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Supplementary Information for

Early metal use and crematory practices in the American Southeast: Implications for long-distance exchange and emergent complexity

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Additional Analyses Conducted on Materials from the McQueen Shell Ring

Radiometric Dating of Human Bones

For AMS dating, pretreatment for calcined bone samples follows (1), which adopts the suggestions of (2). Samples (~1200–2500mg) were sonicated in >18.2 MΩ water for 30 minutes x 2 to remove surface sediments. The whole samples were soaked in 15 ml 0.25N (~1%) HCl at 80°C for 60 minutes to removed diagenetic carbonate. After rinsing and drying, the samples were ground by hand in a mortar and soaked in 1 M acetic acid overnight.

As a check on the level of calcination and the likelihood of the samples retaining in vivo carbonate, subsamples of processed bone powder were scanned by Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) at the Materials Characterization Lab at Penn State on a Bruker Vertex V70. Spectra were generated in the mid-IR (4000 - 400 cm-1) range on several processed samples to identify that most suitable samples for dating judging by the infrared splitting factor calculated from the phosphate peaks at ~700-500 cm-1.

Roughly 350 mg of samples were hydrolyzed in 2 ml of 85% orthophosphoric acid at 80°C in evacuated blood sampling vials to evolve CO_2, entered onto a vacuum line for cryogenic purification and sealed in quartz tubes with CuO and Ag wire and the CO_2 was combusted at 900°C to remove sulfides. Conversion to graphite was done by hydrogen reduction onto an Fe catalyst at 550°C for 3 hours (3) and reaction water drawn off with Mg(ClO4)2, (4). Graphite is pressed into Al targets for AMS measurement at KCCAMS (Fig. S1).

Chemical Analyses of Copper Object

To determine the chemical makeup of the McQueen object, we first developed elemental signatures from raw materials attained from known sources, which included two sets of samples. The first was a set of 60 source samples from the Great Lakes, central Appalachians, and northern Maritimes. Samples were analyzed at the Institute for Integrated Research on Materials, Environment, and Society (IIRMES) at California State University, Long Beach using a New Wave Research UP213 Laster Ablation system coupled with a GBC OptiMass 8000 ICP time of flight mass spectrometer. Additional comparative source data was drawn from the second set of samples that include 24 native copper specimens from the Great Lakes and southern Appalachians analyzed at the Elemental Analysis Facility at the Chicago Field Museum of Natural History using an Analytik Jena quadrupole mass spectrometer and a New Wave UP213 laser ablation system.

Archaeological samples included seven fragments from the copper artifact recovered at the McQueen Shell Ring. Analysis of these archaeological materials was also conducted at the Elemental Analysis Facility at the Chicago Field Museum of Natural History using the same instruments used to analyze source materials.

Artifacts and source samples were preablated with the laser collimated to a 100 μm beam to remove weathered products and other surface contaminants, before sampling with an 80 μm beam. Five samples were taken from each artifact and source specimens to compensate for heterogeneity. Quantitative data were obtained using an internal standard (cu 65) and three external standard reference materials: NIST 500 Unalloyed Copper, NIST 1107 Naval Brass, and NIST 1110 Red Brass. These external standards contained known concentrations for 12 elements, including iron (Fe 57), cobalt (Co 59), nickel (Ni 60), copper (Cu 63), zinc (Zn 66),

arsenic (As 75), silver (Ag 107), tin (Sn 120), antimony (Sb 121), tellurium (Te 128), lead (Pb 208), and bismuth (Bi 209).

Although the datasets from the two different labs should be comparable, comparative studies revealed slight discrepancies between data generated at the Field Museum and at IIRMES. These studies showed that only 10 elements could be consistently compared across datasets, as tellurium and bismuth varied slightly from one lab to the other. To compensate for the variability between datasets, two different analyses were performed; the first being a more precise analysis using materials solely analyzed at the Field Museum, the second being less precise but comprised of a greater number of source samples. This second analysis included samples studied at both IIRMES and the Field Museum; tellurium and bismuth results were excluded.

In both studies, the results of the five samples per artifact and source specimens were averaged to compensate for heterogeneity and the resulting means were transformed to enhance normality as described in previous analyses (5, 6, 7). These transformed data were then subject to discriminant function analysis using SPSS Version 22.

The first statistical analysis included materials studied at the Field Museum, which produced three functions accounting for 100% of the variance (Wilks' lambda = 0.004). Functions one and two accounted for 88% of the variance. Source specimens were correctly assigned to their distinct geological provenance in 95.8% of the cases. Copper from the Great Lakes and copper from the Appalachians were never mistaken in this analysis, demonstrating that the study distinguishes between these two regions in 100% of the cases (Table S1).

The elemental composition of the McQueen Shell Ring copper was found most consistent with the Great Lakes samples, specifically with the Minong Mine source on Isle Royale and the Michipicoten Island source. Both of these sources are associated with the Keweenawan volcanic deposits on the northern side of the Lake Superior Syncline. None of the McQueen Shell Ring copper was consistent with the geological source representing the southern side of the Lake Superior Syncline or from the native copper sources in the southern Appalachians.

The second statistical analysis used the source data analyzed at both the Field Museum and IIRMES, but excluded tellurium and bismuth data, and produced nine functions accounting for 100% of source sample variance (Wilks' lambda = 0.015). Functions one and two accounted for 79.3% of the variance. Source specimens were correctly assigned to their geological provenance in 81% of the cases. Although less accurate than the first analyses, it is important to note that Isle Royale and southern Appalachian sources were never confused for one another based on elemental composition (Table S2). Comparing the McQueen Shell Ring data to this larger yet coarser source data once again demonstrates that the artifact copper is most consistent with Lake Superior sources. All of the copper were found to again trace their highest probability of association with the Minong Mine on Isle Royale (probability values ranging from p = .64 to .95). The Minesota Mine of the southern Keweenaw was found to be the second most probable source for four of the artifact fragments, yet that probability was quite low (p = .03 to .12). The southern Appalachians were found to be the second most probable source for three of the artifact fragments, yet the probability was again found to be low (p = .04 to .34). Sources from the Canadian Maritimes and central Appalachians show minimal similarity to the McQueen samples.
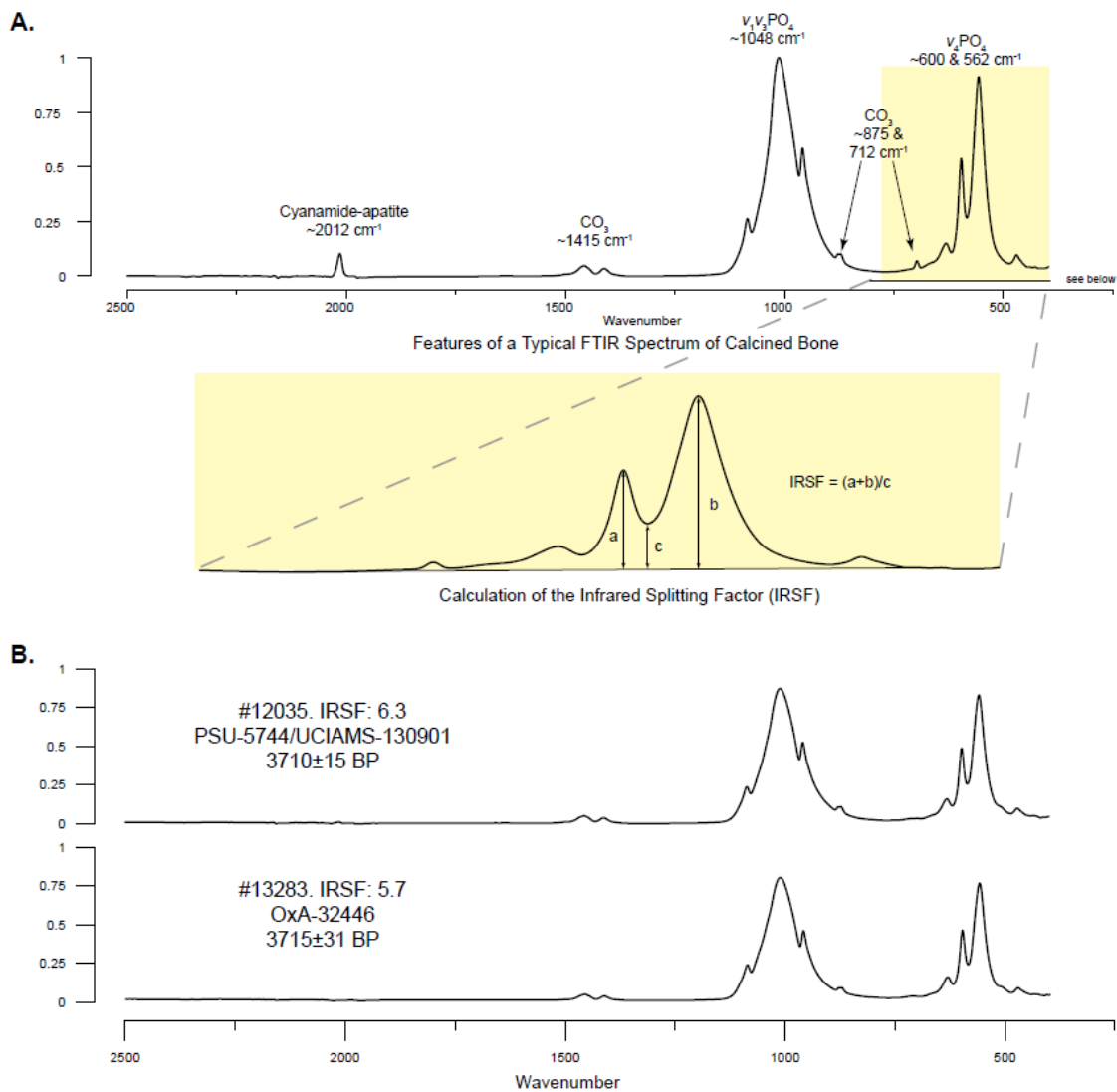
A.

$v_1 v_3 PO_4$
~1048 cm⁻¹

$v_4 PO_4$
~600 & 562 cm⁻¹

CO_3
~875 &
712 cm⁻¹

Cyanamide-apatite
~2012 cm⁻¹

CO_3
~1415 cm⁻¹

1
0.75
0.5
0.25
0

2500   2000   1500   1000   500

see below

Wavenumber

Features of a Typical FTIR Spectrum of Calcined Bone

IRSF = (a+b)/c

a   c   b

Calculation of the Infrared Splitting Factor (IRSF)

B.

1
0.75
0.5
0.25
0

#12035. IRSF: 6.3
PSU-5744/UCIAMS-130901
3710±15 BP

1
0.75
0.5
0.25
0

#13283. IRSF: 5.7
OxA-32446
3715±31 BP

2500   2000   1500   1000   500

Wavenumber

Fig. S1. (*A*) Typical Fourier-Transform Infrared (FTIR) spectrum of calcined bone showing characteristic phosphate and carbonate peaks in the 1500–400 wavenumber range after (8). Detail of 800–400 wavenumber region shows the method of calculating the infrared splitting factor (IRSF), and measure of phosphate crystalinity and transformation during calcination. Values above 5 and the presence of carbonate peaks suggest that diagenesis has not altered the in vivo carbonate signature; (*B*) FTIR spectra and IRSF for the two specimens of calcined bone processed for AMS ^{14}C dating of the carbonate fraction. Acceptable IRSF and presence of carbonate peaks indicates lack of post-depositional alteration of in vivo carbonate.

Table S1. Group membership of copper object and known copper sources using smaller dataset.

	Group	Predicted Group Membership				Total
		Keweenaw	Appalachian	Michipicoten	Isle Royale	
Original	Keweenaw	6	0	0	0	6
Count	Appalachian	0	5	0	0	5
	Michipicoten	1	0	5	0	6
	Isle Royale	0	0	0	7	7
	McQueen	**0**	**0**	**2**	**5**	7
Original	Keweenaw	100	0	0	0	100
Percent	Appalachian	0	100	0	0	100
	Michipicoten	16.7	0	83.3	0	100
	Isle Royale	0	0	0	100	100
	McQueen	**0**	**0**	**28.6**	**71.4**	100

Table S2. Group membership of copper object and known copper sources using larger dataset.

	Group	Predicted Group Membership										Total
		S.App	IR	NS	Mich	C.App	NFL	MM	CM	Ch.M	Snake	
Count	S. Appalachian	25	0	0	0	0	0	0	0	0	0	25
	Isle Royale	0	36	2	1	1	0	3	1	0	0	44
	Nova Scotia	1	0	2	0	0	0	0	0	0	0	3
	Michipicoten	0	0	0	5	1	0	0	0	0	0	6
	C. Appalachian	0	0	0	1	3	0	0	2	0	2	8
	Newfoundland	0	0	0	0	0	4	0	0	0	0	4
	Minesota Mine	0	0	0	1	0	0	3	0	1	0	5
	Centennial Mine	0	0	0	0	0	0	0	4	0	2	6
	Champion Mine	0	0	0	0	0	0	2	0	8	0	10
	Snake River	0	0	0	1	0	0	0	1	0	8	10
	McQueen	**0**	**7**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	7
%	S. Appalachian	100	0	0	0	0	0	0	0	0	0	100
	Isle Royale	0	81.8	4.5	2.3	2.3	0	6.8	2.3	0	0	100
	Nova Scotia	33.3	0	66.7	0	0	0	0	0	0	0	100
	Michipicoten	0	0	0	83.3	16.7	0	0	0	0	0	100
	C. Appalachian	0	0	0	12.5	37.5	0	0	25	0	25	100
	Newfoundland	0	0	0	0	0	100	0	0	0	0	100
	Minesota Mine	0	0	0	20	0	0	60	0	20	0	100

Centennial Mine	0	0	0	0	0	0	0	66.7	0	33.3	100
Champion Mine	0	0	0	0	0	0	20	0	80	0	100
Snake River	0	0	0	10	0	0	0	10	0	80	100
McQueen	**0**	**100**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**100**

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