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RADIOCARBON DATING OF COPPER-PRESERVED ORGANICS

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ABSTRACT. The small but vital role of ^{14}C dating in archaeometric research is clearly shown in the copper project reported herein. The ^{14}C ages place a time perspective on the "Old Copper Culture Complex," substantiating early Libby dates that had been questioned. The respective roles of INAA, PGE and Pb isotope work are briefly summarized. A long tradition of heat treatment from Paleoindian stone to Archaic copper is suggested.

INTRODUCTION

The multidisciplinary copper research program reported here was implemented by a consortium of research facilities, universities, private enterprise and government to better characterize copper materials from the Great Lakes Region of North America. The main objectives of the project were:

1. *Non-Destructive Chemical Analyses*

Samples from copper artifacts were obtained from various locations in Ontario and analyzed at the SLOWPOKE Reactor Facility using instrumental neutron activation analyses (INAA). The elemental concentration data were placed in general fields that were predetermined by Hancock *et al.* (1991a, b) with respect to gold, silver, arsenic and antimony. We clearly separated copper from European and North American origins. Chemical characterization precludes the possibility of accidently mixing European with American materials.

2. *Measurement of Platinum Group Elements*

The IsoTrace Facility analyzed the platinum group element (PGE) distribution in samples of European and North American copper, and the data showed clear separations consistent with those obtained by the SLOWPOKE Reactor Facility. This unique application is believed to be the first use of accelerator mass spectrometry (AMS) for this kind of problem.

3. *Determination of Lead Isotope Ratios*

Copper samples from both European and North American sources were analyzed at the Lead Isotope Laboratory. The resulting data are consistent with the other two elemental analyses and also represent a unique application.

4. *Radiocarbon Dating of Copper-Preserved Organics*

The IsoTrace Facility ^{14}C dated organic materials preserved by copper salts from "Old Copper" artifacts to determine their ages. Copper spear points from the Renshaw and South Fowl Lake sites had preserved cordage, bark twine and wood in their tangs. These materials yielded dates that were internally consistent (Fig. 1; Tables 1, 2, 3). The samples taken were only of milligram size leaving the remainder for other kinds of analyses. We discuss here the AMS ^{14}C dating of these organic remains.

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TABLE 1. IsoTrace ^{14}C AMS Results

Sample	Material	Weight (mg)	IsoTrace (TO no.)	^{14}C age (yr BP)
Anderson #1	Wood splinter	12	-2216	5940 ± 90
Renshaw #1	Plant fiber	29	-2213	4590 ± 50
Renshaw #2	Wood fragments	23	-2214	*
Renshaw #3	Twined cordage	66	-2215	4630 ± 60
Renshaw #4	Wood fragments	30	-2441	4420 ± 60

*This sample was lost during laboratory processing.

TABLE 2. Calibrated Age Ranges with Probabilities

Probability	Calibrated age (cal BC)	68.3% Confidence interval (cal BC)	95.5% Confidence interval (cal BC)
Anderson #1: 5940 ± 90 BP			
62%	4930	4942–4771	5068–4666
100%	4892	4909–4774	5066–4667
100%	4885	4909–4774	5066–4667
100%	4842	4909–4774	5066–4667
100%	4809	4909–4774	5066–4667
Renshaw #1: 4590 ± 50 BP			
100%	3356	3374–3338	3383–3299
Renshaw #3: 4630 ± 60 BP			
75%	3488	3504–3408	3527–3310
100%	3371	3382–3347	3526–3312
Renshaw #4: 4420 ± 60 BP			
55%	3250	3304–3237	3342–2914
100%	3085	3105–3020	3340–2915
100%	3071	3105–3020	3340–2915
100%	3039	3105–3020	3340–2915
74%	2945	3002–2925	3341–2915

TABLE 3. Summary of Calibrated Ages

Sample	Material	IsoTrace (TO no.)	Calibrated age (cal BP)	68.3% error	95.5% error
Anderson #1	Wood splinter	-2216	6800	+60, −70	+220, −180
Renshaw #1	Plant fiber	-2213	5310	+20, −20	+30, −60
Renshaw #3	Twined cordage	-2215	5320	+10, −25	+155, −60
Renshaw #4	Wood fragments	-2441	5020	+40, −45	+275, −150

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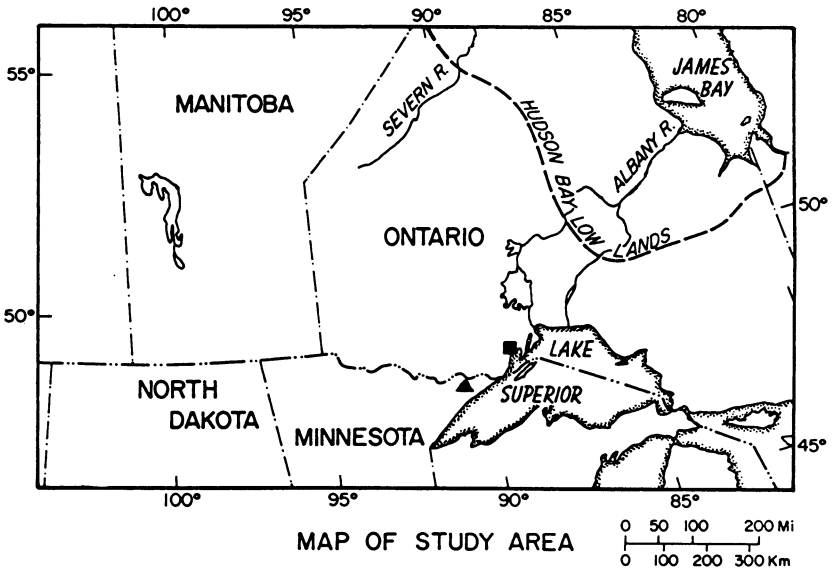

Fig. 1. Map of the research area: ▲ – South Fowl Lake site; ■ – Renshaw site

Background

Preserved recognizable organic remains are rare in archaeological contexts. An extraordinary environment for the preservation of organic materials is one created by the toxic qualities of copper salts associated with the weathering of copper materials. Under certain conditions, copper artifacts can provide this unique environment of preservation. As a rule, the organics preserved are those encapsulated by, or in close proximity to, copper metal. Thus, the amount of material preserved tends to be very small. Prior to the advent of AMS, small sample size was a deterrent to ^{14}C dating.

Copper materials associated with the "Old Copper" complex or industry, the subject of a long chronological debate (West 1929, 1932; Flaskerd 1940; Miles 1951; Wittry 1951; Griffin 1961, 1964; Giddings 1968), provided the bases for this study. Age determinations attributable to this Archaic-period variant were possible with the advent of ^{14}C dating. Libby (1955) and Ritzenthaler and Wittry (1952) reported the first ^{14}C dates from "Old Copper" cultural material, charred wood directly associated with an Archaic burial from the Oconto site. Libby's early date for the complex (5560 ± 600 BC (uncalibrated): Sample numbers C-837 and C-839 combined) was questioned by researchers (*cf.* Johnson 1955; Griffin 1961), but results reported here substantiate his early result.

The samples and their sites

Organic materials preserved by copper salts in copper artifacts from the Renshaw and South Fowl Lake archaeological sites provide a unique opportunity to use AMS ^{14}C dating for gaining insights into ancient humans who occupied what is present-day Ontario (Pavlish & Banning 1980). We chose samples that contained small amounts of preserved plant material.

South Fowl Lake

The Fowl Lakes are located on the extreme northeastern boundary of Minnesota and Ontario (Fig. 1). The copper artifacts recovered from the South Fowl Lake site have been attributed to the Old

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Copper Culture Complex, a regional term for an Archaic-period manifestation. One copper sample, named the Anderson point after its collector, had a well-preserved wood splinter lodged in its tang (Platcek 1965).

Renshaw

The Renshaw archaeological site, DaJi-1 (Canadian Borden No. designation), is one of less than 100 known Archaic-period habitation sites in the western Lake Superior region, and is one of the few to have been excavated. The site is near Thunder Bay, Ontario on a gravel ridge within 1 km of the present Lake Superior shoreline (Fig. 1).

Four copper samples from the Renshaw site produced close-proximity microenvironments that preserved three associated organic materials. Sample DaJi-1 #1 is a unilaterally barbed copper harpoon point with a well-preserved plant-fiber binding (hafting?) of bark wrapped around its shaft. Sample DaJi-1 #2 is a leaf-shaped copper spear point with wood fragments preserved in its tang. Sample DaJi-1 #3 is a one-of-a-kind small copper toggle-like harpoon spear point with remarkably well-preserved grass-based twined cordage threaded along its internal length (Fig. 2). Sample DaJi-1 #4 is a spear point with a well-preserved 0.25-g piece of wood shaft in its tang.

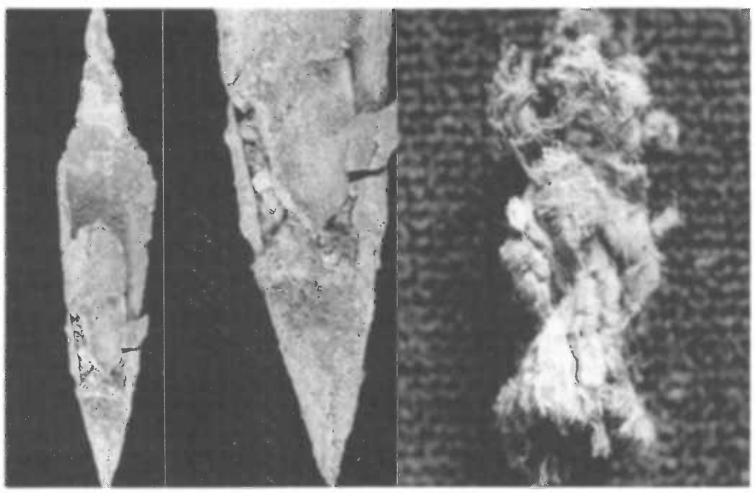

Fig. 2. The harpoon point from the Renshaw site and the location of the cordage are shown along with a closeup of the material after its removal. Only a small portion of the material was required for dating.

Analytical Procedure

Sample Processing

Each sample for ^{14}C dating was physically removed from the copper artifacts with dental tools while being observed under a microscope. The milligram-sized samples were pretreated with the standard acid-alkali-acid (AAA) method to remove all soluble contaminants. The residue was combusted to carbon dioxide in an ampoule combustion system with clean copper oxide and converted to acetylene by lithium carbide synthesis. Electrical dissociation of the acetylene gas in an AC high-voltage discharge produced two graphite targets on 2.5-mm-diameter aluminum pellets, ready for insertion into the ion source.

Mass Spectrometric Analyses

The individual graphite targets were placed on a movable stage (Wilson *et al.* 1984) in an evacuated sample chamber. The stage has a capacity for 5 samples and 2 reference standards. Only 1 of the 2 machine-ready targets from an individual sample was included in each accelerator run.

Sixteen positions were sequentially sampled on each graphite target. For every position, ^{14}C was measured for 10 s; the ^{12}C and ^{13}C currents were measured before and after. The currents were averaged at every position and the ratios and errors of ^{14}C to ^{12}C and ^{13}C to ^{12}C were determined. The age of the sample was then calculated using the Libby half-life of 5568 yr and expressed in standard ^{14}C yr before present (BP), present being defined as AD 1950. Table 1 presents these results with sample weights (Beukens 1971; Beukens, Gurfinkel & Lee 1986).

Results and Conclusions

The results in ^{14}C yr cannot be compared directly to calendrical years, as they use the Libby half-life of 5568 yr instead of the actual characteristic half-life of 5730 yr, and they do not take into account the variable ^{14}C production due to variations of cosmic-ray intensity. Calibration curves of ^{14}C measurements on dendrochronologically dated wood ranging from AD 1950 to 7000 BC are available (de Jong, Becker & Mook 1886; Kromer *et al.* 1986; Linick, Suess & Becker 1985; Linick *et al.* 1986; Pearson & Stuiver 1986; Pearson *et al.* 1986; Stuiver *et al.* 1986). Figure 3 shows the section of interest for these copper artifacts produced by C14CAL, an analytical dendrochronological calibration program designed by R. P. Beukens utilizing data provided by Pearson *et al.* (1986: 911–934); de Jong, Becker and Mook (1986: 939–941) and Kromer *et al.* (1986: 954–960) for the time regions of interest. The absolute probability as a function of age was calculated from the calibration data, and is presented in Figure 4 for the South Fowl Lake, Anderson Point and Renshaw dates. The solutions with 100% probability represent those ages where the ^{14}C ages intersect with the calibration curve. As the curve is not a simple linear function, multiple solutions may occur with varying degrees of probability. The most likely solutions (peaks with a probability of greater than 50%) and their statistical ranges, as derived from the calculated probability as a function of age, are shown in Table 2. By convention, these calibrated ages are expressed in cal AD or cal BC, to distinguish them from historical ages. Another acceptable way to express them is in calibrated years before present (cal BP), where present is defined as cal AD 1950.

The direct dating of the organic materials preserved in archaeological copper materials permits ^{14}C dating without questions of context. The results indicate that the Renshaw site materials were last used and deposited between 5 and 5.3 ka cal BP, and that the Anderson point is *ca.* 6.8 ka cal BP. Table 3 shows these results.

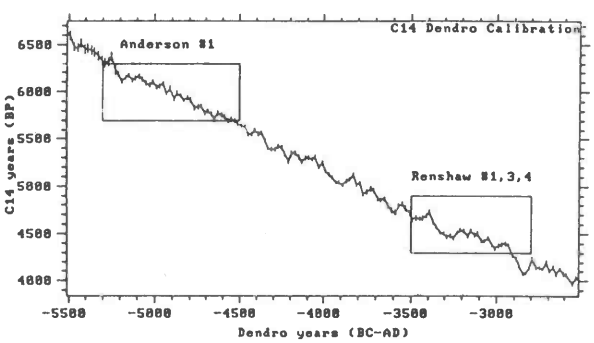

Fig. 3. Part of the dendrochronological calibration curve with the regions of interest emphasized

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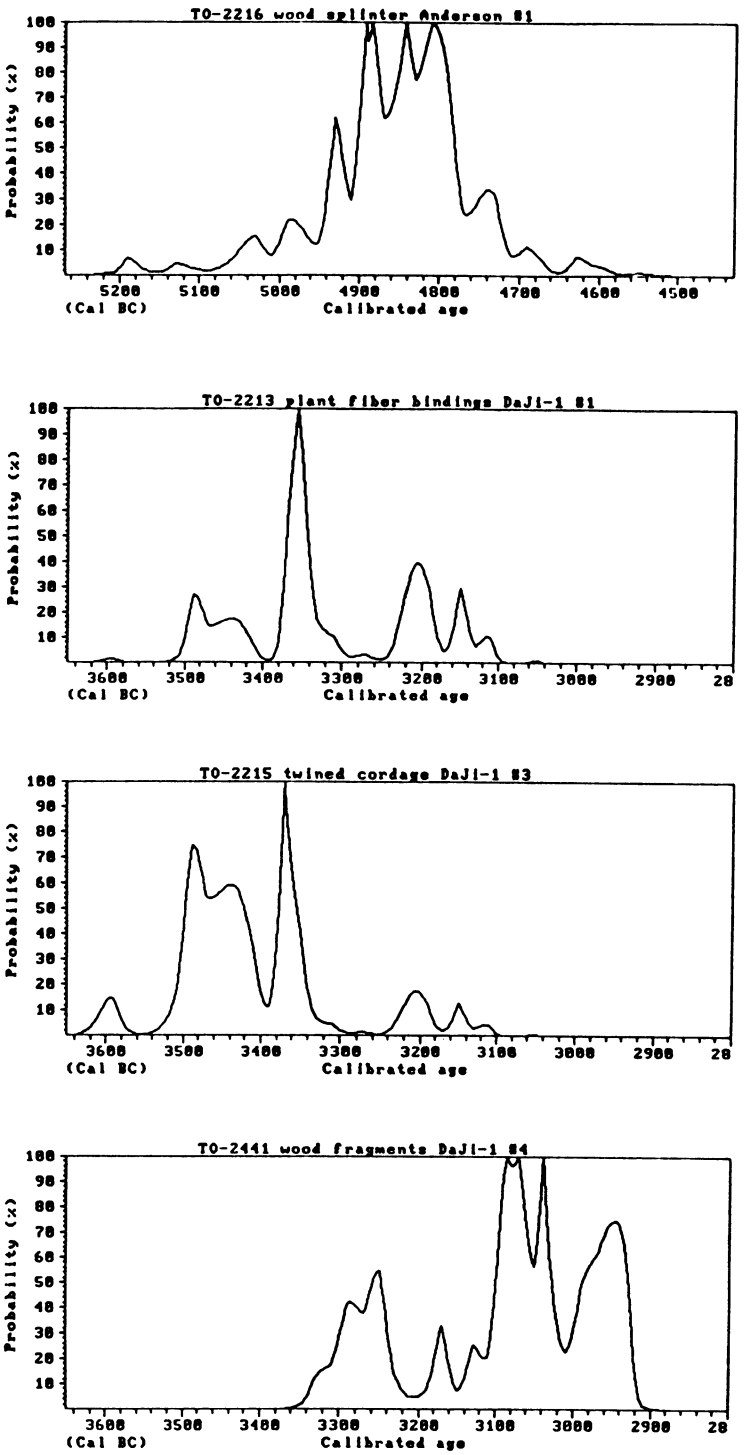

Fig. 4. The probability curves for the intersection of ^{14}C ages with tree-ring ages for the samples analyzed at IsoTrace

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What are the implications of these directly dated copper artifacts? Copper was one of the first metals to be integrated into ancient tool technology. Little evidence exists of Eurasian utilization before smelting processes developed early in the second millennium BC (Tylecote 1987; Renfrew 1973). However, on the basis of the direct date obtained on the Anderson point (5940 ± 90) (Table 1) (Platcek 1965), the prehistoric populations of the Lake Superior region of North America appear to have been utilizing materials in the Fowl Lakes region on the present-day Minnesota - Ontario border by *ca.* 7 ka cal BP.

Prior to this work, most researchers would have attributed the appearance of large utilitarian copper tools to *ca.* 5 ka cal BP. The direct dating of the Anderson point removes any questions of context association and substantiates the earlier claims for the greater antiquity of copper use in the Lake Superior region. Libby's (1955) early date (5560 ± 600 BC) for the complex (Ritzenthaler & Wittry 1952) has been questioned (*cf.* Johnson 1955; Griffin 1961). Further, that low-temperature annealing had to be used on the otherwise unworkable native copper supports the idea that a long, continuous heat-treating tradition existed in the Great Lakes region of North America (Pavlish & Sheppard 1983; Purdy 1982).

While the Renshaw ^{14}C ages are not separable at the 95.5% confidence level (Tables 1, 3), the preserved wood, bark and grass cordage from the copper materials establishes the antiquity of this component of the site at *ca.* 5.3 ka cal BP. These results extend evidence for Archaic occupations at the site back by *ca.* 1.7 ka. A previous estimate, based on a ^{14}C-dated hearth feature from the Lake Algoma beach strand, was assumed contemporaneous due to geomorphic association (Arthurs 1979). The age range of occupation at both the South Fowl Lake and the Renshaw sites reaffirm a picture of long, discontinuous occupation by Archaic copper users in the Lake Superior region of North America.

Acknowledgments

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