on residue and on annuals				
23PL4	790 ± 20	–115	No	No
14WB322	1110 ± 25	–412	Yes	184 ^{14}C yr
14RY10	665 ± 15	–18	No	No
14CY102	705 ± 15 (2)	–13	No	No
25FT56	660 ± 60	–75	No	No
25FT56	610 ± 15	–25	No	No
25FT56	610 ± 20	–25	No	No
14OT5-H1[b]	675 ± 15	+91	No	No
14OT5-H2[b]	1070 ± 15	–304	Yes	144 ^{14}C yr
Sites with ^{14}C ages on residue and charcoal				
14SA403	755 ± 15	+105	No	No
14OT308	715 ± 15	+15	No	No
14LC301	990 ± 15	–27	No	64 ^{14}C yr[c]
14LC301	935 ± 15	+28	No	9 ^{14}C yr[c]
Sites with ^{14}C ages on residue only				
23PL13	900 ± 20	n/a	n/a	No
23PL13	885 ± 20	n/a	n/a	No
23BN2	905 ± 15	n/a	n/a	No
23BN2	860 ± 20	n/a	n/a	No
23BN2	850 ± 20	n/a	n/a	No
14CY2	725 ± 20	n/a	n/a	No
25FR6	1015 ± 20	n/a	n/a	89 ^{14}C yr
25FR6	910 ± 15	n/a	n/a	No
25RW1	595 ± 20	n/a	n/a	No

[a]Largest variance between dates on annuals from a single lodge in the southern Central Plains tradition.
[b]Comparisons on a whole-site basis (see text for explanation).
[c]Not significantly different from 926 ± 20 BP using Ward and Wilson's (1978) technique.

residue formation to result in a significant FRO (Philippsen 2008; Hart et al. 2013). As Fischer and Heinemeier (2003) correctly state, for an FRO on a residue ^{14}C age to be as great as that obtained by assaying fish bone, fish must have been the only resource contributing carbon to the residue.

For an FRO to occur, there must have been an ancient carbon reservoir in the bodies of water at the time in question. Concentrations of carbonate (CO_3^{-2}) and bicarbonate (HCO_3^-) ions vary through time in any given body of water depending on the extent that carbon-containing bedrock and unconsolidated materials are weathered. This can change markedly through time (Mullins et al. 2011), which affects the concentration of ancient carbon in aquatic organism tissue (Hart et al. 2013). Also of significance is that at any given time, carbonate and bicarbonate ion concentrations and thus total alkalinity ($CaCO_3$ mg/L), can vary considerably from drainage basin to drainage basin, even within the same region (Philippsen 2008; Keaveney and Reimer 2012), and spatially and at water column depth within lakes (Zigah et al. 2012). Concentrations of ancient carbon in fish within any given body of water will also vary both within and between species (Keaveney and Reimer 2012).

In general, the amount of carbon contributed to residue formation varies between resources depending on percent fat, carbohydrates, and proteins, each of which contains a different percent carbon (Hart et al. 2007a). The rapidity with which carbon from each resource cooked in a pot mobilizes also varies from resource to resource (Hart et al. 2009). Carbon from one resource may contribute more to residue formation when cooking times are short, while another resource may contribute more carbon when cooking times are long. As a result, there is not a linear relationship between the proportion of a raw resource cooked in a pot and the percent carbon it contributes to residue formation.

Recent modeling of the impacts of ancient carbon on AMS ^{14}C ages from residues indicates that offsets between the actual ^{14}C age of a residue and modeled ^{14}C ages vary widely depending on the percent of dead carbon contributed by fish to the modeled residue (see Hart et al. 2013 for details). These models are informed by knowledge gained through experiments on residue formation over the last decade (Hart et al. 2007a, 2009; Lovis et al. 2011). No FREs are established to our knowledge for the relevant Central Plains drainages at the time period in question. However, we can estimate the amount of fish necessary to obtain specific offsets at varying dead carbon percentages (DCP) in fish. The results of a two-resource varying proportional mixing model using lean fish with varying DCP and maize with a ^{14}C age estimate of 725 ± 15 BP are presented in Table 3. The DCP in each modeled residue is presented in Table 4. To obtain a statistically significant FRO when DCP in fish is 1, fish needs to account for a minimum of 80% of the raw resources cooked in a pot, which results in a carbon contribution of 52% to residue formation. When DCP in fish is 5, for a statistically significant FRO, fish must account for a minimum of 30% of the raw resources, which results in fish contributing 10% of carbon in the residue. In both cases, residue DCP is 0.52.

Ignoring the issue surrounding 14WB332 for the moment, Roper's (2013:156) comparisons of ^{14}C ages on annual plants to those on residue include differences of 115 to 442 ^{14}C yr. An offset of 115 ^{14}C yr for an age estimate of 725 ± 15 BP requires that a residue have a DCP of 1.38 and for an offset of 442 ^{14}C yr, a DCP of 5.27. The offset model indicates that the minimal amount of raw fish with a DCP of 2 needed for a 115 ^{14}C yr offset is 89%. At a DCP of 4, raw fish would need to account for 66% of the raw resource mix to produce a 115 ^{14}C yr offset and, at a DCP of 20, 22%. To produce an offset of 442 ^{14}C yr, fish with a DCP of 10 would need to account for 80% of the raw resources cooked in a pot, and 56.5% of the raw resources with a DCP of 20.

Extensively analyzed residues in New York (Hart et al. 2007b; Reber and Hart 2008), New Jersey (Messner et al. 2008; Messner 2011), Michigan (Raviele 2010), and the northern Plains (Boyd and Surrette 2010) suggest it is unusual that a single resource contributed all carbon to residue formation. This is consistent with the ethnographic and ethnohistoric records, which often refer to stew-like preparations (Parker 1910; Kinietz 1940). Adding to this is evidence that the interior walls of pots in central New York were frequently sealed with pine resin, which contributed carbon to residue formation (Reber and Hart 2008). While there is yet to have been detailed analyses of residues from the Central Plains Tradition, the ethnographic and ethnohistoric records for this region frequently refer to multiple boiled resource preparations in pottery vessels/iron kettles (Will and Hyde 1917; Wilson 1917). It seems reasonable to infer that multiple resources commonly contributed to residue formation during the period of time in question. If so, the concentrations of dead carbon from fish needed to produce offsets in the hundreds of years would be unlikely. However, because Roper (2013) has not established the extent of any ancient carbon reservoirs from the period of time in question by obtaining ^{14}C assays on fish bone from the various drainages, we cannot calculate the DCP in fish and thus firmly establish the likelihood of significant FROs in cooking residues.

Table 3 Freshwater reservoir ^{14}C yr offsets by dead C percent for modeled residues with lean fish and context ^{14}C age of 725 ± 15 BP.[a]

% raw fish	$\%C_{Fish}$ in residue	Dead C percent in fish														
		1	2	3	4	5	10	11	12	13	14	15	20	21	22	23
10	3	3	5	8	10	12	24	27	29	32	34	37	49	51	53	56
20	7	6	11	16	21	27	53	58	63	68	74	79	105	111	116	121
30	10	9	18	26	35	43	86	95	104	112	121	130	173	182	191	199
40	15	13	26	38	51	64	127	140	153	166	178	191	256	269	282	295
50	21	18	36	53	71	89	178	196	214	232	250	268	359	377	395	414
60	28	24	48	72	96	120	242	266	291	315	340	365	490	515	541	566
70	39	32	64	97	129	161	326	359	392	426	459	493	664	699	733	768
80	52	43	87	130	174	218	441	486	531	577	623	670	905	953	1002	1050
90	71	59	118	178	238	298	607	671	734	798	863	928	1262	1331	1400	1469
100	100	84	168	252	338	425	872	964	1057	1152	1248	1344	1846	1950	2055	2162

[a]See Hart et al. (2013) for details on model construction.

Table 4 Dead carbon percent in the modeled residues in Table 3.

% raw fish	$\%C_{Fish}$ in residue	Dead C percent in fish														
		1	2	3	4	5	10	11	12	13	14	15	20	21	22	23
10	3	0.029	0.058	0.087	0.116	0.145	0.29	0.319	0.348	0.377	0.406	0.435	0.580	0.609	0.638	0.667
20	7	0.063	0.126	0.189	0.252	0.315	0.63	0.693	0.756	0.819	0.882	0.945	1.260	1.323	1.386	1.449
30	10	0.103	0.207	0.310	0.413	0.517	1.034	1.137	1.240	1.344	1.447	1.551	2.067	2.171	2.274	2.377
40	15	0.152	0.304	0.456	0.608	0.760	1.521	1.673	1.825	1.977	2.129	2.281	3.041	3.193	3.345	3.497
50	21	0.212	0.424	0.636	0.848	1.060	2.120	2.332	2.544	2.756	2.968	3.180	4.240	4.452	4.664	4.875
60	28	0.287	0.575	0.862	1.150	1.437	2.875	3.162	3.450	3.737	4.025	4.312	5.750	6.037	6.325	6.612
70	39	0.386	0.771	1.157	1.542	1.928	3.856	4.242	4.627	5.013	5.399	5.784	7.712	8.098	8.484	8.869
80	52	0.518	1.037	1.555	2.073	2.592	5.183	5.701	6.220	6.738	7.256	7.775	10.366	10.884	11.403	11.921
90	71	0.708	1.415	2.123	2.831	3.538	7.077	7.785	8.492	9.200	9.908	10.615	14.154	14.861	15.569	16.277

OTHER EXPLANATIONS FOR OFFSETS

Roper (2013:159) admits that the FRE may not account for all of what she believes are too-old ^{14}C ages on residues. She suggests two other means by which ancient carbon may have contributed to residue formation resulting in age offsets: nixtamalization of maize and leachate from shell temper.

Nixtamalization

Nixtamalization of maize is a process that has recently acquired experimental attention relative to residue formation (Lovis et al. 2011). Such alkaline processing of maize to produce hominy is usually effected through use of wood ash or lime produced from limestone or shell. The Lacondon Maya is the only ethnographically documented group in the Americas to regularly employ shell for nixtamalization; the remainder use lime from limestone or use wood ash (Katz et al. 1974). Lime (CaO) for nixtamalization is obtained by heating calcium carbonate ($CaCO_3$) in the form of limestone or shell at temperatures of 600 to 900°C (Herbert 2008). Calcium carbonate is 12% carbon, while lime contains no carbon (see Herbert 2008; Ellwood et al. 2012), and its use in nixtamalization would not affect ^{14}C assays on residues. There is no ethnographic evidence for lime-based nixtamalization in the Central Plains (Katz et al. 1974).

According to Katz et al. (1974), the ethnographic Pawnee and the Omaha both used wood ash for nixtamalization. The Pawnee were earth lodge dwellers occupying parts of the Missouri River system, the Platte and Republican rivers in the modern states of Kansas and Nebraska, closely related to Roper's area of interest. Clearly, wood ash derived from contemporary trees cannot contribute dead carbon to residue formation. The introduction of decades-old carbon from wood ash, however, could potentially result in slight offsets. A proportional mixing model based on a ^{14}C age of 725 ± 15 BP indicates that a statistically significant offset would require a 40% carbon contribution of ash from 100-yr-old wood and 80% from 50-yr-old wood to residue formation (Table 5). Ash from 25-yr-old wood would not result in a significant offset in any proportion. Traditional nixtamalization uses little lime, only 0.1% to 5% by maize weight (Rosentrater 2006). Given that wood ash contains only 5% to 30% carbon (Siddique 2008:303), the large proportion of ash from old wood needed in the formation of residue to produce a statistically significant offset is extremely unlikely to have occurred.

Shell Temper Leaching

Shell temper in pottery can pose a potentially complex problem, one that may be viewed beyond any explanatory value of "leachates." Depending on location of origin (in combination these are separable as marine, freshwater, terrestrial, and estuarine), and the taxon from which the shell temper derives, there may in fact be a substantial and highly variable ^{14}C age offset on the shell. This has been explored for individual chronologically sensitive regional species subjected to AMS dating, particularly ostracods and gastropods, with resulting variable dead carbon content (Gillespie et al. 2009; Pigati et al. 2010). ^{14}C ages obtained on shell have been viewed in general as a long-standing problem, particularly for freshwater and terrestrial shells because of the vagaries of ancient carbon being incorporated into the shell (Michels 1973). Moreover, the uptake of ancient carbon that may be incorporated into shell production is normally from material in solution and ultimately derived from limestone. That said, recent research suggests that several species of terrestrial gastropods can produce reliable ^{14}C ages (Pigati et al. 2010; Rakovan et al. 2013). On the other hand, ^{14}C ages of freshwater mussel may require a reservoir correction (e.g. 340 ± 20 ^{14}C yr in a subregion of California; Culleton 2006). Importantly, these examples are assays on shell alone, not on cooking residues with variable percentages of ancient carbon from shell-temper leachate.

Table 5 ^{14}C ages from incorporation of wood ash carbon of varying ages in cooking residues.[a]

% carbon	100-yr-old wood		50-yr-old wood		25-yr-old wood	
from ash	pMC	^{14}C age	pMC	^{14}C age	pMC	^{14}C age
0	0.915810	725	0.915810	725	0.915810	725
10	0.914709	735	0.915259	730	0.915539	728
20	0.913608	745	0.914708	735	0.915268	730
30	0.912507	755	0.914157	740	0.914997	732
40	0.911406	765	0.913606	745	0.914726	735
50	0.910305	775	0.913055	750	0.914455	737
60	0.909204	785	0.912504	755	0.914184	740
70	0.908103	795	0.911953	760	0.913913	742
80	0.907002	805	0.911402	765	0.913642	745
90	0.905901	815	0.910851	770	0.913371	747
100	0.904800	825	0.910300	775	0.913100	750

[a]Based on a 15-yr standard deviation. Shaded values indicate statistically significant differences between the age of the modeled residue with no carbon from wood ash using Ward and Wilson's (1978) technique.

A major problem with shell as temper is the need to prevent the transformation of $CaCO_3$ into CaO (Herbert 2008). The latter's expansion when transformed into calcium hydroxide ($Ca[OH]_2$) causes spalling and the potential failure of pots. Low firing at <650°C, particularly under reducing atmospheres, prevents the transformation of $CaCO_2$ to CaO (Herbert 2008).

The relative proportion of aplastic:plastic in the fabric is a consideration for Roper's supposition. As noted, this is not necessarily constant and may vary between vessels within and between pottery traditions. Such variation is particularly evident between the several eastern North American pottery manufacturing traditions employing shell as the aplastic (e.g. Mississippian and Oneota/Upper Mississippian). In terms of the potential effects of such variation in proportional density, one might infer that the greater the area of exposed shell temper on a vessel interior, then the higher the probability that there will be a significant offset in ^{14}C ages on residues incorporating ancient carbon from the leachate. Several questions arise in terms of the leachate. How long does it take shell exposed to heated water to leach from the fabric of pottery vessel interior surfaces and enter solution? Is there a transfer of ancient carbon from shell leachate into cooking residues? If so, is this incorporation systematic? Is any ancient carbon from leachate removed from the residue during HCl treatments prior to ^{14}C assay? These in themselves would be interesting experiments to perform in tandem with measurements of the various carbon contents of experimental residues.

Regardless of any such issues, ancient carbon from shell would need to represent the same DCP in residue as that from fish. It seems very unlikely that concentrations of ancient carbon from shell temper would constitute the DCP necessary to result in 115 to 442 ^{14}C yr offsets that Roper (2013) suggests given the amount of shell exposed to potential leaching is small and that $CaCO_2$ is only 12% carbon. For example, a 340 ^{14}C yr offset on freshwater shell for a ^{14}C age of 725 BP results from a shell DCP of 4.02. According to our model, an offset of 115 ^{14}C yr with DCP of 4.02 would require that residue carbon from shell be 33.8%, the equivalent of shell accounting for 63% of the raw resources cooked in a pot. Of further note is evidence that pottery wall interiors may be sealed to make them impermeable (Schiffer et al. 1994). Such sealing, for which there is evidence in New York (Reber and Hart 2008), would seemingly minimize shell temper leaching. The oil to which Roper (2013) refers in the analysis of the shell-tempered vessel from 14WB322 may be such a sealant.

SUMMARY

In her assessment of ^{14}C ages on cooking residues from the southern distribution of the Great Plains Tradition, Roper (2013) suggests that 13 of 23 (56.5%) such ages are questionable. This is based on comparison with contextual ^{14}C ages on annual plants or wood charcoal or on her current hypothesis of the tradition's timespan. By taking into account the differences in ^{14}C ages of annual plants from single-lodge contexts and the oldest ^{14}C age for an annual plant in the region, we reach a very different conclusion. In our analysis, none of the 11 ^{14}C ages on residues with single-lodge context ^{14}C ages on annual plants have offsets that exceed the variances between ^{14}C ages from single-lodge contexts on annual plants. Of the 23 total ^{14}C ages on residues, five ages are older than the oldest ^{14}C age on an annual plant from the southern Central Plains Tradition, the remaining 18 ages are not. Of those that are older, one is ambiguous because it may represent residue from fire fuel rather than from cooking food. Two others are not significantly different from the oldest ^{14}C age on an annual plant. This leaves 2 of 22 (9.1%) ^{14}C ages on cooking residues that are seemingly at odds with the regional chronology. It is of interest that both of these are from lodges lacking other ^{14}C ages. Roper was previously willing to consider one of these ^{14}C ages as potentially accurate (Roper and Adair 2012). Our modeling based on experience with experimental residue formation suggests it is improbable that old carbon from nixtamalization or ancient carbon from shell temper leachate would result in significant offsets. It also seems improbable that enough ancient carbon would have been incorporated into these residues from cooking fish with terrestrial resources to result in offsets in the hundreds of years. In the absence of clear evidence that these ^{14}C assays incorporate dead C from fish, they should not be dismissed simply because they do not fit the currently hypothesized chronology for a culture-historic taxon.

CONCLUSIONS

In both this and prior work, we have attempted to understand the processes that lie behind potential errors in AMS assays on carbonized food residues. We neither dispute the potential presence of an FRE, nor do we dispute that any ^{14}C age can be inaccurate, including AMS ages obtained on residues. However, in order to gain an appropriate understanding of this phenomenon and its effects it takes more effort than simply comparing a date on residue to dates on annual plants, or stating that certain or all such assays do not fit a hypothesized chronology to ascertain that a ^{14}C age is inaccurate (e.g. Hohman-Caine and Syms 2012; Roper 2013). Rather, we believe this is an issue that requires systematic research through focused evaluation of research designs and outcomes. We are willing to entertain the alternative hypothesis that there are significant offsets of AMS dates on cooking residues under certain conditions, that if present they are probably related to FRE, and we need to understand when and how this occurs without throwing out the proverbial baby with the bathwater to support temporal hypotheses often hinging on decades of ^{14}C ages obtained on associated datable materials.

It is well established that the potential for FRE can vary both temporally and spatially among water bodies. In instances where FRE is called into explanation for "unacceptable" ^{14}C ages, we have demonstrated little if any statistical validity adheres to the argument (Hart and Lovis 2007a), and when systematic comparisons have been undertaken at the regional level between AMS ages on residues and associated context dates, we have found only a low frequency of asynchrony (Hart and Lovis 2007b). We have, likewise, in this discussion called into question nixtamalization and shell temper as significant sources of old or ancient carbon in residue formation. The initial catalyst for much of this debate has surrounded the potential of fish in a food mix to contribute ancient carbon to residue formation that results in earlier than expected ages (e.g. Fischer and Heinemeier 2003; Philippsen 2008; Philippsen et al. 2010). Modeling of the potential FROs from fish as a component of resource mixes, both here and elsewhere, reveals that such effects vary not only by individual fish species' fat content, but that for statistically significant offsets to occur fish must accommodate large proportions of the food mix depending on DCP. We additionally argue that rather than using associated detrital charcoal ages as the benchmark against which to evaluate the accuracy of AMS assays on carbonized residues, ^{14}C ages obtained from residues be used to rectify errors in ^{14}C chronologies regardless of the impact of such revision on threshold cultural events (Hart et al. 2013).

Established historical chronologies have attained almost law-like status, not just in the Central Plains but more broadly, and we recognize that it is difficult to reject old traditions. Such chronologies are hypotheses that are in continual need of testing. Obtaining ^{14}C ages on pottery residues has the potential to aid in the testing of hypothesized chronologies. However, even as research on traditional ^{14}C dating identified issues that required deeper inspection and interpretation, so does the AMS dating of residues. We urge further systematic research designed to better refine our understanding of these issues. Understanding the systematics of the FRE will allow appropriate application of AMS dating procedures to residue samples with low probability of FRE effects, and also allow more accurate assessments of AMS residue ^{14}C ages for specific time intervals keyed to measured FRE on a location-by-location basis within specific drainage basins.

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