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Copper mining on Isle Royale 6500–5400 years ago identified using sediment geochemistry from McCargoe Cove, Lake Superior

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Abstract

Isle Royale, in Lake Superior, contains evidence of indigenous copper mining; however, the timing and geographical extent of mining activity is poorly known. We analyzed metal, carbon, nitrogen, and organic matter concentrations to document past mining pollution in sediment cores recovered from McCargoe Cove; a long, narrow inlet of Lake Superior on Isle Royale that receives drainage from a watershed that contains numerous ancient copper mines. At McCargoe Cove, concentrations of lead, copper, and potassium increase in the sediments after AD 1860 and between 6500 and 5400 years before AD 1950 (yr BP). Metal pollution increases at McCargoe Cove exceed natural (or background) levels and coincide with radiocarbon dates associated with copper artifacts and existing lead pollution reconstructions from lakes on the Keweenaw Peninsula. Interestingly, a coherent cessation of lead emissions at multiple study sites after ~5400 yr BP coincides with the onset of dry conditions found in regional paleoclimate proxy records. After ~5000 yr BP, lead concentrations on both Isle Royale and the Keweenaw Peninsula remain at background levels until the onset of modern lead pollution ~AD 1860.

Keywords

archaeology, lead, Michigan, Old Copper Complex, pollution, prehistoric copper mining, sediments

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Introduction

Copper use in the regions surrounding Lake Superior represents one of the oldest examples of metalworking (Figure 1), yet the timing and pattern of past copper mining activity is poorly constrained (Beukens et al., 1992; Martin, 1993; Pompeani et al., 2013). Indigenous peoples mined copper from open bedrock features such as trenches and pits and heated or annealed the copper with wood fires to aid in extraction and processing (Laronge, 2001; Martin, 1999; Schroeder and Ruhl, 1968). High densities of pre-contact (or prehistoric) mines are found along Minong Ridge on Isle Royale (Gillman, 1873; Lane, 1900; Winchell, 1881). Excavations of these pits revealed depths up to 20 m and included tools such as rock hammers (i.e. hammerstones) and deposits of charcoal. Field surveys show that the mine pits are concentrated along a 3-km section of Minong Ridge starting from the western shoreline of McCargoe Cove (Figure 2) (Gillman, 1873).

Previous lead (Pb) pollution reconstructions from lake sediments on the Keweenaw Peninsula document several periods of heightened sediment Pb loadings associated with copper mining from 8000 to 5000 yr BP (Pompeani et al., 2013). The restricted geographic distribution of the Keweenaw Peninsula study area relative to the larger Michigan Copper District region limited the scope of the investigation and raised new questions regarding the timing, intensity, and spatial pattern of the ancient copper mining industry. For example, on the Keweenaw Peninsula, Pb emissions were not detected after 5000 yr BP, even though copper artifacts are dated to this period (Crane and Griffin, 1965; Martin, 1993). A reduction in Pb emissions suggests that an intensive copper industry was absent or had shifted to other regions after 5000 yr BP. To explore the spatial pattern of ancient metalworking, we recovered lake sediments from McCargoe Cove; a long, narrow inlet of Lake Superior located on Isle Royale.

The Portage Lake Volcanic bedrock was targeted for mining because it contains large deposits of native copper ‘fissure veins’ and vesicles containing secondary native copper (Figure 1) (Pompeani et al., 2013; Rosemeyer, 2009). Copper mines and related piles of poor rock, tailings, and soil (i.e. overburden) are frequently found around Lake Superior where the Portage Lake Volcanic bedrock is exposed or near the surface. Poor rock contains low copper concentrations and is commonly piled near the mine entrance (or adit). Tailing refers to the remaining source rock and residues associated with the copper ore that remains after

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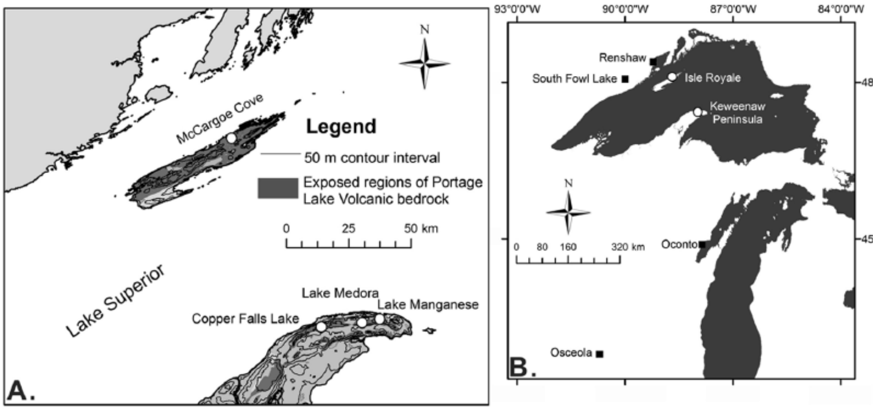

Figure 1. (a) Maps showing the location of the Keweenaw Peninsula and Isle Royale with sediment core locations (circles). Dark gray areas are regions where Portage Lake Volcanic (PLV) bedrock is exposed at the surface or covered by shallow Quaternary deposits. The PLV is the primary copper-bearing rock exploited by prehistoric miners (Hill, 1847; Pompeani et al., 2013; Whittlesey, 1862). (b) Map of the Upper Great Lakes region with study locations (circles) noted in relation to archaeological sites (squares) mentioned in the text.

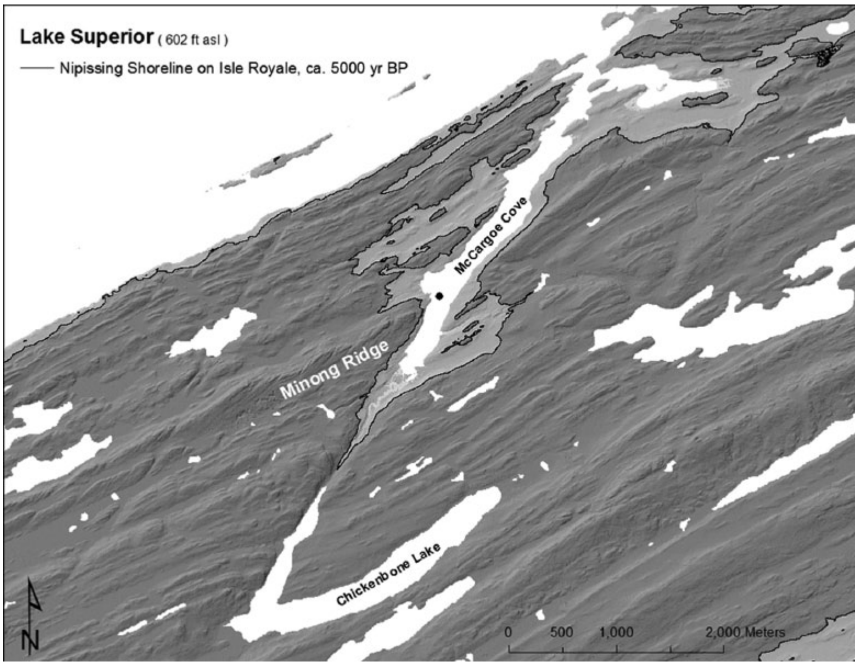

Figure 2. Topographic map of the study location. The black circle in McCargoe Cove marks the location of the sediment core. Black contour line indicates the approximate Lake Superior shoreline during Nipissing Highstand ~5000–4500 yr BP (Blewett, 2009; Breckenridge, 2013).

processing (i.e. stamp mill, smelting, annealing, etc.). Runoff from indigenous overburden piles and mine pits on Minong Ridge flows directly into McCargoe Cove, providing a unique location in which to measure past sedimentological and geochemical disturbances associated with pre-contact mining. Hereafter, this is referred to as the Old Copper mining period.

Background

Setting

Isle Royale is a freshwater archipelago comprised of a main island and approximately 200 smaller islands that stretch for ~70 km along the northwestern portion of Lake Superior. The copper-bearing Portage Lake Volcanic metabasalt bedrock formed topographic ridges that remained as islands in Lake Superior following deglaciation around 12,000 yr BP (Clayton, 1983; Lewis and Anderson, 1989). The surface elevation of Lake Superior varied substantially following deglaciation (Lewis et al., 2008). The Nipissing, known as the highest lake-level transgression during the last 8000 years, peaked sometime between 5000 and 4500 yr BP (Figure 2) (Blewett, 2009; Breckenridge, 2013). After ~4000 yr BP, water levels fell to near modern and remained there until today. Numerous inland lakes and wetlands separated by bedrock ridges that parallel a southwest-northeast trend are found on Isle Royale. January temperatures average −11°C, and July temperatures average 14°C with large temperature gradients between coastal and inland portions of the island (Flakne, 2003). Soils are poorly developed, especially on bedrock ridges, limiting vegetation cover. In areas with sufficient soil to support trees, such as around McCargoe Cove, boreal forests are present including species such as white birch (*Betula papyrifera*), aspen (*Populus tremuloides*), balsam fir (*Abies balsamea*), white pine (*Pinus strobus*), white spruce (*Picea glauca*), sugar maple (*Acer saccharum*), with occasional occurrences of red oak (*Quercus rubra*) (Flakne, 2003).

Evidence for ancient copper mining in Michigan

The earliest references to copper in the Great Lakes area come from Jacques Cartier's second voyage to the region in AD 1535–1536. Cartier noted the presence of copper among the native peoples inhabiting the Gulf of St Lawrence (Biggar, 1924; Griffin, 1961). In AD 1610, Samuel de Champlain met with Native Americans on the St Lawrence River who offered him a bar of copper that they said was from a source near a river draining into a large lake. For nearly 200 years following Cartier's and Champlain's accounts of copper, the French and British, with guidance from native groups, mined copper in the southern Lake Superior region with limited success (Biggar, 1925; Lankton, 2010). Although native peoples guided Europeans to pieces of float copper, there is no record of active copper mines (Whittlesey, 1863) or successful copper mining activity during the early European contact period with Native Americans (Griffin, 1961; Lankton, 2010). However, archaeological evidence indicates that the indigenous peoples of the Upper Great Lakes used copper at the time of contact with Europeans (Martin, 1999).

In AD 1843, the Lake Superior Anishinaabeg (Ojibwe) peoples relinquished lands that included the Keweenaw Peninsula and Isle Royale, marking the beginning of modern copper prospecting in the region (Lankton, 2010). Accounts and maps drawn by Samuel Hill in AD 1847 provide some of the earliest written evidence for pre-contact copper mines on the Keweenaw Peninsula (Hill, 1847). Excavations of the pits, first reported by John Foster and Josiah Whitney in AD 1850, confirmed that they were produced by humans, and suggested that they were abandoned for centuries (Foster and Whitney, 1850). In AD 1862, Michigan State Geologist Charles Whittlesey published a map of the mines on the Keweenaw Peninsula (Whittlesey, 1862). This was followed by publications by Whittlesey (1863) and Hagar (1865), which further described the remains and attempted to obtain minimum ages for the mines by counting rings within tree stumps on top of the overburden piles. These tree-ring counts suggested that the overburden piles were produced several hundred years ago. Explorations in other regions of the copper districts around Lake Superior revealed even more extensive workings, such as Minong Ridge on Isle Royale (Gillman, 1873; Holmes, 1901; Lane, 1900; Winchell, 1881).

Radiocarbon dating the prehistoric industry

The development of radiocarbon dating established the temporal context of copper use around the Upper Great Lakes. Willard Libby was the first to radiocarbon date charcoal preserved with copper artifacts from Oconto archaeological site (Figure 1). These analyses returned dates of 5600 ± 600 and 7510 ± 600 ^{14}C yr BP (or ~6400 and 8400 yr BP) (Libby, 1954; Stuiver et al., 2010). Subsequent radiocarbon measurements of organic matter associated with copper artifacts confirmed the dates obtained by Libby (Binford, 1962; Mason and Mason, 1961). Additional work expanded the number of radiocarbon measurements by dating charcoal and wood preserved in copper pit mines on Isle Royale, extending the potential age range for copper mining to younger periods (Crane and Griffin, 1965).

The development of accelerator mass spectrometry (AMS) radiocarbon dating made it possible to measure smaller masses of organic macrofossils associated with copper artifacts. Copper is a known bactericide and fungicide that helps to preserve organic matter in the case of the Old Copper societies. Beukens et al. (1992) were among the first to pioneer techniques to date organic matter preserved with copper artifacts. The median calibrated AMS radiocarbon age of ~6800 yr BP (5940 ± 90 ^{14}C yr BP) from South Fowl Lake is still considered one of the oldest reliable dates for worked copper in North America (Beukens et al., 1992; Martin, 1999; Stuiver et al., 2010). More recently, carbon preserved at the Oconto site, including a piece of string, produced five AMS radiocarbon ages ranging between 8400 and 5600 yr BP (Pleger, 2001). At another prominent Old Copper site in Osceola, Wisconsin (Figure 1), an estimated 500 individuals were buried with copper objects. Two pieces of charcoal preserved in the grave pit at this site had ages of ~4600 and 3700 yr BP (4080 ± 70 and 3450 ± 250 ^{14}C yr BP) (Kuehn, 2002; Stoltman, 1997). In general, these and other radiocarbon measurements (Martin, 1993) indicate that copper use in the Upper Great Lakes region probably occurred over a period of several thousand years, beginning by the Early Archaic (~11,500–6700 yr BP) (Pleger and Stoltman, 2009).

Little is known about the Archaic period (~11,500–2000 yr BP) on Isle Royale because most archaeological surveys focused on the present shoreline where pre-contact sites are limited to Woodland contexts (~2000–500 yr BP) (Clark, 1995, 1996). Archaic sites are restricted to the elevated beach ridges and the higher areas above them because the relative water level of Lake Superior has decreased since the Nipissing transgression (~5000 yr BP). An Archaic human presence on Isle Royale is inferred from radiocarbon measurements on charcoal preserved at the bottom of prehistoric copper mine pits near McCargoe Cove (Crane and Griffin, 1965). However, little is known about the occupational and subsistence technologies used by Archaic societies on Isle Royale, in part, because no burials have been discovered that can be directly attributed to the prehistoric copper mining societies. Differences in hammerstone styles found on Isle Royale and the Keweenaw Peninsula have been noted (Martin, 1999). For example, Keweenaw Peninsula hammerstones usually show evidence of hafting (i.e. grooves carved into the rock for a strap wrapped around a handle), whereas hammerstones on Isle Royale typically consist of a rounded igneous or metamorphic cobble with no evidence of hafting. Recent excavations on Isle Royale at the inland beach ridges do not reveal artifactual evidence typical of the Old Copper Complex (Clark, 1995), which is mainly found to the south of Lake Superior and typified by the copper-using cultures associated with human burials found at Oconto and Osceola Cemeteries in Wisconsin (Figure 1b) (Pleger and Stoltman, 2009). Additionally the lithic artifact assemblages associated with Archaic contexts on Isle Royale appear to be more related to northern Lake Superior groups, including the Shield Archaic (Clark, 1996). Radiocarbon measurements associated with copper artifacts found north of Lake Superior at the Renshaw Site in Thunder Bay, Ontario, and at South Fowl Lake in Minnesota reveal that they were produced in the Archaic period (Figure 1b) (Beukens et al., 1992). In summary, the artifact record from Isle Royale is sparse and current archaeological research indicates no outstanding connection between the Old Copper Complex material cultures found in Wisconsin and Michigan beyond the use of copper technologies. Therefore the label 'Old Copper' used in this study is not intended to denote individuals or cultures responsible for the mining remains, but rather as a short descriptor for the interval when prehistoric mining pollution is detected during the Archaic period.

Methods

Fieldwork

In June 2012, five 1-m-long overlapping Livingstone cores and a polycarbonate surface-sediment core spanning 3.6 m was taken at a water depth of 9.4 m in McCargoe Cove (48.0923°N, 88.7044°W) about 0.1 km northeast of Minong Ridge (Figure 2). The sediment cores were wrapped in plastic wrap and sealed in ABS tubes for transport to the Department of Geology and Planetary Science at the University of Pittsburgh. The flocculate upper surface sediments were extruded in the field at 0.5-cm intervals to 30 cm depth and stored in Whirl-Paks® for transport.

Radiometric dating

The age profile for the upper 16 cm was determined using ^{210}Pb assays, while the lower 2.5 m was dated using six AMS radiocarbon measurements on terrestrial macrofossils. Radioisotope (^{210}Pb and

^{214}Pb) activities were interpreted using the constant rate of supply (CRS) model by direct gamma counting using a high-purity, broad-energy germanium detector (Canberra BE-3825) in the Department of Geology and Planetary Science at the University of Pittsburgh following a 3-week equilibration period in airtight Petri dishes (Appleby and Oldfield, 1978; Binford, 1990; Lima et al., 2005). Sediment sub-samples extracted for radiocarbon dating were disaggregated with 7% H_2O_2 and sieved through a 125-μm screen to isolate terrestrial macrofossils. The macrofossils were picked using a small brush under a binocular microscope and were pretreated following standard acid-base-acid procedures (Abbott and Stafford, 1996). Radiocarbon samples were measured at the W. M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory.

Loss-on-ignition

In the laboratory, 1-cm^3 sub-samples were taken at 3-cm intervals and dried at 60°C for 48 h. Loss-on-ignition (LOI) was measured by combusting the dried sediments at 550°C for 4 h and at 1000°C for 2 h to determine weight percent organic matter and carbonate content (Dean, 1974; Heiri et al., 2001).

X-ray diffraction analyses

The mineralogy of the core was investigated by powder x-ray diffraction (XRD) using a Philips PW3710 X'Pert® x-ray diffractometer at the University of Pittsburgh Swanson School of Engineering. Three 1-cm-thick samples were taken at a mean depth of 51.5, 217.5, and 297.5 cm and pretreated using 7% H_2O_2 for 12 h at room temperature to remove organic matter. The sediments were then washed with deionized water, frozen, lyophilized, and homogenized before XRD analyses. The spectra were analyzed using X'Pert Graphics and Identify® software to identify mineral assemblages present.

Carbon and nitrogen analyses

Dry homogenous sediment sub-samples for carbon and nitrogen analyses were treated with 1 M HCl for 12 h at room temperature, centrifuged, and the resulting supernatant was decanted. The sediments were rinsed with deionized water, frozen, and lyophilized. The dry pretreated sub-samples were then analyzed using Elemental Combustion System 4010 interfaced to a Delta V advantage mass spectrometer through the ConFlo IV system to determine total organic carbon and total nitrogen concentrations at the Stable Isotope Laboratory at Idaho State University. The furnace temperature was kept at 1000°C, while the reduction oven was kept at 650°C. The gases generated from the combustion were carried in a helium stream into a GC column held at 60°C. The gases were then separated before being diluted in the ConFlo IV and passed to the mass spectrometer for analysis. A total of 47 samples were obtained down the core at 10-cm resolution and at 2-cm resolution during periods of interest (6500–5400 yr BP and 90 to −55 yr BP).

Metal analyses

Sub-samples for metal analyses were taken at 3-cm intervals down core. After preliminary analyses, one interval of interest (6500–5400 yr BP) was resampled continuously at 1-cm resolution. All the samples (n = 105) were frozen, lyophilized, and homogenized, and ~0.1 g of dry sediment was used for geochemical analyses. The metals were extracted by mixing homogenized dry sediment with 10% sub-boil distilled trace metal grade HNO_3 in 15-mL polypropylene tubes and constantly agitated at room temperature for 12 h. Metals extracted from sediments using dilute HNO_3 are sensitive to inputs from human activities (Graney et al., 1995; Monna et al., 1999). Metal concentrations in the resulting supernatant were measured on a Perkin/Elmer NexION 300× Inductively Coupled Plasma-Mass Spectrometer at the Department of Geology and Planetary Science at the University of Pittsburgh. Detection limit is <1 μg/g for lead (Pb), copper (Cu), potassium (K), titanium (Ti), magnesium (Mg), and iron (Fe). Standards, blanks, and duplicates were measured during the analyses to ensure reproducibility.

Anthropogenic Pb enrichment factor (EF) indices were calculated using the methods in Shotyk et al. (1996), Weiss et al. (1999), and Boës et al. (2011). Multiple references (e.g. Ti, Fe, Mg, and organic matter) and site-specific background concentrations were used to produce four indices of Pb enrichments. The indices were then averaged to calculate a mean anthropogenic Pb EF with 95% confidence intervals (Pompeani et al., 2013). Background levels of Ti, Fe, Mg, and organic matter were estimated by taking the average of the entire record, whereas background (or natural) values for Pb, Cu, and K were calculated using the period from 5400 to 100 yr BP when there was minimal variation in metal concentrations. Spatial patterns of Pb input were determined by comparing the geochemical record from McCargoe Cove with those from lakes on the Keweenaw Peninsula (Pompeani et al., 2013).

Whole rock metal analyses

Three small samples of rock from the surface of separate mine pits were obtained to characterize the metal composition of the bedrock surrounding the copper deposits on Minong Ridge. Samples were stored in labeled Whirl-Paks for transport. In the laboratory, the samples were washed with deionized water, dried, and shipped to ALS Minerals for total metal analysis (procedure ME-MS41).

Results

Age model

A total of six radiocarbon and nine CRS ^{210}Pb dates were used to calculate an age–depth model (Tables S1 and S2, see Supplementary Files, available online). The ages were input into the CLAM package for R (Blaauw, 2010; Stuiver et al., 2010) to generate a linear point-to-point age model and determine 95% confidence intervals for the interpolated ages (Figure 3). Four dates suggest that from ~8800 until 4000 yr BP, sedimentation rates in the cove were around 0.1 mm/yr. From 4000 to −55 yr BP, sedimentation rates increased to an average of 0.6 mm/yr.

Visual sedimentology

The sediments are reddish gray (Munsell color 5 yr 5/2) from 360 to 260 cm and composed of minerogenic material with interbedded layers of sand. Above 260 cm (or ~7000 yr BP), the core transitions from red to dark brown (7.5 yr 3/2) sediments with no sand layers present above this stratigraphic level. An abrupt transition occurs at 250 cm (~6000 yr BP) to a gray-colored (10 yr 5/1) layer, which gradually changes to brown (7.5 yr 3/2) sediments that remain from 245 to 0 cm (~5000 yr BP to the present).

XRD, organic matter, and carbon-to-nitrogen ratios

The detrital mineral content of the sediment primarily consists of plagioclase series mineral assemblages. In particular, the three samples from depths 51.5, 217.5, and 297.5 cm (820, 5600, and >9000 yr BP (last age is extrapolated)) contain Na end-member plagioclase and alkali feldspar mineral matter ($CaAl_2Si_2O_8$, $NaAlSi_3O_8$, and $KAlSi_3O_8$). Organic matter concentrations are lower on average from 8800 to 4000 yr BP (~5%), and carbonate is below detection levels in the sediment. Organic matter gradually

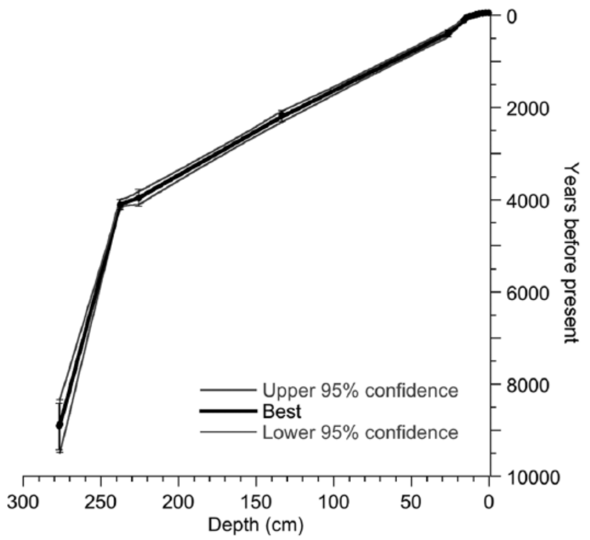

Figure 3. Age model for the McCargoe Cove sediment core used a linear point-to-point function in CLAM to generate ages with 95% confidence intervals (Blaauw, 2010). Black dots represent radiocarbon and ^{210}Pb ages.

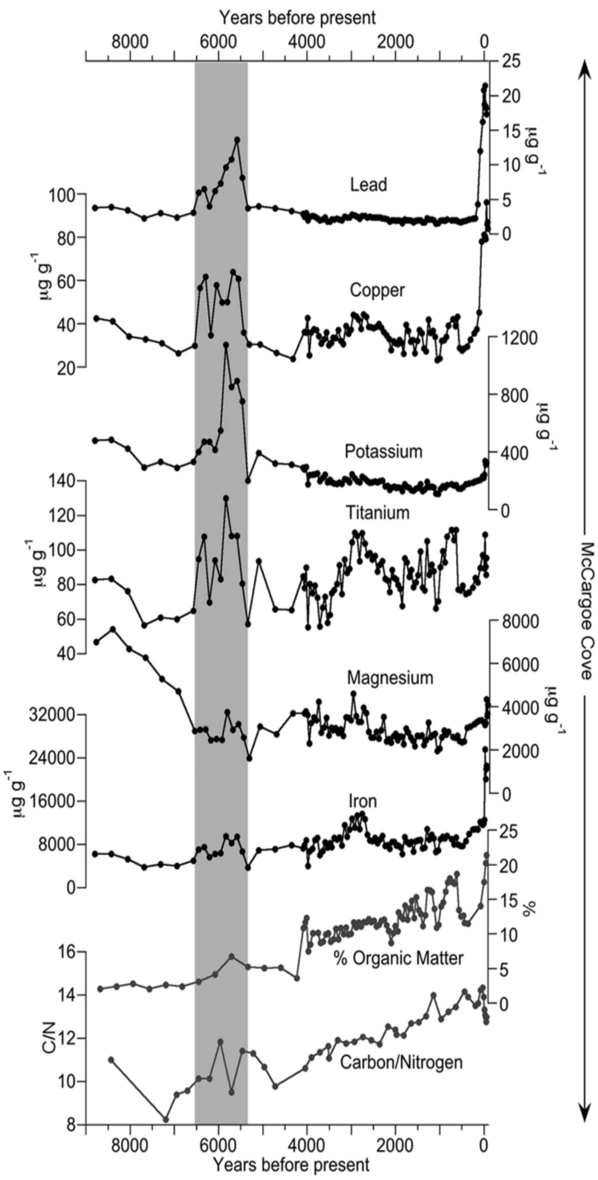

Figure 4. Proxy results from the McCargoe Cove sediment core. The gray box highlights the time period in which metal pollution associated with prehistoric mining can be detected.

increases from 4000 to −55 yr BP reaching ~12% by weight. Carbon-to-nitrogen (C/N) ratios are ~11 around 8500 yr BP but transition to ~10 from 7000 to 6000 yr BP. Sediment C/N ratios increase to values of 11–12 and become more variable after 6000 yr BP before returning to lower values by ~4000 yr BP. Thereafter, C/N ratios increase to higher values (~13) until the present.

Sediment metal concentrations

Titanium, magnesium, and iron. Titanium (Ti), Mg, and Fe concentrations remain relatively stable over the 8400-year record, with the exception of Mg, which was higher from 8400 to 6500 yr BP, and Fe, which increases after 0 yr BP (AD 1950) (Figure 4). From about 6500 yr BP to the present, Ti, Mg, and Fe vary around their core average plus or minus two standard deviations (2σ) (Table S3, available online).

Lead, potassium, and copper. Lead, Cu, and K concentrations are relatively high between 6500 to 5400 yr BP and 90 (AD 1860) to −55 yr BP (AD 2005). If these periods are omitted, sediment Pb, Cu, and K concentrations remain within their background average ±2σ (Table S3, available online). In sediments from 90 to −55 yr BP, Pb and Cu concentrations increase from ~10 to 3 times above background concentrations, respectively, whereas K does not increase above background levels (Figure 4). From 6500 to 5400 yr BP, Pb, Cu, and K concentrations rapidly increase to peaks of 14, 64, and 1140 µg/g, respectively, which is a ~7-, 2-, and 6-fold increase above background values. Concentration changes of this magnitude are not recorded in Ti, Mg, Fe, and organic matter from 6500 to 5400 yr BP.

Whole rock metal concentrations. Bedrock samples collected along the western shoreline of McCargoe Cove contained average concentrations of Pb, Cu, and K around ~10, 530, and 2200 µg/g, respectively. Average Ti, Mg, and Fe concentrations were ~4200, 12,800, and 44,700 µg/g (Table S4, available online).

Discussion

Human influences on environmental metal cycling

Lake sediment record changes in metal inputs from the environment and human activities (Graney et al., 1995; Renberg, 1986), as well as from recycling within the lacustrine system (e.g. redox) (Kalff, 2002). Here, we use Pb, Cu, and K as proxies for mining and annealing activities. Two distinct periods of elevated Pb, Cu, and K inputs are recorded after 90 yr BP (AD 1860) and from 6500 to 5400 yr BP. If the periods associated with recent and prehistoric mining (i.e. 90 to −55 yr BP and 6500–5400 yr BP) are omitted, sediment Pb, Cu, and K scatterplots with Ti, Mg, Fe, and organic matter cluster around a consistent range, referred to here as natural or background variability. Metal concentrations associated with human loadings plot outside the range of background variability (Table S3, available online) (Figure 5).

Constraining natural variability. Organic matter concentrations are compared with the metal proxies because it provides sorption sites in the sediments and, therefore, changes in the amount of organic matter could affect metal concentrations in the sediments (Bloom, 1981; Bowen, 1979). The combination of lower C/N ratios, which are affected by changes in the source of organic matter (Meyers, 1997), and lower organic matter concentrations from ~8800 to 4000 yr BP suggests both a decrease in productivity and an increase in the relative contribution of algal (N-rich) material (Figure 4). After ~4000 yr BP, organic matter concentrations rise and C/N ratios increase, reflecting greater production and/or preservation of organic matter and an increase in the flux of terrigenous (C-rich) organic matter to sediments.

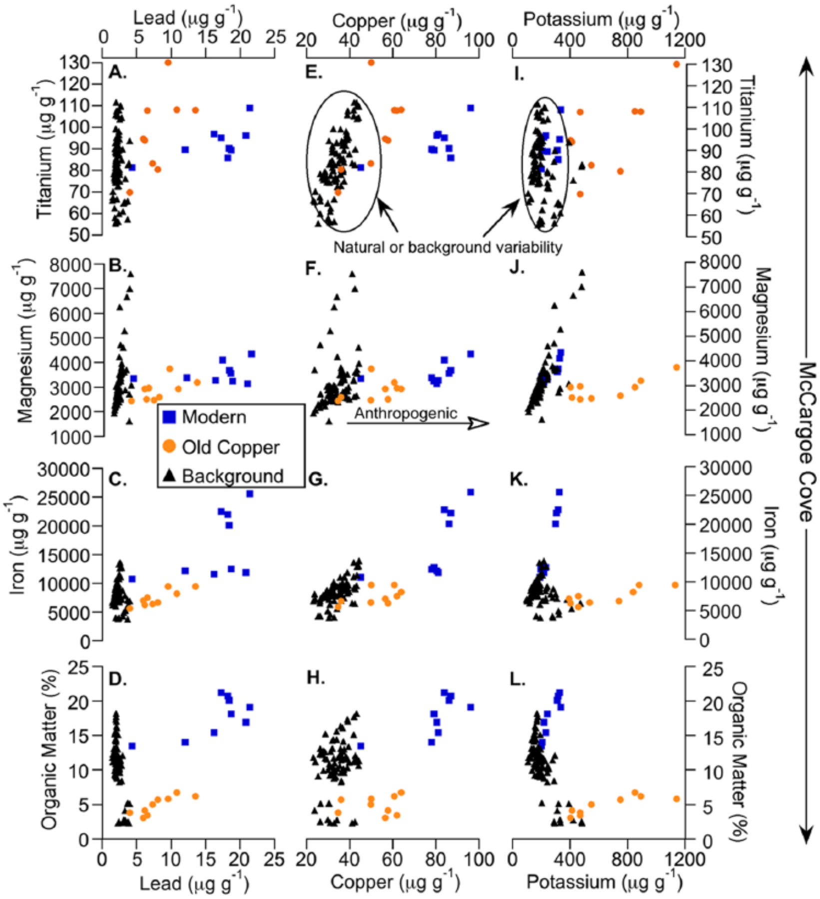

Figure 5. Scatterplot matrix of the proxy metal and organic matter concentrations grouped into three time periods: Modern (90 to −55 yr BP), Old Copper (6500–5400 yr BP), and Background (8800–6500 yr BP and 5400–90 yr BP). Periods of human-related metal loadings at McCargoe Cove generally plot outside the range of natural or background variability.

Changing concentrations of Ti, Mg, and Fe in McCargoe Cove sediments are interpreted to reflect shifts in the relative importance of processes influencing the delivery of metals to the basin, because these elements are found in high concentrations in the bedrock surrounding the copper lodes (Table S4, available online). For example, Ti concentrations weakly correspond with changes in organic matter concentrations (r^2 = 0.13) and are interpreted to reflect changes in soil erosion, particularly because higher organic matter concentrations are associated with higher C/N ratios (r^2 = 0.67) (Figure 4). Magnesium concentrations in the sediments are relatively high from 8800 to 6500 yr BP when organic matter concentrations are low. Increasing organic matter and C/N ratios starting around 4000 yr BP correspond with lower Mg, indicating either a dilution effect or a reduction of Mg delivered to the McCargoe Cove. Iron concentrations remain relatively unchanged throughout the entire record, except for small increases around 2700 yr BP and after 0 yr BP (AD 1950). The minor increases in Fe concentrations observed around 2700 yr BP occur at the same time that Ti and Mg concentrations increase. Therefore, we use Ti, Mg, Fe, and organic matter concentrations to account for a multitude of processes that influence the fluxes and preservation of metals in the sediments of McCargoe Cove.

Proxies of human activities. Increases in Pb and Cu concentrations from 90 to −55 yr BP (AD 1870–AD 2005) are likely the result of the use of leaded gasoline and recent mining/smelting activities (Kerfoot and Robbins, 1999; Nriagu, 1996; Vermillion et al., 2005). Lead, Cu, and K concentrations increase from 6500 to 5400 yr BP corresponding with several radiocarbon dates associated with copper artifacts found in the region (Beukens et al., 1992; Libby, 1954; Pleger, 2001) and Pb EF increases identified in lake sediments from the Keweenaw Peninsula (Pompeani et al., 2013). Because of our limited understanding of the activities associated with ancient copper mining, we can only speculate as to the pathways in which metals were delivered to the sediment.

After 90 yr BP (AD 1860), copper inputs were probably related to some combination of leaching from rock debris and disturbed soils (transport enhanced by association with organic ligands), and/or atmospheric inputs from ore processing and/or smelting (Figure 4). Therefore, we assume increases in Cu concentrations from 6500 to 5400 yr BP also resulted from some combination of leaching and/or atmospheric inputs (e.g. annealing and wood burning) (Figure 5). For example, annealing and hammering of native copper produces copper oxides (Peterson, 2003). In addition, numerous overburden piles were deposited on the surface of Minong Ridge, providing a potential source of dissolved copper to the McCargoe Cove. The limited understanding of Old Copper mining techniques and the wide variety of minerals associated with native copper ore make it difficult to predict emissions and leaching of metals in the past. Nonetheless, we assume that increases in Cu concentrations after 90 yr BP and from 6500 to 5400 yr BP resulted from some combination of processes related to copper mining.

Interestingly, K concentrations increase to 1140 µg/g around 5800 yr BP. The lack of an increase in K concentrations during the historic mining period suggests that K is insensitive to deforestation and leachate from overburden recently deposited in the catchment (Figure S1, available online) (Holmes, 1892). Thus, a plausible mechanism must be invoked to explain the increase in K concentrations from 6500 to 5400 yr BP. Burning biomass, including wood, has been observed to preferentially release K (Calloway et al., 1989; Fine et al., 2001; Harrison et al., 2012; Kleeman et al., 1999; Larson and Koenig, 1994; Song et al., 2005) and produce water soluble potash (i.e. KOH). Potassium has also been used to infer biomass burning in ice cores (Eichler et al., 2011; Kehrwald et al., 2012). Therefore, we propose that K increases at McCargoe Cove during Old Copper mining were likely related to some combination of inputs from wood fires (e.g. potash and wood smoke) and/or unknown processes related to ancient mining and annealing techniques.

The lack of an increase in K concentration in historic sediments raises questions about the differences between modern and prehistoric mining techniques (Figure 5i–l). For example, the lack of a modern increase in K concentration in the sediments can be attributed to the relatively short duration of recent copper mining (i.e. from AD 1875 to AD 1885) and low human populations relative to the apparent length of Old Copper mining period (i.e. ~900 years). Or perhaps, higher K concentrations resulted from forest fires, which emit K aerosols (Pio et al., 2008). However, these episodic events cannot explain the duration of the sustained K enrichment (~600 years) during the Old Copper mining period because forest fires are short (<1 year), and there are no K concentration increases in the sediments deposited during recent forest fires (Figure S1, available online) (NPS, 2004).

In recent times, sources of Pb to the sediment were the result of inputs from regional and global Pb emissions (Pacyna and Pacyna, 2001), in part from burning fossil fuels and smelting, along with possible contributions from leaching recently deposited overburden piles in the catchment (Table S4, available online). During the Old Copper mining period, Pb compounds could have come from overburden leachate or particulates volatized from fire associated with mining and annealing. Rising Pb concentrations from 6500 to 5400 yr BP contrasts with modern Pb pollution in that it is associated with higher concentrations of K (Figure 5), which is insensitive to inputs from overburden leachate. The association with higher K concentrations suggests that the source of Pb from 6500 to 5400 yr BP was derived from some combination of wood burning and/or unknown processes related to mining and annealing.

Lead, Cu, and K concentrations follow unique trends during the Old Copper mining period. For example, maximum Cu and K concentrations occur ~5800 (±200) yr BP, while Pb peaks ~5600 (±200) yr BP (Figure 4). The observed lag in higher metal concentrations might be explained by changes in the nature and/or location of metalworking activities (i.e. technologies, ore composition (Table S4, available online), and/or extraction rates) that influenced the relative fluxes of Pb, Cu, and K to the core site. However, this needs to be tested with additional proxies and archaeological data. Alternatively, the lag in the timing of peak Pb concentrations relative to the peak in Cu and K concentrations could be explained by the longer residence time of Pb in soils (Bowen, 1979). This does not appear to be consistent with the data, because Cu concentrations had doubled relative to background average values by 6300 yr BP, while Pb concentrations had tripled, and K remained near background levels. In general, the increases in Pb, Cu, and K concentrations produced by human activities far exceed background variability, providing a useful way to differentiate anthropogenic and natural metal inputs (Figure 5).

Anthropogenic Pb EFs

Recent Pb increases. Lead was normalized to three reference metals (Ti, Fe, and Mg) and organic matter to calculate a mean anthropogenic EF (Figure 6) (Boës et al., 2011; Pompeani et al., 2013; Shotyk et al., 1996). Recently, Pb began to increase at McCargoe Cove around 90 yr BP corresponding with the initiation of copper smelting on the Keweenaw Peninsula (AD 1860)

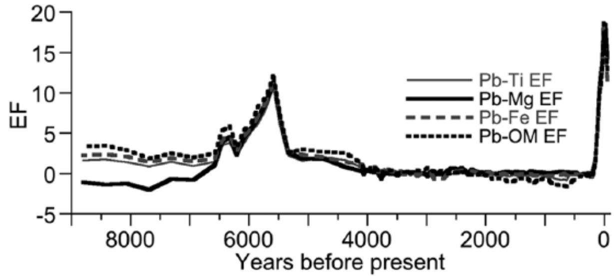

Figure 6. The anthropogenic lead (Pb) enrichment factor (EF) indices (Boës et al., 2011; Weiss et al., 1999) used to calculate the mean anthropogenic Pb EF. Titanium (Ti), magnesium (Mg), iron (Fe), and organic matter (OM) are used to account for background (or nonhuman) variability.

(Lankton, 2010) and mining in the catchment (AD 1875–AD 1885). Lead EFs continued to increase and eventually peaked at 18 around AD 1950 (Figure 7), likely as a result of the use of leaded gasoline and the global rise in Pb emissions (Pacyna and Pacyna, 2001). The removal of lead additives from gasoline and the closure of the mining and smelting industries in the late 20th century led to substantial declines in Pb concentrations in the sediments after ~AD 1980. The absence of mining pollution in centuries leading up to European arrival is consistent with tree-ring age estimates of the overburden piles (Hagar, 1865; Whittlesey, 1863), which suggest that they were deposited at least centuries prior to the middle 19th century.

Prehistoric Pb increases. Prior to recent increases starting around AD 1860, Pb EFs remained between ~1 and 2 for the last ~5400 years. Starting ~6500 yr BP, Pb EF values began to increase at an average rate of ~0.2%/yr to a value of 11 by ~5400 yr BP. Prior to 6500 yr BP, Pb EF values were <2 EF.

Regional Pb EF comparison

Lake sediment cores from the Keweenaw Peninsula (Copper Falls Lake, Lake Medora, and Lake Manganese) record increases after about ~100 yr BP, and subsequent declines after ~AD 1980, except Lake Medora, which records increases over the duration of the 20th century (Figure 1). Increases in lead EFs are recorded at two sites on the peninsula ~8000 and ~7000 yr BP (Copper Falls Lake and Lake Manganese) (Figure 7). At McCargoe Cove, higher Pb EF are recorded from 6500 to 5400 yr BP followed by increases at Lake Medora from 6100 to 5900 yr BP. Thereafter, Pb emissions appear to shift to Copper Falls Lake from 5800 to 5500 yr BP and to Lake Manganese ~5000 yr BP. The lack of measurable copper mining pollution after 5000 yr BP could imply that the copper exploited by later pre-contact societies came from other geologic deposits (Levine, 2007a, 2007b) and/or that copper mining activities in the Lake Superior region (and subsequent metal pollution) remained at levels that are below detection. In general, Pb, Cu, and K indicate that copper mining activities at McCargoe Cove on Isle Royale occurred during the Early and Middle Archaic periods (i.e. from 6500 to 5400 yr BP) and correspond with Pb EF records from the Keweenaw Peninsula (Figure 7) (Pleger and Stoltman, 2009; Pompeani et al., 2013).

Comparisons with Minong Ridge mine pit dates

We compared Pb EF values at McCargoe Cove with published radiocarbon dates of charcoal recovered from pit mines on Minong Ridge (Figure 2). Two radiocarbon dates obtained from charcoal preserved at the bottom of mine pits on Minong Ridge (Crane and Griffin, 1965) correspond to periods of Pb increases in

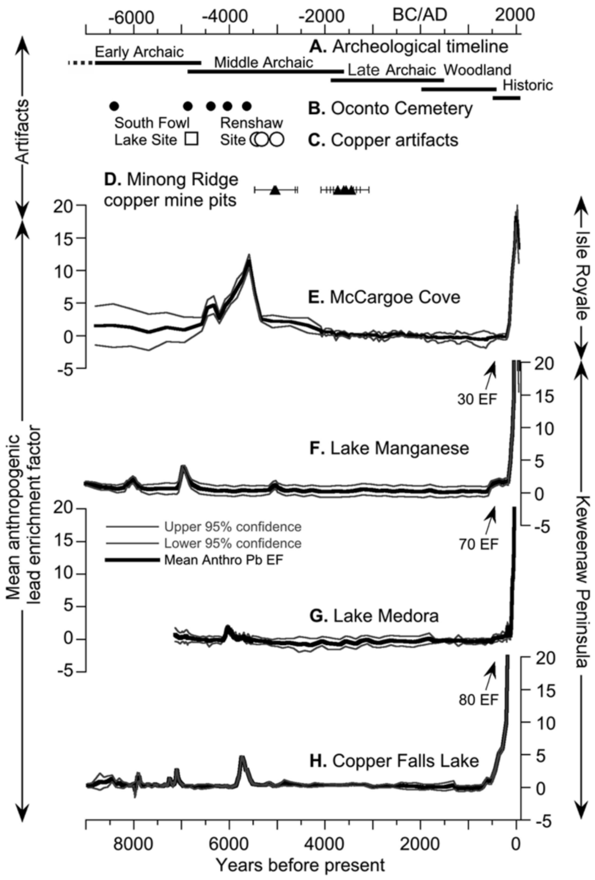

Figure 7. (a) Regional archaeological timeline (Pleger and Stoltman, 2009). (b) Radiocarbon ages from Oconto Cemetery, which included numerous individuals buried with copper artifacts (Pleger, 2001). (c) Radiocarbon ages of organic material preserved with copper artifacts from South Fowl Lake and Renshaw sites (Figure 1) (Beukens et al., 1992). (d) Radiocarbon measurements of charcoal preserved within prehistoric pit mines on Minong Ridge (Crane and Griffin, 1965). Mean anthropogenic lead (Pb) enrichment factors (EFs) for (e) McCargoe Cove, (f) Lake Manganese, (g) Lake Medora, and (h) Copper Falls Lake (Pompeani et al., 2013).

the sediment of McCargoe Cove; however, the other three reported dates appear to post-date the peak in Pb EF values (Figure 7d). Therefore, we propose that these dates, and potentially other radiocarbon dates from the mine pits and trenches (Crane and Griffin, 1965), mark the infill of the mine pits or possible contamination by more recent carbon (producing radiocarbon dates younger than the age of deposition), rather than being reflective of the active copper mining period.

Implications of the McCargoe Cove record

Lead concentrations increase from 6500 to 5400 yr BP at McCargoe Cove and at two other lakes on the Keweenaw Peninsula (i.e. Lake Medora, Copper Falls Lake), demonstrating that a detectable mining industry extended across several parts of the Michigan Copper District during this period (Figure 7). Increasing metal pollution associated with mining beginning ~6500 yr BP supports archaeological evidence for copper metalworking by at least the Early Archaic Period (Pleger and Stoltman, 2009; Pompeani et al., 2013). The rapid decrease in metal pollution inputs from 5500 to 5400 yr BP suggests an abrupt decline in mining and annealing activities at this location.

The disparate timing of Pb EF increases at the four reconstruction sites (Figure 7) could be related to inherent uncertainties in the sediment age models. Alternatively, the spatial and temporal patterns may be explained by how humans decide to look for and exploit resources. Specifically, as mining activity grew at McCargoe Cove and other localities around Lake Superior, we hypothesize that the most accessible (e.g. location, purity, workability) copper was targeted first, followed by other comparable areas. For example, our field observations on Minong Ridge and other written accounts noted that the Old Copper miners used the strike of the copper veins to predict the location of additional copper loads covered by shallow surficial deposits (Gillman, 1873; Whittlesey, 1863). As mining activity grew and the copper deposits were depleted and/or became more difficult to exploit, producing decreasing returns (Tainter et al., 2006), the mine site would eventually be abandoned. Thus, as the miners discovered and exploited new deposits in different locations, over time, pollution loading would increase in nearby lakes, while more distal sites would not record detectable pollution inputs. In some cases, multiple periods of Pb EF increases indicate that some localities (Copper Falls Lake) were worked over several temporally distinct periods. After mining was abandoned, pollution levels would decrease, consistent with geochemical evidence found in sediment cores from multiple mining locations. Despite thousands of years of mining, copper is still found in the region. Therefore, diminishing return rates from mining only partially explain the permanent reduction of mining pollution after 5000 yr BP.

Another line of evidence that could explain the rapid decline of mining pollution can be found in regional paleoclimate records from Elk Lake (45.890°N, 95.832°W) in western Minnesota (Smith et al., 1997, 2002), Crawford Lake (43.468°N, 79.949°W) in southern Ontario (Yu et al., 1997), and Fayetteville Green Lake (43.033°N, 75.967°W) in New York (Kirby et al., 2002). At Elk Lake, the presence of shallow water ostracods (i.e. *Limnocythere staplini*) and higher carbonate $\delta^{18}O$ indicates the onset of dry conditions starting around 5400 yr BP. After ~5400 yr BP, low lake levels and more saline water prevailed for about two centuries (Smith et al., 2002). In addition, low lake levels and sediment carbonate $\delta^{18}O$ at Crawford Lake suggest a period of dry conditions and low lake levels beginning at ~5500 yr BP (~4800 ^{14}C yr BP) (Yu et al., 1997). Dry conditions at Crawford Lake persisted for ~3000 years, as evinced from a hiatus in sediment deposition from shallow water cores. At Fayetteville Green Lake, a reduction in the delivery of moist Gulf air masses and an increase in the frequency of cross-continental, moisture-poor, low-$\delta^{18}O$ precipitation occurs after ~5200 yr BP indicated by a shift to more negative sediment $\delta^{18}O$ (Kirby et al., 2002). Interestingly, the onset of drier conditions at Elk Lake, Crawford Lake, and Fayetteville Green Lake coincide or follow the decline in Pb emissions at Lake Medora, Copper Falls Lake, and McCargoe Cove. When interpreted in combination, the sediment Pb reconstruction records from Isle Royale, the Keweenaw Peninsula, and paleoclimate proxies from around the Great Lakes provide tentative evidence that the regional cessation of more than 3000 years of mining pollution around Lake Superior coincided with the onset of sustained dry conditions in the Midwest.

Conclusion

Metal pollution detected at multiple locations on both Isle Royale and the Keweenaw Peninsula demonstrates mining activity occurred across the greater Lake Superior region from 6500 to 5400 yr BP (Figure 7). After 5000 yr BP, lake sediment records from McCargoe Cove on Isle Royale do not contain any significant Pb increases until European settlement, consistent with earlier findings from lakes on the Keweenaw Peninsula (Figure 7) (Pompeani et al., 2013). Changing spatial and temporal patterns of pollution could be related to shifts in the location of copper mining activity during the prehistoric mining period. Therefore, identifying and separating human from natural changes will improve interpretations of lake sediment proxies from the region. Notably, the final cessation of Pb emissions at multiple lakes coincide with the onset of sustained dry conditions detected at several sites around the Great Lakes (Kirby et al., 2002; Smith et al., 1997, 2002; Yu et al., 1997), raising the possibility that metalworking activity associated with hunter-gatherer economies in North America was susceptible to influences of climate change.

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