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Identifying American native and European smelted coppers with pXRF: a case study of artifacts from the Upper Great Lakes region

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ABSTRACT

In North America, it is critical for archaeologists to differentiate between American native copper and European smelted copper. Indeed, native copper, a rather pure metal, was not smelted in this region, unlike European copper objects that later became available to Native Americans during trading encounters. Until now, archaeologists with a low budget wishing to use a totally non-invasive approach have relied on visual inspection and archaeological contextualization of the objects to distinguish American native copper from European smelted copper. This paper assesses the reliability of portable x-ray fluorescence (pXRF) as a fast, effective, and completely non-destructive method of differentiating the two types of copper present at Northern American sites through a case study of two sites from the Upper Great Lakes region. To establish group attribution with pXRF, results obtained on a subset of objects with LA-ICP-MS are used. Results indicate that for the specific purpose of differentiation between native and European copper types, pXRF can be used reliably, without sample preparation and despite surface corrosion. Therefore, pXRF provides a non-destructive way to clarify European trade item distribution and continuity of native copper object use among Indigenous peoples of North America during the colonial period.

1. Introduction

In North America prior to European contact, Native peoples did not smelt copper ore, but practiced cold-working, annealing, and other forms of non-pyrotechnic metallurgy on nuggets and sheets of native copper available mostly in the Great Lakes area (Martin, 1999: 23–30; Pleger and Stoltman, 2009: 707–709; Rapp et al., 2000). Later, European objects made from smelted copper, such as trade kettles, became available to Native Americans during trading encounters; Native people often dismantled and modified copper trade items to create personal adornments and other objects (Anselmi, 2008; Ehrhardt, 2005; Turgeon, 1997).

Differentiating these two different types of copper is useful in two situations:

1) Recognition of possible “protohistoric” sites, where smelted European copper might be the only trade item present in the assemblage, likely obtained through down-the-line trade.
2) Demonstrating persistence of traditional copper-working technology in later historic periods among Native American peoples who also were obtaining items originally manufactured in Europe.

Different approaches have been developed to identify American native and European smelted copper. Archaeologists have visually documented Native American metalworking techniques applied to copper artifacts to categorize technological styles of working native and smelted copper (Latta et al., 1998; Anselmi, 2008). In addition, sophisticated analytical techniques such as Instrumental Neutron Activation Analysis (INAA) (Wayman et al., 1985; Hancock et al., 1991, 1993, 1994; Cooper et al., 2008; Michelaki et al., 2013 (INAA of copper and brass)), Particle X-Ray Induced Emission (PIXE) (Gersch et al., 1998; Ehrhardt et al., 2000; Fleming and Swann, 2000), Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) (McKnight, 2007; Dussubieux et al., 2008; Hill, 2012) and X-Ray Fluorescence (XRF) (Ehrhardt and Kaiser,

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2011; Abel and Burke, 2014) have been applied to determine the composition of metal artifacts. Previous research established that North American native copper contains very low levels of impurity in contrast with European smelted copper. To accurately separate the two types of copper, it is therefore necessary to use an analytical method with a good sensitivity for a large range of elements. Other requirements of researchers and curating institutions may include minimum destructiveness and large sample output to obtain significant results.

The popularity of portable XRF (pXRF) has been growing tremendously over the past decade, and it has been hugely successful to source obsidian (e.g. Kellett et al., 2013; Millhauser et al., 2011; Moholy-Nagy et al., 2013). For some other materials the use of pXRF is not as straight forward and the lack of sensitivity for some key elements in ceramic (e.g. Speakman et al., 2011) or problems such as the presence of surface corrosion or patina on metals (e.g. Charalambous et al., 2014; Martinón-Torres et al., 2014; Smith, 2013) could greatly affect the interpretation of the results. XRF in general is an analytical technique that measures the surface composition of an artifact, only penetrating a few microns to a few mm into the sample depending on the energy of the primary X-ray beam and the sample matrix. Compositions should be measured on cleaned and polished surfaces. Carrying out XRF analysis without sample preparation could be problematic in the case of copper or copper-based artifacts as they can be heavily corroded with a layer of oxidized material that can be 30 microns thick or more (Dussubieux et al., 2008). The composition of the corrosion layer is usually depleted in copper and can be enriched in a variety of trace elements (Moreau and Hancock, 1999). A previous study showed that it was possible to differentiate European smelted copper and North American native copper using portable XRF on artifact surfaces after removal of corrosion material (Ehrhardt and Kaiser, 2011). However, such cleaning is unacceptable in some cases. This paper assesses the feasibility of using pXRF as a fast and effective method of identifying cold-worked native versus European smelted coppers without any sample preparation. PXRF was applied to 43 copper artifacts from two archaeological sites in the Upper Great Lakes region and 18 of them were re-analyzed using LA-ICP-MS. Based on the comparison between the pXRF and LA-ICP-MS results, the nature of the metal used for the 25 samples only analyzed with pXRF was identified. A brief discussion of the archaeological implication of this study is provided.

2. Archaeological contexts

Copper-base metal artifacts appear on archaeological sites in North America beginning in the Middle Archaic period (c. 5000 BC) (Pleger and Stoltman, 2009), but smelted copper and brass did not become available until European explorers brought kettles and other metal items. In the Midwest, European-made materials are rare in archaeological assemblages dated prior to AD 1650; sites with a few trade items in an otherwise Native-made assemblage are considered "protohistoric." One reason that very few protohistoric sites have been identified in the Midwest may be inability to differentiate between native and smelted copper artifacts without compositional analysis. Archaeologists may classify copper objects as "native" when found in contexts with other locally-made artifacts, and as "European" only if other trade items are present, but in protohistoric contexts, this method of contextual differentiation is ineffective. To demonstrate the usefulness of the archaeometric approach, two known protohistoric contexts were selected for this study (Fig. 1).

Both sites, Rock Island (47 WN 128) and Clunie (20 SA 722), have protohistoric components evidenced by clearly European-made items, such as glass beads. These sites were selected because their copper-based metal assemblages potentially included both cold-worked native copper and European-made smelted copper artifacts.

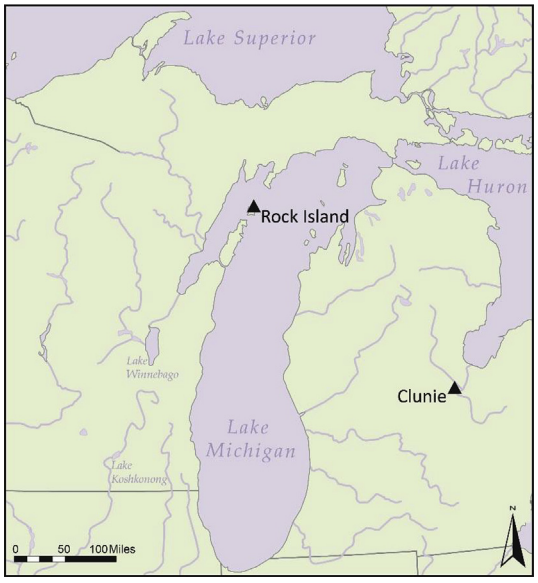

Fig. 1. Locator map for archaeological sites of origin for metal samples.

Rock Island is a multi-component village site on an island off the tip of the Door Peninsula in Wisconsin, with prehistoric Woodland and Oneota components (Mason, 1990, 1991), along with extensive historic-era occupations. Excavators Carol I. and Ronald J. Mason divided the historic occupations into four periods that coincide with major historical events and dominant occupation by different tribes (Table 1, adapted from Mason, 1986). The assemblages from the first two historic periods contained significant proportions of Native-made ceramic and lithic materials and relatively few trade items, including some copper artifacts. Copper was also present in the prehistoric components, demonstrating continuous use of such metal objects and working methods on site. More than 1000 copper-based metal artifacts were recovered from all periods of habitation at the Rock Island site.

Sample selection of Rock Island copper-based metal artifacts was designed to answer the following archaeological research questions:

1) Were smelted copper objects obtained in the proto-historic period at Rock Island, prior to AD 1670? Since a few other European-made trade goods were identified in association with Lake Winnebago Trailed Oneota ceramics, smelted copper could have been present as well.
2) Did the use of native copper persist in late 17th and 18th century occupations of Rock Island? European-made trade items, including cut copper and brass scrap are abundant in this period, but native copper objects also might be present in the assemblage. Continuity of copper-working might include materials as well as methods.

Table 1
Periods of occupation at the Rock Island site.

Period	Dates	Tribal affiliation
1	Post 1641–Pre 1650/51	Potawatomi
2	1650/51–1653	Huron-Petun-Odawa, or Proto-Wyandot
3	c. 1670–1730	Potawatomi
4	1760–1770	Odawa