Environmental Science & Technology

Article

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Lake Sediments Record Prehistoric Lead Pollution Related to Early Copper Production in North America

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Supporting Information

ABSTRACT: The mining and use of copper by prehistoric people on Michigan's Keweenaw Peninsula is one of the oldest examples of metalworking. We analyzed the concentration of lead, titanium, magnesium, iron, and organic matter in sediment cores recovered from three lakes located near mine pits to investigate the timing, location, and magnitude of ancient copper mining pollution. Lead concentrations were normalized to lithogenic metals and organic matter to account for processes that can influence natural (or background) lead delivery. Nearly simultaneous lead enrichments occurred at Lake Manganese and Copper Falls Lake ~8000 and 7000 years before present (yr BP), indicating that copper extraction occurred concurrently in at least two locations on the peninsula. The poor temporal coherence among the lead enrichments from ~6300 to 5000 yr BP at each lake suggests that the focus of copper mining and annealing shifted through time. In sediment younger than ~5000 yr BP, lead concentrations remain at background levels at all three lakes, excluding historic lead increases starting ~150 yr BP. Our work demonstrates that lead emissions associated with both the historic and Old Copper Complex tradition are detectable and can be used to determine the temporal and geographic pattern of metal pollution.

■ INTRODUCTION

The copper deposits on the Keweenaw Peninsula (Michigan, United States) are the largest source of native copper in North America.[1] Surveys of the region during the middle and late 19th century identified thousands of mine pits with widespread evidence of prehistoric human activity in the form of hammerstones and tailing piles concentrated along the ~100 km copper-bearing ridge in the interior of the peninsula (Figure 1).[2,3] Surveyors excavating the prehistoric pits uncovered large masses of worked native copper,[4,5] scaffolding,[6] ladders,[7] and other mining tools.[8] Several accounts noted that abundant charcoal deposits surrounded the copper within the pits,[4,5,9] suggesting prehistoric (or pre-European contact) people used fire to aid in extracting and processing the copper. Descriptions of the ancient mine pits indicate they had likely been abandoned for hundreds of years prior to their discovery.[5,10,11] Although research has uncovered no evidence of prehistoric smelting around Lake Superior, it has demonstrated that prehistoric North American peoples heated native copper with fire and worked (or annealed) the metal with rock hammers.[12,13]

Interest surrounding prehistoric mining and use of copper in North America has spawned over a century of research. Three copper-using traditions are recognized based on this work.[14] The first of these traditions, commonly described as the Old Copper Complex (or Culture), occurred during the Middle Archaic period [~7000 to 3700 years before present (yr BP)] and predates the regional appearance of ceramics and agriculture. Copper artifacts from this period are concentrated around the Upper Great Lakes and are characterized by the production of heavy copper-tool technology. Significant sites from this tradition include the Osceola and Oconto cemeteries in Wisconsin.[15] Later, in the Early Woodland period (~2100 to 1500 yr BP), the Hopewell Exchange System (also called the Hopewell Tradition) developed and began to circulate exotic materials, including copper, across extensive trade networks in eastern North America.[14] In particular, numerous ceremonial copper artifacts from this period were found within burial mounds located in the Ohio River Valley.[16] By the Late Woodland period (~1100 yr BP), the agricultural peoples of the Mississippian Tradition or Southeastern Ceremonial Complex predominated the social and political landscape across the Midwest and eastern North America until European contact in the 16th century.[17] Copper artifacts from this period were recovered from excavations at the Spiro (Oklahoma) and Moundville (Alabama) archeological sites, in addition to a copper workshop identified at the archeological site of Cahokia

Received: November 4, 2012
Revised: March 22, 2013
Accepted: April 26, 2013
Published: April 26, 2013

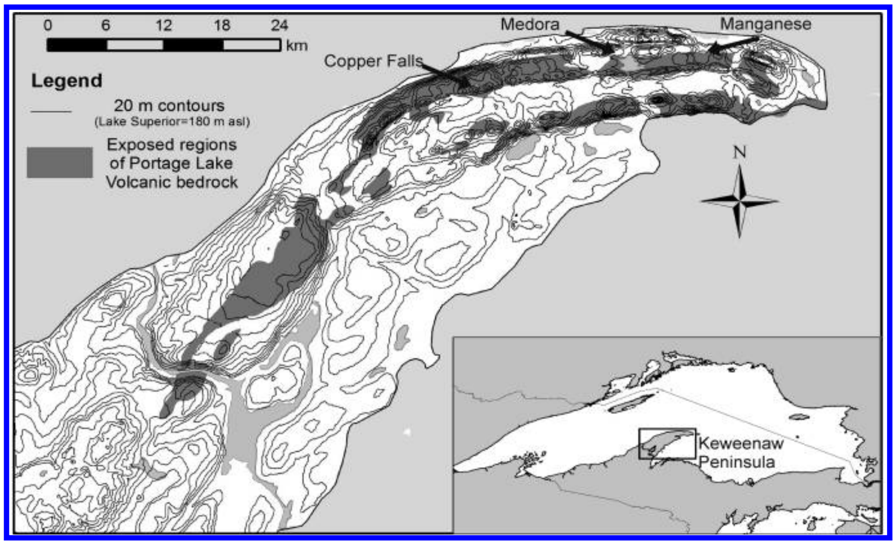

Figure 1. Map of the Upper Great Lakes region (inset) and Keweenaw Peninsula with study lakes noted. Surficial exposures of Portage Lake Volcanic bedrock are highlighted in dark gray. Comparisons with Charles Whittlesey's map[2] confirm that prehistoric mine pits were commonly located on surficial exposures of the Portage Lake Volcanic bedrock, which contained deposits of native "fissure vein" copper.[1]

(Illinois).[18] In general, artifacts from the Old Copper Complex, the Hopewell, and the Mississippian Traditions suggest considerable variability in the geologic source, production technique, and use of copper.[14,19]

Radiocarbon dates of organic matter found associated with copper artifacts indicate that people were using copper in the Upper Great Lakes region by ∼9000 to 7000 yr BP.[20,21] These dates suggest metal use appeared earlier in North America than in Europe,[22] Asia,[23] and South America.[24] Furthermore, the development of copper-working technologies in the Lake Superior region seemingly preceded agriculture and emerged during a time period that has traditionally been associated with hunter−gatherer societies.[12,15]

Here we use lake sediment cores to demonstrate that, on a local scale, measurable levels of atmospheric lead (Pb) pollution were generated at discrete time intervals by preagricultural societies on the Keweenaw Peninsula starting as early as 8000 years ago. Lead is used as a proxy for human activities because it has low background concentrations in the sediments (∼1−2 $\mu g \cdot g^{-1}$). These characteristics make lead especially effective for recording small inputs from human metalworking activities. We applied anthropogenic enrichment factor equations to metal records from three lake sediment sequences to estimate past changes in human-related Pb inputs to the lakes.

Study Sites. The Michigan copper district is located on the northern shore of the Upper Peninsula and on Isle Royale. The principal copper-bearing rock is the Portage Lake Volcanic unit, which is primarily composed of Middle Proterozoic metamorphosed basalt flows.[1] Historic mining on the Keweenaw Peninsula began in 1843 AD, expanded until 1920 AD, and declined until 1997 AD when mining ended.[25] Early mining of the Portage Lake Volcanics focused on the highly pure native copper veins exposed by glacial erosion, with later mining efforts aimed at extracting copper found within vesicles in the bedrock (amygdaloidal) and copper sulfides (Cu_2S, CuS).[25] Although the Charles Whittlesey "Outline Map Showing the Position of the Ancient Mine Pits" accurately portrayed the strike of the Portage Lake Volcanics, it does not note surficial deposits that could inhibit direct access to bedrock.[2] Therefore, we incorporated surficial geology maps to highlight regions where bedrock is exposed at the surface. A comparison of the Whittlesey map with recent geologic surveys confirms that most prehistoric mine pits were located on the Portage Lake Volcanics (Figure 1).

Lake Manganese [47.454° N, 87.883° W, 234 m above sea level (asl), 0.5 km^2], Copper Falls Lake (47.417° N, 88.192° W, 392 m asl, 0.3 km^2), and Lake Medora (47.438° N, 87.976° W, 307 m asl, 6.2 km^2) are located along a 24 km transect that follows the elevated Portage Lake Volcanic ridge within the interior of the Keweenaw Peninsula. Lake Manganese (the northernmost lake) has a maximum depth of 7 m, receives inflow from two small streams that enter the lake from the south, and overflows through an outlet on the northern shore. Copper Falls Lake is topographically elevated, has a maximum depth of 3 m, and has no perennial inflow or outflow. Lake Medora is the largest of the three study lakes; it has a maximum depth of approximately 7 m, no surficial inflow, and one outflow that drains to the south. Lake Manganese and Copper Falls Lake are situated in isolated catchments that were logged multiple times over the last ∼150 years. The catchment of Lake Medora is primarily forested, with the exception of an asphalt highway on the southern side of the shoreline and several seasonal residences.

■ METHODS

Field Work. We characterized the physical and chemical characteristics of each lake using a Hach Hydrolab equipped with temperature, dissolved oxygen, conductivity, and pH sensors. In June 2012, sulfuric acid titrations were conducted on the surface waters of each lake by use of a Hach digital titrator to determine total dissolved bicarbonate and carbonate concentrations (i.e., alkalinity) (see additional text in Supporting Information).

We collected surface sediment profiles from all three lakes in June 2010 using a piston corer fitted with a 6.6 cm diameter polycarbonate tube. Surface sediments were extruded in the field at 0.5 cm intervals to a depth of 50 cm. Overlapping 1 m long cores spanning the remainder of the sediment sequence were obtained from each lake by use of a modified Livingston corer. All cores were collected near the depocenter of the lake basin. The Copper Falls record consists of four 1 m overlapping drives that extend 3.79 m below the sediment−water interface. The Lake Medora and Lake Manganese records consist of three 1 m drives that extend 3.06 and 3.00 m below the sediment−water interface, respectively.

Loss-on-Ignition Analysis. In the laboratory the sediment cores were split into halves and subsampled at 3−4 cm intervals by use of a 1 cm^3 piston-core sampler. The sediments subsamples were then dried at 60 °C for 48 h to remove water. Organic matter and calcium carbonate content as a weight percentage were then measured by loss-on-ignition (LOI) in a muffle furnace at 550 °C for 4 h and 1000 °C for 2 h.[26,27] The 1000 °C burn indicates that carbonate minerals are absent in the sediments at all three sites.

Geochronology. We used ^{210}Pb assays interpreted with the constant rate of supply (CRS) method[28,29] to date the upper 20 cm of sediment from all three surface cores. Radioisotope (^{210}Pb, ^{137}Cs, and ^{214}Pb) activities were determined by direct γ counting on a high-purity, broad-energy germanium detector (Canberra BE-3825) at the University of Pittsburgh. Terrestrial macrofossils for radiocarbon dating were isolated from the sediment, pretreated following standard acid−base−acid procedures,[30] and measured at the W. M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at the University of California, Irvine. Twelve, five, and three radiocarbon dates were obtained from the Copper Falls, Medora, and Manganese sediment cores, respectively. We generated spline age-depth models with 95% confidence intervals using CLAM for R (Figure 2).[31]

Elemental Analyses. Subsamples for metal analyses were collected at variable intervals from the homogeneous organic-rich sediments positioned above the deglacial sediments. The uppermost 20 cm of each core was subsampled for metal analyses at 1−2 cm resolution. Over the remaining lower sections of each core, subsamples were obtained at 3−4 cm resolution. After initial analyses, the sediment record was resampled continuously every 1 cm through prehistoric intervals of interest. Subsamples were frozen, lyophilized, and homogenized prior to extraction from ∼0.2 g of sediment with 10% HNO_3 by constant agitation at room temperature for 24 h in 15 mL polypropylene tubes.[32] Acidified subsamples were centrifuged and the resulting supernatant was used for metal measurements. Metal concentrations in the Copper Falls Lake supernatant were measured on a Perkin-Elmer Sciex Elan 6000 inductively coupled plasma mass spectrometer (ICP-MS) at the University of Alberta. Detection limits are (in micrograms per gram) 0.03 for Pb, 0.09 for Ti, 2.00 for Mg, and 3.70 for Fe. The Lake Medora and Lake Manganese records were measured on the Perkin/Elmer Nexion 300X ICP-MS at the University of Pittsburgh (detection limit is <1 $ng \cdot g^{-1}$ Pb, Ti, Mg, Fe). In addition, standards, blanks, duplicates, and reruns were conducted during analyses to ensure reproducibility within acceptable limits (see additional text and Table S8 in Supporting Information).

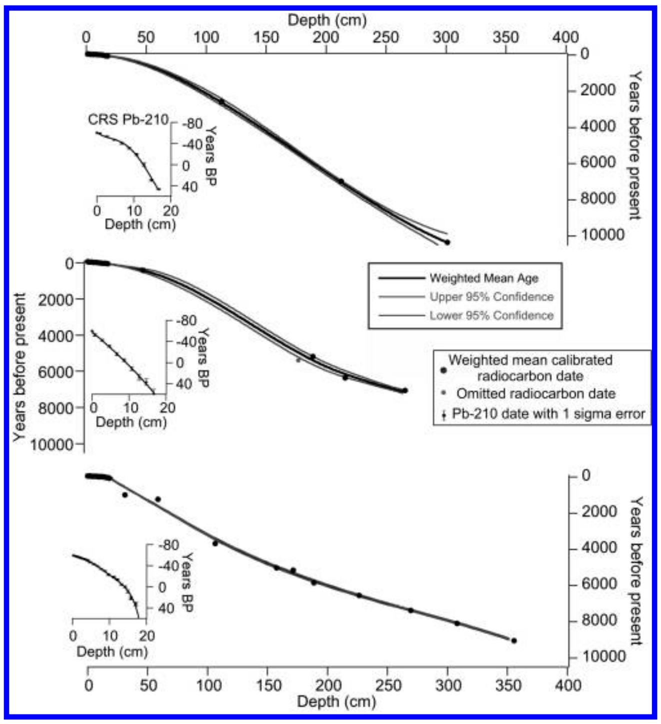

Figure 2. Radiocarbon dates (●) and CRS ^{210}Pb (inset) used to calculate age models. We used a spline (—) to interpolate between dates (with 95% confidence intervals) using CLAM for R.[31].

Anthropogenic Enrichment Factors. Quantifying anthropogenic pollution requires accounting for inputs derived from a multitude of natural (or nonhuman) processes.[33,34] Chemical weathering in the catchment, along with contributions from the atmosphere, are the primary natural sources of weakly bound metals in lake sediments.[35,36] To approximate these inputs, we normalized Pb to background references.[33] Four proxies (i.e., Ti, Mg, Fe, and organic matter) were used for normalizing to capture the variety of natural processes distinctive to each lake.[37] Weak acid extraction methods were utilized to isolate metals that are sorbed to organic matter, mineral surfaces, and ferro-manganese oxides within the sediment.[38−40] Previous studies have demonstrated that concentrations of metals sorbed to sediment surfaces and liberated by weak acid extraction methods are sensitive to anthropogenic inputs.[32,40,41] In contrast, total digestions incorporate metals held within mineral lattices[38] and consequently may reflect physical erosion rates in the catchment or other processes[42] that could obscure an atmospheric signal.[36] Other environmental and geochemical controls within the lake (such as redox conditions in the water column) and catchment can substantially change the flux of weakly bound metals over longer (e.g., millennial) time scales.[36] To account for this, we used weakly sorbed iron (Fe) as a proxy for redox changes. Organic matter was used because metals often sorb to organic matter surfaces within the lake sediment, therefore variations down core could potentially influence metal concentrations.[36] Titanium (Ti) and magnesium (Mg) were used to approximate chemical weathering processes.[37,43] Lead concentrations were applied to anthropogenic enrichment factor equations for Ti, Mg, Fe, and organic matter to produce four indices of human-derived lead enrichment.[33,37,44] All four indices (Figures S2 and S3, Supporting Information) were then averaged to produce a mean anthropogenic enrichment factor (with 95% confidence intervals), hereafter referred to as EF (Figure 5; see additional text in Supporting Information). Anthropogenic EF values ≤1 are generally considered background levels.

RESULTS AND DISCUSSION

Natural Sources of Atmospheric Lead. Understanding the influence of natural sources of metals to lake systems is

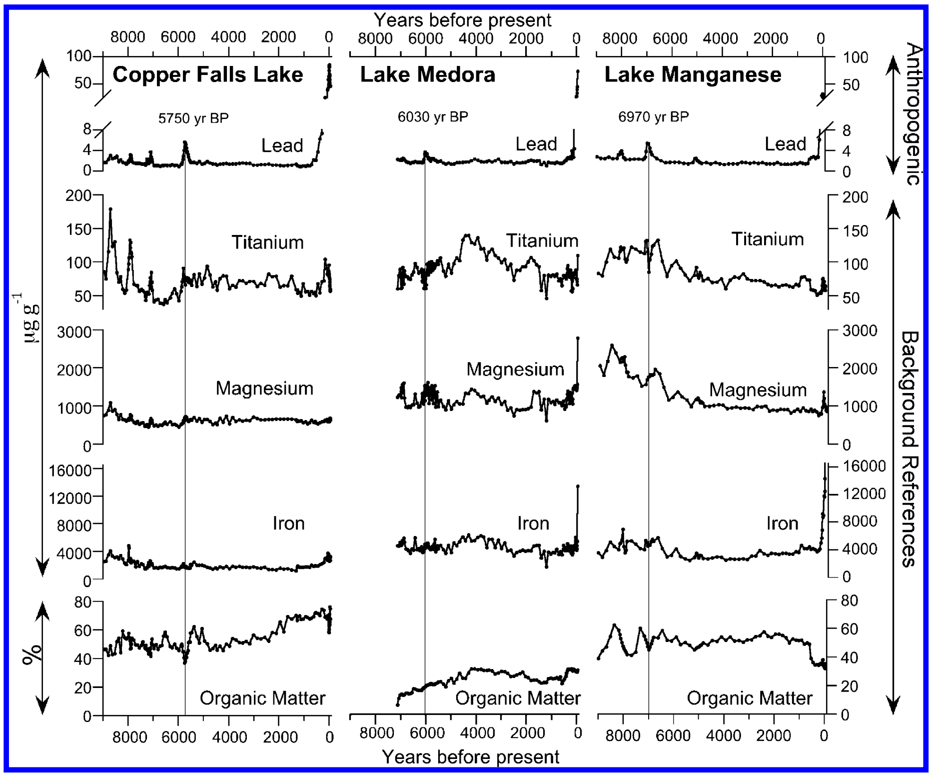

Figure 3. Weakly bound metal records from Lake Manganese, Lake Medora, and Copper Falls Lake. Metals used as proxies for human activity are at the top (i.e., anthropogenic), and references or proxies used to estimate background (or nonhuman) processes are at the bottom.

critical for estimating the influence of human activities on atmospheric metal/metalloid cycles. The principal sources of natural atmospheric metals are wind-blown soil particles, volcanoes, seasalt spray, and forest fires. Research suggests that about 50% of global metal emissions are of natural origin.[34,45] However, for economically important metals such as Pb, the natural fluxes are much smaller than emissions from human activities. Today, about 9% of total global Pb emissions can be attributed to non-human processes, such as volcanic emanations and wind-blown soil particulates.[34,45] Accordingly, we assume that, in the absence of anthropogenic Pb emissions, dissolved fluxes from chemical weathering processes were the predominant Pb inputs to the study sites and that natural atmospheric Pb deposition contributed an insignificant Pb flux to lake sediments on the Keweenaw Peninsula.

Brief Overview of Lead Pollution. Measurements of metal concentrations from a diversity of locations provide evidence for the occurrence of Pb pollution over the past 3000 years.[46,47] Recent lead contamination in the environment was first recognized by Patterson.[48] Subsequent efforts using lake sediment cores, first by Lee and Tallis[49] and later by Renberg,[50] documented the relationship between heavy metal contamination in lake sediments and smelting in Europe. Ice core reconstructions from Greenland confirmed these sediment-based results and further have demonstrated that pollution from early Greek and Roman metallurgy was distributed throughout the northern hemisphere.[51,52] The use of sediment cores to document pollution chronologies has since expanded to other regions.[35,53] For example, lake sediments recovered near ancient copper mining sites in the Hubei province of China record over 2000 years of Pb pollution,[54] and in South America sediment records have been widely applied to understand the timing, magnitude, and technological evolution of mining and metallurgy over the past ~3000 years.[32,35,55] Collectively, these records and others have confirmed that preindustrial mining and metallurgical activities can leave a lasting environmental legacy preserved within natural archives.

Background Levels. Three elements (Ti, Mg, and Fe) with varying geochemical properties and percentages of organic matter were used to identify anthropogenic Pb variability relative to basin-specific background Pb delivery. Site-specific background values were calculated from the average of the entire record, or in the case of the anthropogenic proxies, the average value was taken from 5000 to 150 yr BP (when human influences appear to be minimal) (see additional text in Supporting Information). Metals (e.g., Ti) and organic matter do not necessarily covary within and among the lake sites. This lack of covariance implies that inter- and intrasite disparity in the lake settings (e.g., differences in hydrology, productivity, and bedrock composition) influence changes in background metals and organic matter concentrations but cannot explain the variability exhibited by lead (Figure 3).

Historic Lead Pollution. As a test of lake and sediment sensitivity to airborne pollution, we compared the Pb EF records to historic metalworking activities that are known to have influenced atmospheric metal concentrations in the Midwest and Upper Great Lakes region. For example, the rise in Pb sediment concentrations at ~150 yr BP (which is present in all three records) likely reflects historic Pb smelting in Midwestern North America that continued until the 20th century (Figure 4).[41,56,57] The small increases in Pb that occur from ~500 to 150 yr BP may have resulted from age model uncertainties or bioturbation. After 100 yr BP (1850 AD), the abrupt rise in anthropogenic Pb corresponds closely with the opening of the Portage Lake Smelting Works in 1860 AD, followed by other copper smelters in the late 19th century.[25,43]

 dx.doi.org/10.1021/es304499c | Environ. Sci. Technol. 2013, 47, 5545−5552

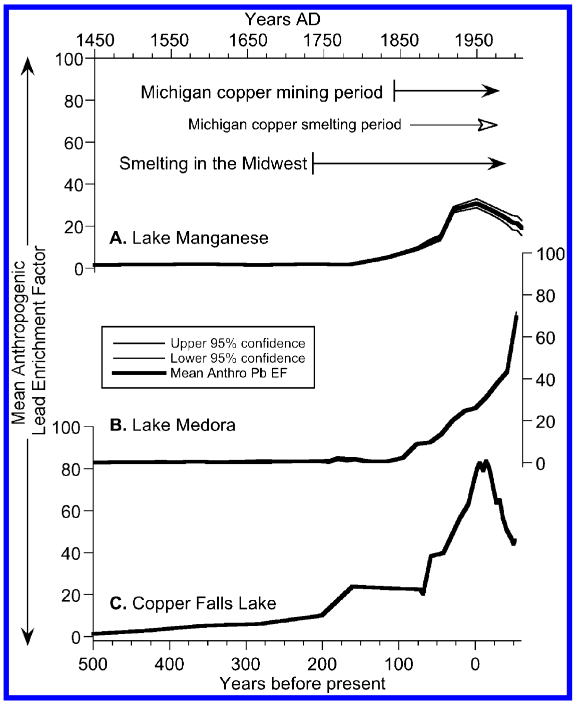

Figure 4. Recent mean anthropogenic lead (Pb) enrichment factor (EF) record from the study lakes in relation to historical events.[25,57,63]

The introduction of the internal combustion engine and widespread burning of tetraethyl-leaded gasoline in the middle 20th century likely further contributed to the increase in Pb to the sediments during this time. Notably, the discontinuation of leaded gasoline use after 1976 AD[58] and the economic decline of the mining industry[25] produced substantial Pb decreases over the last 40 years in the Lake Manganese and Copper Falls Lake sediment records. At Lake Medora, however, anthropogenic Pb values increased throughout the 20th century, which we attribute to asphalt road runoff in the catchment.[59] Nevertheless, the correspondence between the lake sediment Pb EF records and historical events is generally strong (Figure 4), demonstrating that sediments from all three lakes are sensitive archives of pollution from human activities.[25]

Prehistoric Lead Pollution. The oldest reproducible prehistoric Pb EF excursion occurs in both the Lake Manganese and Copper Falls Lake records ~8000 yr BP (Figure 5; note that the Lake Medora record does not span this period). The age of this 2 EF increase in Pb is broadly consistent with the 8800 yr BP age of charcoal found adjacent to worked copper recovered 15 km southeast of Copper Falls Lake.[21] Between ~7300 and 7100 yr BP, anthropogenic Pb EF values again increase to ~3 EF within Copper Falls Lake, followed by increases at Lake Manganese (to 4 EF) between ~7000 and 6700 yr BP. Thereafter, Pb remains at background levels for ~400 years until the Middle Archaic period, when concentrations increase to an EF of ~2 at Lake Medora (6300 to 5900 yr BP) and ~5 at Copper Falls Lake (5800 to 5500 yr BP). Interestingly, Lake Manganese did not record Pb increases during these times, except for a small (~2) EF rise around 5000 yr BP. Comparison of Pb EF data with radiocarbon dates of copper artifacts from Middle Archaic archeological sites such as South Fowl Lake, Renshaw, and Oconto Cemetery[20,60] reveals a strong temporal correspondence between the artifactual and geochemical records (Figure 5). We therefore conclude that these lakes, and likely others on the Keweenaw Peninsula,

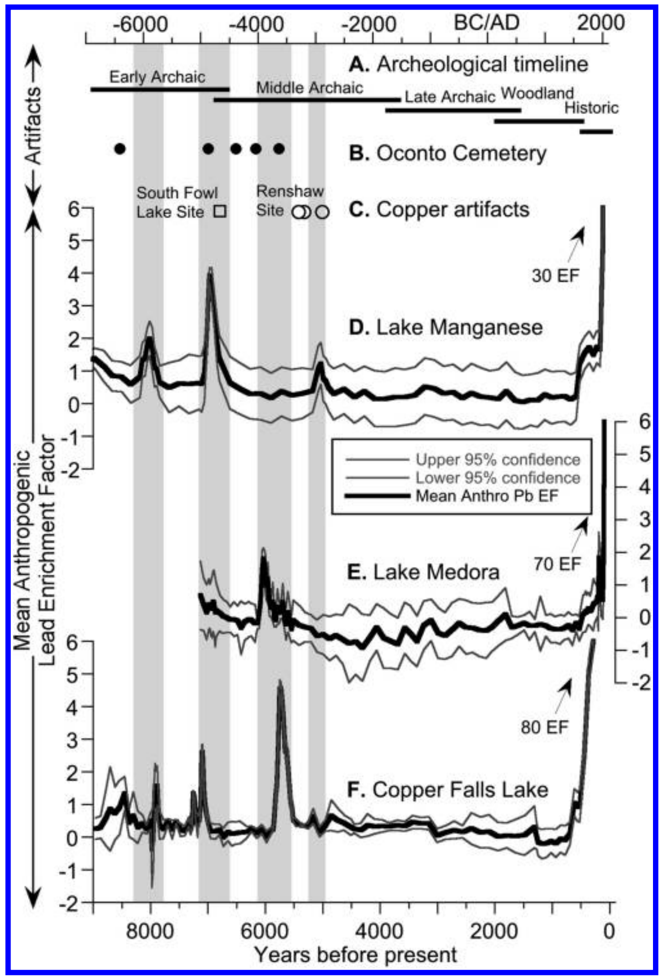

Figure 5. (A) Archeological timeline adapted from ref 15. (B) Radiocarbon dates (●) from Oconto Cemetery.[60] The site included numerous individuals buried with copper artifacts and is considered the archetypal example of the Middle Archaic Old Copper Complex.[15] (C) Radiocarbon dates of wood and twine (□, ○) preserved with copper artifacts from South Fowl Lake (Minnesota) and Renshaw (Ontario) sites.[20] (D) Lake Manganese, (E) Lake Medora, and (F) Copper Falls Lake mean anthropogenic lead (Pb) enrichment factor (EF) from all four background references (see additional text and Figures S2 and S3, Supporting Information).

record the timing and geographic extent of ancient copper mining activities within their sediments.

The exact source of human-mobilized Pb during these periods is difficult to discern. One potential source of Pb is catchment disturbance and subsequent leaching from soils or tailings. However, no apparent sedimentological changes (such as sand layers) occur during prehistoric Pb EF increases, suggesting minimal changes in overall sediment sources during these periods. Furthermore, the background metal (i.e., Ti, Mg, Fe) and organic matter variations are not associated with Pb increases. This suggests that changes from chemical weathering, redox conditions, or variations in organic matter concentrations cannot explain trends exhibited by Pb in the sediments (Figure 3). In addition, field observations around Copper Falls Lake indicate that the exposures of copper veins and mine tailing piles were located outside of the catchment (to the north) and at a lower elevation than the lake site. This suggests that the leaching of mine tailings probably had a limited impact on the prehistoric Pb record at Copper Falls Lake, although less is known about the occurrence of prehistoric mine tailings in relation to Lake Manganese and Lake Medora. Available evidence therefore suggests that prehistoric Pb inputs were, in part, derived from atmospheric sources.

Crystallographic analyses of copper artifacts demonstrate that prehistoric peoples processed copper by annealing (i.e., heating with fire),[13,61] likely to increase the malleability of the metal for processing and extraction. During annealing and hammering, impurities such as Pb associated with the native copper were likely volatized and carried in plumes of heated air and wood smoke particulates that were dispersed in the local airshed by wind. We hypothesize that the relatively low efficiency and energetic intensity of this technique limited the distance of Pb transport. Consequently, Pb emissions were minimal and annealing/mining activities occurring in one locality may not have significantly affected Pb concentrations in lake sediments from other areas of the peninsula. This is consistent with anthropogenic EF calculations at all three lakes, which demonstrate that human-derived Pb at each site is unique with respect to timing and magnitude, yet generally consistent with the archeological record (Figure 5).

Implications of the Keweenaw Records. Annealing activities associated with copper mining and processing on the Keweenaw Peninsula likely produced lower emissions than did the smelting practices in South America,[32] Europe,[62] and Asia.[54] Despite lower emissions, discrete increases in Pb are recorded in lakes near mine pits during several periods from ~8000 to 5000 yr BP. In some cases, lead enrichments in sediments from nearby watersheds are offset by several hundred years. For instance, a prominent Pb enrichment found in the sediments of Copper Falls Lake (e.g., ~5700 yr BP) is absent at Lake Manganese and occurs at a significantly different time period (at 95% confidence, Figure 2) than the Lake Medora enrichment at ~6300 yr BP. In sediment from ~8000 and ~7000 yr BP, nearly simultaneous anthropogenic lead enrichments are recorded at Lake Manganese and Copper Falls Lake. Together, these records suggest that intensive copper extraction and annealing emerged concurrently near Lake Manganese and Copper Falls Lake; whereas from ~6300 to 5000 yr BP the focus of metalworking activities shifted across the peninsula (Figure 5). These reconstructions demonstrate that, on a local scale, prehistoric Pb emissions grew and diminished multiple times over the course of decades to centuries. Developing additional lake records of Pb pollution will help to elucidate what is an apparently complex temporal and spatial pattern of human metalworking pollution.

If prehistoric metalworking activity is proportional to pollution emissions, then discrete increases in Pb between 8000 and 5000 yr BP (Figure 5) imply that human societies associated with the Old Copper Complex maintained the most intensive copper industry known in the prehistory of the Keweenaw Peninsula. No measurable increases in Pb concentrations occurred at any of the three lakes from ~5000 yr BP until the historic period, even though copper-using traditions (e.g., Hopewell; ~2100 to 1500 yr BP) existed at later periods in North America.[14] During times in which anthropogenic Pb is absent in the lake sediments, people might well have still annealed or mined copper, although at a lower intensity that produced negligible emissions relative to background levels. For example, copper artifacts dated to the Woodland period (e.g., ~1470 yr BP)[21] have been recovered on the Keweenaw Peninsula, but the sediment records suggest that the copper resources along the peninsula were not intensively mined or processed during this period. Given that Pb emissions appear to have been localized, it is possible that the mine pits that produced this copper have yet to be identified. Regardless, the existence of Pb pollution in the Archaic period (~8000 to 5000 yr BP) on the northern Keweenaw Peninsula is noteworthy, because it predates all known anthropogenic lead emissions in the world (e.g., refs 44, 55, and 62). Furthermore, the timing of the oldest anthropogenic Pb enrichments (~8000 yr BP in the Copper Falls Lake and Lake Manganese records) predates the oldest known evidence for copper smelting in Eurasia (i.e., in Serbia, ~7000 yr BP),[22] indicating that early copper-working techniques probably emerged at similar times at multiple locations.

Geochemical and artifactual records from Europe, South America, and Asia provide insight into the occurrence of metal use and associated pollution. These studies have demonstrated that atmospheric Pb pollution occurred over the last 3000 years. The Keweenaw Peninsula lake records presented here provide evidence that prehistoric Pb pollution is detectable in North America and occurred over a period of about 3000 years starting by at least ~8000 yr BP. This predates archeological evidence for agriculture in this region,[12,15] suggesting that early metal specialization and related metalworking pollution in prehistoric North America was not associated with or dependent upon agriculture.

■ ASSOCIATED CONTENT

Supporting Information

Additional text, three figures, and eight tables describing water column measurements; prehistoric and historic anthropogenic lead EF series; Pb-210 and radiocarbon data for Copper Falls Lake, Lake Medora, and Lake Manganese; site-specific background values; and reproducibility. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Christopher Purcell and Jordan Abbott for assistance in the field; Colin Cooke, Matthew Finkenbinder, Aubrey Hillman, Ellen Fehrs, Jeffrey Tubbs, and Katherine Haas for help with the research and writing of the paper; and two anonymous reviewers. This work was funded by the Henry Leighton Memorial grant through the University of Pittsburgh Department of Geology and Planetary Science, a graduate student research award from the Geological Society of America, and instrumental support from the National Science Foundation (EAR-IF 0948366).

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