Journal of Archaeological Science: Reports 6 (2016) 332–341

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry analysis of copper-based artifacts from Southern Ontario and the chronology of the indirect contact period

Alicia L. Hawkins [a,*], Joseph A. Petrus [b], Lisa Marie Anselmi [c], Gary Crawford [d]

[a] School of the Environment, Laurentian University, 935 Ramsey Lake Road, Sudbury, ON P3E 2C6, Canada
[b] Department of Earth Sciences, Laurentian University, 935 Ramsey Lake Road, Sudbury, ON P3E 2C6, Canada
[c] Department of Anthropology, SUNY Buffalo State, Buffalo, NY 14222, USA
[d] Department of Anthropology, University of Toronto at Mississauga, 3359 Mississagua Road, Mississauga, ON L5L 1C6, Canada

ARTICLE INFO

Article history:
Received 15 May 2015
Received in revised form 10 February 2016
Accepted 20 February 2016
Available online xxxx

Keywords:
LA-ICP-MS
Native copper
European copper
Brass
Late Iroquoian
Indirect contact period
Ontario

ABSTRACT

Samples of copper-based artifacts from four components from three Late Iroquoian archaeological sites in southern Ontario were analysed using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry. Compositional analysis showed that the concentrations of Ni, Zn, As, Ag, Sn, Sb, Au, Bi, Co, In and Pb clearly differentiate North American native copper from European-introduced smelted copper and brass. Together with radiocarbon dates, this indicates the presence of trade metals on Iroquoian sites in the early to mid sixteenth century, well in advance of a European presence in the region. The small sample analysed suggests that red brass appears earlier than yellow brass, and trade metals may be found at sites in the Lake Ontario drainage before they are found in the southern Georgian Bay area.

1. Introduction

The later contact period in Ontario (ca. 1580 to 1650 CE) is relatively well dated using glass bead chronology (Fitzgerald et al., 1995; Kenyon and Kenyon, 1983) but it is clear that European metal items were traded during a period of indirect contact in advance of the beginning of trade in glass beads (Birch and Williamson, 2012; Fox et al., 1995). Exactly when this trade began is not clearly established, because most chronological assessments of Ontario Iroquoian sites are made using pottery seriation. The radiocarbon calibration curve for the sixteenth century is relatively flat, further complicating the matter. Copper-based metal (primarily smelted copper or brass) is found on many Ontario Iroquoian sites in greater and smaller quantities; however, the longstanding use and exchange of native copper in eastern North America make it impossible to determine its origin without chemical analysis. The simple and relatively effective scratch test described by Fitzgerald and Ramsden (1988) may allow separation of copper from brass, but it cannot differentiate between native copper and European trade copper. Thus, methods such as Instrumental Neutron Activation Analysis (INAA), X-Ray Fluorescence (XRF), and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS), provide means by which to determine the chemistry, and therefore origin, of copper-based metal artifacts. When coupled with a program of radiocarbon dating, such analysis may allow us to determine more precisely when metal trade materials reached the lower Great Lakes marking the inception of the period of indirect contact.

This article presents results of LA-ICP-MS analysis of 37 samples from 24 copper-based metal objects from three sites in Ontario: Ellery, Emmerson Springs, and Wallace (Fig. 1). Together with previously unpublished radiocarbon dates from these sites, we aim to address the question of the timing of the period of indirect contact in southern Ontario. INAA has been an important tool in understanding the use of copper-based metal in Ontario, and we examine the degree to which results obtained by LA-ICP-MS are comparable with those obtained by INAA. The suite of elemental concentrations that can be obtained by the two types of analysis are different, and we consider if elements other than those identified in INAA studies may be helpful to distinguishing European smelted copper from North American native copper.

* Corresponding author.
E-mail addresses: ahawkins@laurentian.ca (A.L. Hawkins), jpetrus@laurentian.ca (J.A. Petrus), anselmlm@buffalostate.edu (L.M. Anselmi), g.crawford@utoronto.ca (G. Crawford).

http://dx.doi.org/10.1016/j.jasrep.2016.02.022

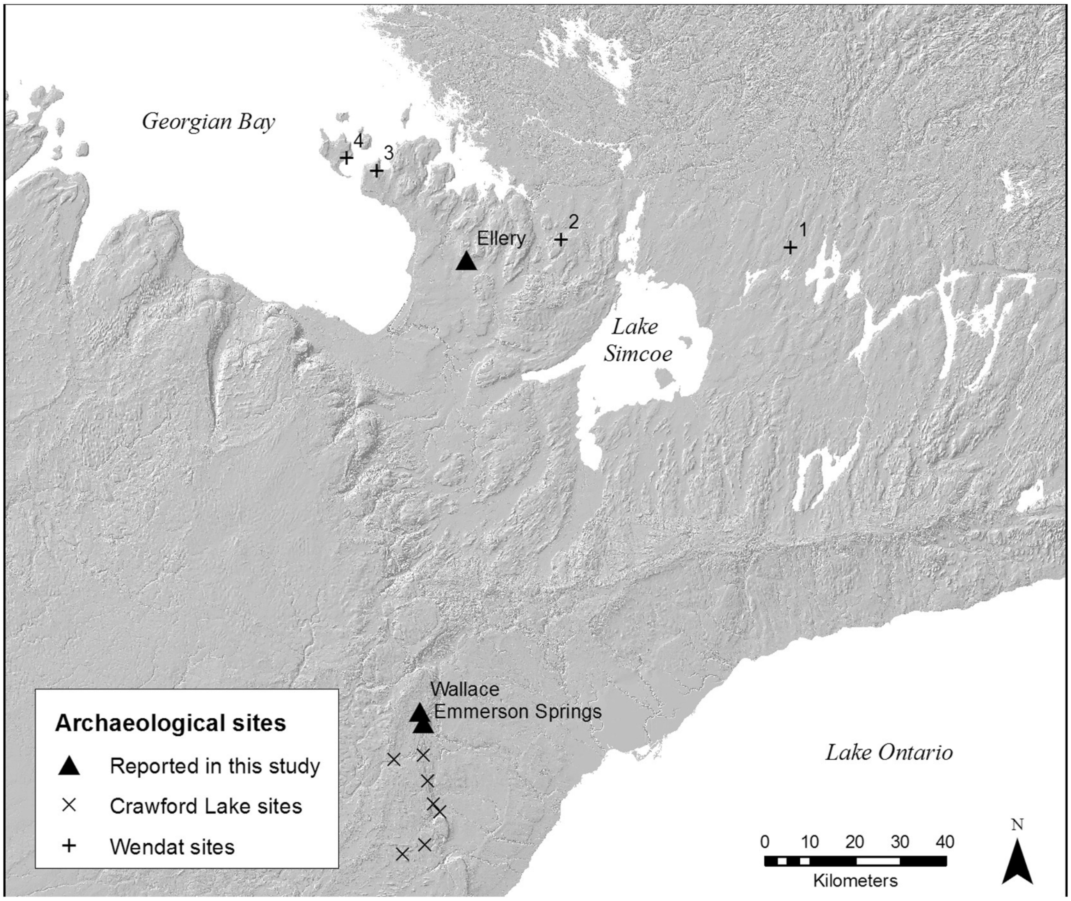

Fig. 1. Location of the sites with copper analysed by LA-ICP-MS and other sites mentioned in the text. Wendat sites: 1 - Benson, 2 - Ball, 3 - Robitaille, 4 - Ste. Marie II. Map data from the Ontario Geological Survey 2010. Surficial geology of southern Ontario; Ontario Geological Survey, Miscellaneous Release Data 128 — Revised.

2. Copper characterization studies in Eastern North America

A number of different analytical methods have been applied to determine compositions of archaeological copper-based metals in North America. These include Instrumental Neutron Activation Analysis (INAA), Particle Induced X-ray Emission spectrometry (PIXE), X-ray fluorescence (XRF) and Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS). Analysts frequently employ metallography (e.g., SEM) in concert with compositional analysis (e.g., Dussubieux et al., 2008; Ehrhardt, 2005; Wayman et al., 1985). The goals of these different examinations include characterizing North American source materials and artifacts deriving from them (e.g., Hill, 2009; Lattanzi, 2013; McKnight, 2007); distinguishing between native copper and European smelted copper (e.g., Abel and Burke, 2014; Dussubieux et al., 2008; Dussubieux and Walder, 2015; Fleming and Swann, 2000; Ehrhardt, 2005; Fox et al., 1995; Gersch et al., 1998; Hancock et al., 1991, 1993; Wayman et al., 1985); and characterization of the composition of copper-based alloys (brasses and gunmetals) (e.g., Anselmi et al., 1997; Hancock et al., 1995a; Pavlish et al., 1998; Michelaki et al., 2013). Only the latter two study types are pertinent to this paper.

In Ontario, the bulk of the research on the composition of archaeological copper has been conducted using INAA, which provides quantified estimations of the bulk concentrations of many elements in an artifact. INAA of copper-based metals has two limitations: a) it is not possible to obtain concentrations of lead and b) large objects cannot be analysed whole and must be sub-sampled. PIXE also provides quantified estimations of the concentrations of elements relevant to distinguishing native copper from European smelted copper. The detection limits (LOD) are higher than for INAA, but PIXE has the advantage of detecting lead (Fleming and Swann, 2000; Gersch et al., 1998). X-ray fluorescence (XRF) provides semi-quantitative results and can distinguish native copper from European smelted copper on the basis of the presence or absence of a number of elements, including lead (Abel and Burke, 2014). Table 1 summarizes the elements found to be useful for distinguishing different native copper from European smelted copper using these three techniques.

Table 1
Elements considered useful to separate native copper from European smelted copper using different analytical techniques.

Analytical method	Distinguishing elements and levels in native copper	References
INAA	As (≤105 ppm)[a]	Hancock et al. (1991),
	Sb (≤55 ppm)[a]	Wayman et al. (1985)
	Au (≤130 ppb)	
	Ag (≤300 ppm)	
	Co (≤1–6 ppm)	
	Ni (below LOD)	
	In (below LOD)	
	Cd (below LOD)	
	Se (below LOD)	
PIXE	Ag (<300 ppm)	Ehrhardt (2002), Fleming and
	As (<100 ppm)	Swann (2000), Gersch et al. (1998)
	Sb (below LOD)	
	Pb (below LOD)	
	Ni (at or below LOD)	
XRF	Pb (below LOD)	Abel and Burke (2014)
	As[b]	
	Sb[b]	
	Bi (below LOD)	

[a] Some sources of native copper have elevated levels of As, Sb, Sn and Hg.
[b] Elevated concentrations of As and Sb in a sample with high Pb indicates European copper.