Environmental Science & Technology

Article

pubs.acs.org/est

Environmental Legacy of Copper Metallurgy and Mongol Silver Smelting Recorded in Yunnan Lake Sediments

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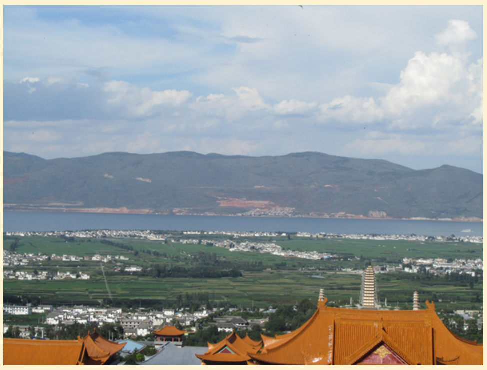
Supporting Information



ABSTRACT: Geochemical measurements on well-dated sediment cores from Lake Er (Erhai) are used to determine the timing of changes in metal concentrations over 4500 years in Yunnan, a borderland region in southwestern China noted for rich mineral deposits but with inadequately documented metallurgical history. Our findings add new insight into the impacts and environmental legacy of human exploitation of metal resources in Yunnan history. We observe an increase in copper at 1500 BC resulting from atmospheric emissions associated with metallurgy. These data clarify the chronological issues related to links between the onset of Yunnan metallurgy and the advent of bronze technology in adjacent Southeast Asia, subjects that have been debated for nearly half a century. We also observe an increase from 1100 to 1300 AD in a number of heavy metals including lead, silver, zinc, and cadmium from atmospheric emissions associated with silver smelting. Culminating during the rule of the Mongols, known as the Yuan Dynasty (1271−1368 AD), these metal concentrations approach levels three to four times higher than those from industrialized mining activity occurring within the catchment today. Notably, the concentrations of lead approach levels at which harmful effects may be observed in aquatic organisms. The persistence of this lead pollution over time created an environmental legacy that likely contributes to known issues in modern day sediment quality. We demonstrate that historic metallurgical production in Yunnan can cause substantial impacts on the sediment quality of lake systems, similar to other paleolimnological findings around the globe.

INTRODUCTION

Metal contamination in agricultural soils is an increasingly pressing concern for China as recent reports suggest that as much as 200 000 km^2, or one-sixth of China's arable land, is affected by excessive accumulation of heavy metals.[1] Modern day trace metal pollution from industrial activities has been widely documented in a number of lakes in Yunnan province, China.[2−4] This pollution has noted consequences on sediment quality[5] and aquatic ecosystem health,[6] with metal accumulation occurring in agricultural settings, including terraced rice paddy wetlands.[7] However, Yunnan is particularly rich in mineral resources and has a long history of metallurgy. Western Yunnan in particular is home to some of the earliest copper-based metallurgy sites in the province,[8] though the age of these sites has been debated.[9] It is unclear to what extent modern industrial pollution can be regarded as a continuation of early activities since the impact that historic and prehistoric mining may have had on the landscape remains undocumented and most likely underestimated due to poor historical records.[10,11] Lake sediment geochemistry has been used elsewhere in the world to reconstruct mining and metalworking activities,[12−14] yet relatively few records of this type exist in China.[15,16]

Yunnan has rich deposits of metals including copper, tin, lead, gold, silver, and iron, many of which are mined and processed near the city of Dali, in the western half of the province[17] (Figure 1B). Today, a number of ore bodies are mined in western Yunnan including the Mrchangjing and Zhacun gold mines, the Yongping copper mine, and the Jinding lead and zinc mine[18] (Figure 1B; Table 1). Lake Er (Erhai) is located in the northwest portion of Yunnan with the modern city of Dali situated on the southern shores of the lake (Figure 1B). Erhai is ideally located to answer questions about the history of mineral resource use in Yunnan since historically there were metal smelting and production facilities in the vicinity of Dali[19] and modern day nickel, copper, and platinum

Received: October 9, 2014
Revised: January 10, 2015
Accepted: February 16, 2015
Published: February 16, 2015

DOI: 10.1021/es504934r
Environ. Sci. Technol. 2015, 49, 3349−3357

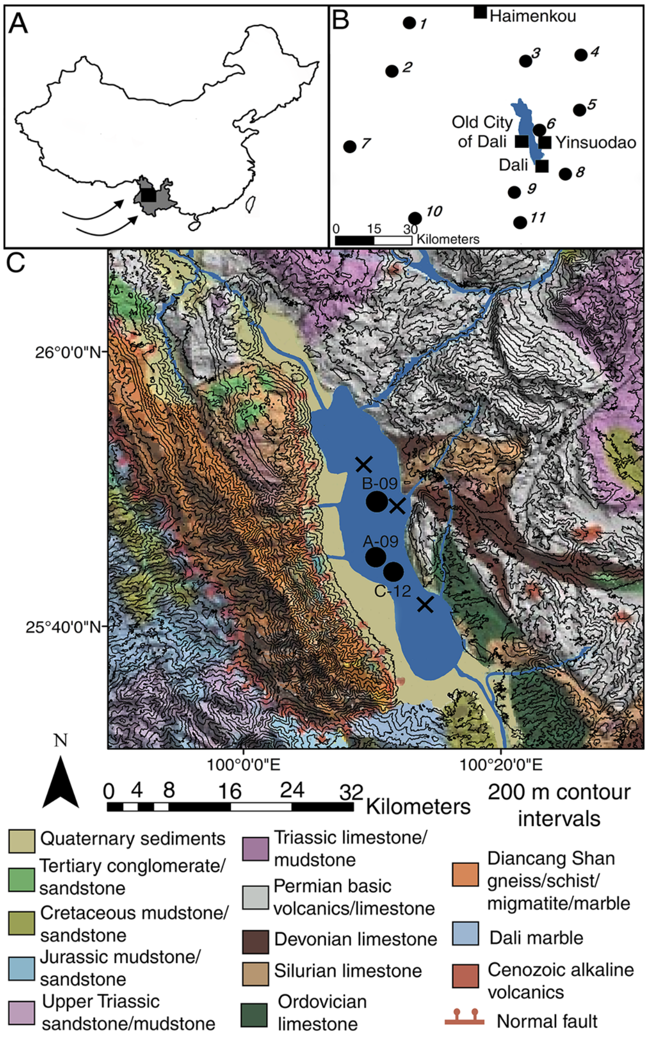


Figure 1. (A) China with Yunnan Province shaded in gray. Erhai (square) with dominant wind direction. (B) Major ore bodies (see Table 1) and archeological sites Haimenkou and Yinsuodao in relation to Dali and Erhai. (C) Erhai and coring locations A-09, B-09, and C-12. Previous coring locations by Dearing et al.[31] marked by Xs. Geologic map adapted with permission from ref 24. Copyright 2010 The Geological Society of America, Inc.

Table 1. Ore Bodies of Northwestern Yunnan Displayed in Figure 1[23,67]

number in Figure 1	name	deposit
1	Jinding	Pb, Zn, Sr, gypsum
2	Baiyangchang	Co, Cu, Ag
3	Beiya	Au
4	Heqing	Mn
5	Baofengsi	Pb, Zn, pyrite
6	Huangcaoba	Ni, Cu, platinum group metals
7	Tiechang	Sn
8	Mrchangjing	Au
9	Shihuangchang	As
10	Yongping	Cu, Co
11	Zhacun	Au

metal mining takes place on the eastern side of the lake at the Huangcaoba mine.[20]

Regional Setting. Erhai (25°47′ N, 100°11′ E, 1964 m elevation) is a relatively deep (21.5 m) lake with a catchment area of 2560 km^2 (Figure 1C).[21] The Erhai basin is tectonic in origin and formed as a pull-apart basin.[22] The Diancangshan Mountains are on the western side of the catchment, composed of high-grade metamorphic rocks and bound by a normal fault.[23,24] The northern and eastern sections of the catchment are composed of Quaternary sediments, Permian basic volcanics and limestones, and Triassic sandstones and mudstones.[23,24] The lake receives inflow from 38 streams and outflows through the Xier River to the south.[5] Since 1980, algal blooms, eutrophication, and other water and sediment quality issues have been noted.[25,26] The climate of the region is dominated by the Indian Summer Monsoon with 70% of precipitation falling between June and September.[27] Temperatures are stable and mild, averaging 9 to 21 °C.[28] Previous research on Erhai sediment cores found that lake levels varied by only 1−3 m over the late Holocene.[29] While this is a tectonically active region and several earthquakes have occurred historically,[30] the small fluctuations in lake level suggest that, over the last several thousand years, tectonic activity had a limited impact on water levels.

Previous research on sediment cores from Erhai by Dearing et al.[31] included palynological analysis and measurements of grain size, magnetic properties, and geochemistry. They identified a rise in metalworking at 1400 BC with an increase in copper concentration from 12 to 14 μg/g.[31] Additionally, an increase in lead concentration at 550 AD from 4 to 14 μg/g was inferred to represent a change from bronze to silver metalworking. However, this previous study relied on an age model based on a combination of radiocarbon measurements on bulk sediment and shell material, both of which are subject to reservoir effects, and correlation with paleomagnetic features from three cores recovered from different locations in the lake[32−34] (Figures 1 and S1, Supporting Information). Shell material and bulk sediment are subject to radiocarbon reservoir effects, where ancient carbon from carbonate rocks and soils is incorporated into samples, making them appear older than the true age of deposition.[35] Other research on Yunnan lakes identified a pronounced reservoir effect of several thousand years from bulk sediment dates.[36−38] Because limestone exists in the Erhai catchment,[23] bulk sediment and shell radiocarbon dates are susceptible to these problems. Additionally, several age reversals appear in the sediment profile, but these were not taken into account in the age model, which relied on a polynomial line of best fit drawn through all the dates (Figure S1, Supporting Information). In the Dearing et al.[31] study, the three cores were separated by as much as 20 km and some of the cores were collected from the deepest part of the lake while others were collected along the shoreline where there are significantly different sediment accumulation rates (Figure 1C). Given the potential issues with the Dearing et al.[31] age model, there is a clear need to reassess the findings using radiocarbon measurements on identifiable terrestrial macrofossils that are unaffected by reservoir effects.

Archeological and Historical Context. The results of archeological excavations and palynological analysis suggest that Erhai's lakeshores were occupied during the Neolithic.[39] One of these Neolithic/Bronze Age settlements is the Yinsuodao shell midden on the southeastern shore[40] (Figure 1B). Metal slag and complex copper and bronze artifacts found there date to no later than 1200 BC,[40] suggesting that metal production existed in the area during the middle of the second millennium BC. Similar evidence of copper-based metalworking as early as second millennium BC was found at the Haimenkou site,[41] located near Lake Jian, ~50 km north of Erhai (Figure 1B). Elemental analyses of materials from these two sites indicate that copper was the earliest metal to be used in western Yunnan.[42] Alloyed bronzes made of mixtures of copper and tin were later used, but pure copper items were used throughout the Bronze Age.[43] Prior to the middle of the first millennium BC, lead was usually a trace metal (<5%) in standard bronze recipes.[43] Archeological materials from the Erhai region show influence from the Eurasian steppes;[42] however, due to the lack of archeological data marking the transition between Neolithic and Bronze ages in Yunnan and the absence of geochemical records associated with smelting activities near Erhai, the timing of the earliest metallurgical activities in Yunnan remains unclear.[44] The current interpretations of the beginnings of Yunnan metallurgy are particularly relevant to ongoing debates about the onset of metallurgy in Southeast Asia, a region that is geographically and culturally connected to Erhai through the Great Mekong exchange system.[9,44,45]

Similar metallurgical features and artifact types at Yinsuodao and Haimenkou indicate that the metal industry was part of the second and first millennia BC technological complex in western Yunnan, which had close associations with cultures along the Jinsha (upper Yangzi) valleys north and east of Erhai.[45] Lead isotope studies suggest that the Baiyangchang ore body (Figure 1B) was a source for metal production at Haimenkou.[19] Many of these Western Yunnan objects became the prototypes of bronze for the Dian culture (350 BC to 100 AD),[43] located on the shores of Lake Dian, ~250 km southeast of Erhai. Bronze artifacts remained in use even after iron was introduced into the region toward the end of the first millennium BC. Copper, tin, lead, and silver probably continued to be extracted from these mines and used in parallel with other ore deposits widely dispersed over Yunnan.[46,47] An immense silver industry arose during the Nanzhao and Dali kingdoms (738–1253 AD) and silver utilitarian and religious objects were produced along with iron and bronze utensils and weaponry.[47] With the invasion of the Yuan Dynasty (the Mongols) in 1253 AD, the Dali Kingdom was conquered and Yunnan nominally became part of Chinese territory.[48] The Yuan administration's mismanagement of Yunnan ore resources resulted in the decline of the copper industry.[49] Silver materials from large-scale mining activities in Yunnan were distributed nationwide, but the value of silver was severely deflated due to overproduction.[49] The Ming (1368–1644 AD) and Qing (1644–1911 AD) Dynasties that followed heavily exploited the mineral resources of Yunnan for copper and silver, but historical records are incomplete and the true extent of this activity is unknown.[10]

■ METHODS

To characterize the impact that metallurgy has had on the lake over the past several thousand years and attain more realistic estimates of the timing and scale of metalworking, we recovered sediment cores from three different locations in Erhai (A-09, B-09, and C-12 coring sites; Figure 1C). We measured the sediment concentrations of a suite of weakly bound metals including copper, lead, silver, cadmium, zinc, aluminum, and magnesium. We focus our attention on lead because it has successfully been used to document early preindustrial anthropogenic metallurgical activities[13,50] and is relatively immobile once deposited in lake sediments;[51] however, we supplement our interpretation using other metals.

Field Work. In 2009, three cores were collected at 25°44′34″ N, 100°11′44″ E (A-09) at a water depth of 11 m and one core was collected from 25°48′42″ N, 100°11′42″ E (B-09) at a water depth of 20 m (Figure 1C). At A-09, a 62 cm long core with an intact sediment–water interface was collected using a lightweight percussion coring system (A-09 surf) (Figure S2, Supporting Information). The upper 20 cm was sliced in the field at 0.5 cm intervals and used for geochemical analysis and ^{210}Pb dating. Deeper sediments (A-09 D-1 and D-2) were collected using a steel barrel Livingston corer.[52] At B-09, a 74 cm long surface core was recovered with an intact sediment–water interface using the percussion coring system (B-09 surf) (Figure S2, Supporting Information) and the upper 20 cm was sliced in the field at 0.5 cm intervals and used for geochemical analysis ^{210}Pb dating.

In 2012, five core drives were collected at 25°43′38″ N, 100°12′01″ E (C-12) using a steel barrel Livingston corer (Figure 1C) at a water depth of 11 m, forming a composite record of 259 cm (C-12 D1-D5) (Figure S2, Supporting Information). Overlapping sections at all coring sites were identified on the basis of field measurements and confirmed with stratigraphic correlation of geochemical data. Since sites A-09 and C-12 are separated by <1 km and have a similar water depth, we combined the sediment cores from these two sites into one composite record using field notes and stratigraphic correlation of geochemical data.

Water Content, Bulk Density, and Loss-On-Ignition Analysis. Water content, bulk density, and loss on ignition were measured at 2 cm intervals using 1 cm^3 samples. Samples were dried at 60 °C for 48 h to remove water. Weight percent organic matter and carbonate content was determined by loss-on-ignition at 550 and 1000 °C, respectively.[53]

Geochronology. Eight radiocarbon ages of terrestrial macrofossils were measured on A-09 and C-12 cores (Table S1, Supporting Information). Terrestrial macrofossils, such as leaves and charcoal, were targeted for dating because they are less subject to transport and reworking, and unlike bulk sediment and shells, they are not subject to hard-water effects.[54] These samples were pretreated using the standard acid, alkali, acid procedure,[55] measured at the Keck Center for Accelerator Mass Spectrometry at the University of California Irvine, and calibrated using Calib 7.0.[56] The upper 8 cm of A-09 was dated using a constant rate of supply (CRS) ^{210}Pb age model[57] (Table S2, Supporting Information). A smooth spline was used to produce an age model with the best fit using the clam 2.2 code[58] in the software "R"[59] (Figure 2).

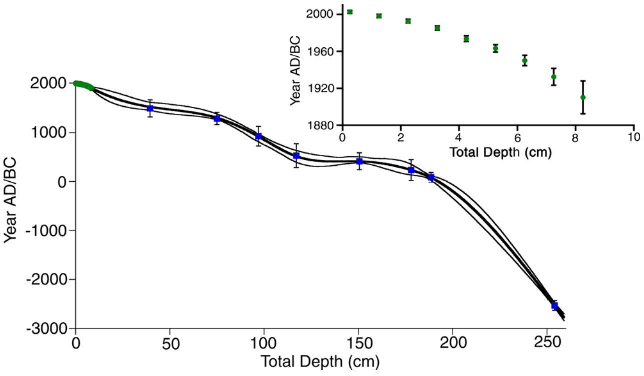


Figure 2. Age-depth model with 95% confidence intervals and radiocarbon dates with 2-sigma error bars from Cores A-09 and C-12 in black. Inset, Core A-09 ^{210}Pb dates with 2-sigma error bars.

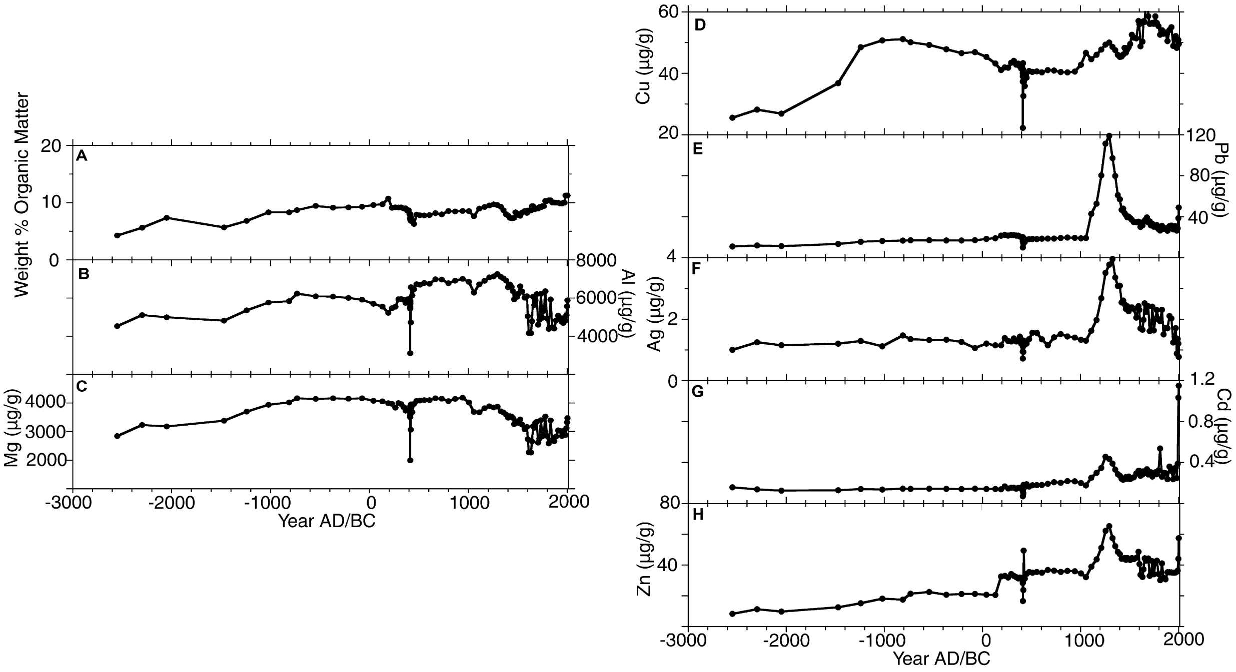


Figure 3. (Left panel) Reference factors measured in the C-12 cores: (A) weight percent organic matter, (B) concentrations of aluminum (Al), and (C) concentrations of magnesium (Mg). (Right panel) Concentrations of metals measured in the C-12 cores: (D) copper (Cu), (E) lead (Pb), (F) silver (Ag), (G) cadmium (Cd), and (H) zinc (Zn).

Elemental Analysis. Half centimeter thick slices were sampled at 3 to 5 cm intervals on sediment cores from all three core sites. Half centimeter thick slices from the upper 30 cm of the C-12 cores were analyzed every 1 cm. All samples were lyophilized and homogenized. Elements were extracted using 6 mL of 1 M HNO_3 overnight, a standard method for extracting weakly bound trace metals from sediments.[60] The supernatant was extracted and diluted before being measured on a PerkinElmer NeXION 300X inductively coupled plasma mass spectrometer at the University of Pittsburgh. Duplicates were run every 20 samples and were generally within 10% of each other. Blanks were run every 20 samples to check for memory effects and were below the detection limits of the instrument.

Anthropogenic Enrichment Factors. To account for changes associated with sediment delivery and source, we calculated anthropogenic enrichment factors based on the reference factors of aluminum (Al), magnesium (Mg), and organic matter. By normalizing metal concentrations to Al and Mg, we can account for changes in erosion, runoff, and sediment source[61] since the Erhai catchment includes mafic igneous rocks, sandstones, and mudstones (Figure 1C), whose weathering would result in Al and Mg. Additionally, metals such as lead are commonly sorbed to organic matter, so changes in organic matter must be accounted for[12,62] (Table S3, Supporting Information). The enrichment factor (EF) was calculated following the methods of Weiss et al.[63] as follows:

$$\mathrm{Pb\,EF} = \frac{\mathrm{Pb\,sample}}{\mathrm{reference\,sample}} \Big/ \frac{\mathrm{Pb\,background}}{\mathrm{reference\,background}}$$

where $\mathrm{Pb}_{\mathrm{background}}$ and $\mathrm{reference}_{\mathrm{background}}$ is site-specific and is defined as the average concentration over the stable preanthropogenic period. The Pb EF is then used to calculate the Pb anthropogenic EF:

$$\mathrm{Pb\,anthro\,EF} = \mathrm{Pb\,sample} - (\mathrm{Pb\,sample}/\mathrm{Pb\,EF})$$

■ RESULTS

Core C-12 is the focus of our discussion because it is closest to the old city of Dali and has the longest recovered sedimentary record, but we use cores A-09 and B-09 to support our conclusions. The results of the composite age model based on ^{210}Pb dating and 8 AMS radiocarbon dates on terrestrial macrofossils indicate that the C-12 cores span 4500 years (Figure 2). Sedimentation rates from 2500 BC to 200 AD average 0.03 cm/year, from 200 to 450 AD increase to 0.30 cm/year, and from 450 AD to the present remain stable at 0.11 cm/year. Sediments from all three sets of cores are homogeneous dark brown/black fine silt and clay and are composed of 5−10% organic matter (Figure 3) with no detectable carbonate. We see no sedimentological evidence in the cores to suggest substantial variations in water level; thus, we conclude that lake level changes have not played an important role in causing variations in metal concentrations for the past 4500 years.

We focus our attention on the concentrations of copper (Cu), lead (Pb), silver (Ag), cadmium (Cd), and zinc (Zn) as these display the most variation (Figure 3). The concentrations of these metals, in particular Pb, are remarkably similar in terms of both depth and magnitude from all three coring sites though core B-09 is much shorter than A-09 and C-12 (Figure S3, Supporting Information). From 2500 BC to 200 AD, the concentrations of Pb, Ag, Cd, and Zn are low and stable, averaging 15.6, 1.2, 0.1, and 29.5 μg/g, respectively (Figure 3). From 200 to 450 AD, concentrations double for all of the aforementioned elements. After 450 AD, the concentrations remain stable until 1100 AD. Beginning at 1100 AD, concentrations of Pb, Ag, Cd, and Zn increase and reach a peak at 1300 AD of 119.1, 3.8, 0.4, and 65.4 μg/g, respectively. From 1300 to 1980 AD, concentrations decline to 26.6 μg/g for Pb, 0.88 μg/g for Ag, 0.25 μg/g for Cd, and 35.7 μg/g for Zn. The last 30 years have slightly higher concentrations of Pb, Ag, Cd, and Zn at 49.1, 0.8, 1.2, and 57.5 μg/g, respectively. Concentrations of Cu display different variations. From 2500 to 2000 BC, Cu averages 26.8 ± 1 μg/g and nearly doubles to 51.1 μg/g beginning ~1500 BC (Figure 3). After a peak at 700 BC, concentrations decline to an average of 41.4 μg/g. At 1000 AD, concentrations increase to a peak of 66.2 μg/g at 1650 AD before declining to 49.5 μg/g in the last 10 years.

■ DISCUSSION

We calculated anthro EFs to account for changes in erosion, runoff, and sediment flux that may have impacted the delivery of metals to the lake. We acknowledge that the weak acid extraction performed on these samples does not represent the total lithogenic proportion of elements such as Al or Mg;[64] rather, we seek to normalize the concentrations of metals such as Pb to natural geogenic processes to account for variations in sediment source and delivery. The high correlation coefficient between the chosen reference factors and metals of interest during the prepollution time period suggests that they can account for part of metal content in the sample (Table S3, Supporting Information). On the basis of the relatively stable and low concentrations of the reference elements (Figure 3), we define background levels as the time period from 2500 BC to 200 AD.

Early Metallurgy. From 2500 BC to 200 AD, the anthro EFs of Pb, Ag, Cd, and Zn were stable and less than three, representing our best estimate of background variations arising from natural, nonanthropogenic sources (Figure 4). Natural sources of these metals in the atmosphere include wind-blown dust, sea salt, volcanic emissions, and forest fires.[65] Approximately 40−50% of Cd and 20−40% of Pb arises from volcanic emissions and 20−30% of Pb and Zn can be attributed to soil-derived dust; the remainder of natural emissions is due to biogenic processes.[65]

From 200 to 450 AD, the anthro EFs of Pb, Ag, Cd, and Zn increase by 3- or 4-fold. This is accompanied by a 10-fold increase in the sedimentation rate. We attribute these increases to be the result of greater sediment influx and/or a change in sediment source to the lake reflecting land use change. Pottery models from grave sites on the shores of Erhai dating to the Han Dynasty (ca. 206 BC to 220 AD) depict irrigated farming practices,[66] which suggests that Chinese-style agriculture first arose in these settlements beginning ~2000 years ago. The initiation of this style of agriculture coincides closely with the land use change inferred in our record.

The Cu anthro EF from 2500 to 2000 BC is less than one (Figure 4), likely recording natural variability associated with biogenic emissions.[65] Beginning at 1500 BC, Cu anthro EF increases to between 6 and 12. While our age control is limited by the lack of a radiocarbon date directly at the increase, we performed age uncertainty analysis (Figure S4, Supporting Information) which showed that the timing of this event is ±400 years. Our interpretation is that the increase is caused by the initiation of copper-based metalworking around the lake, which archeological research suggests began around this time.[40] The lack of a concomitant increase in either Pb or Sn concurs with archeological records that initial metalworking techniques were primarily used for copper-making and were not associated with the production of complex bronze alloys combining more than two or three metals.[8] The absence of increases in other metals (e.g., Zn and Cd) suggests that this increase in copper was linked to atmospheric emissions. Small increases in Al, Mg, and organic matter (Figure 3) may account for part of the Cu increase; however, the magnitude of change is much less than that of the Cu. Given that the beginnings of copper-based metallurgy during the second millennium BC in Yunnan remain an open question,[9,44,45] our results lend substantial support to the initiation of this activity beginning by at least 1500 BC. These data not only add new dimensions to the history of Yunnan metals in the context of Eurasian metallurgy, but they will be crucial for clarifying the much debated chronological issues related to the initiation of copper-based metallurgy in adjacent Southeast Asia.

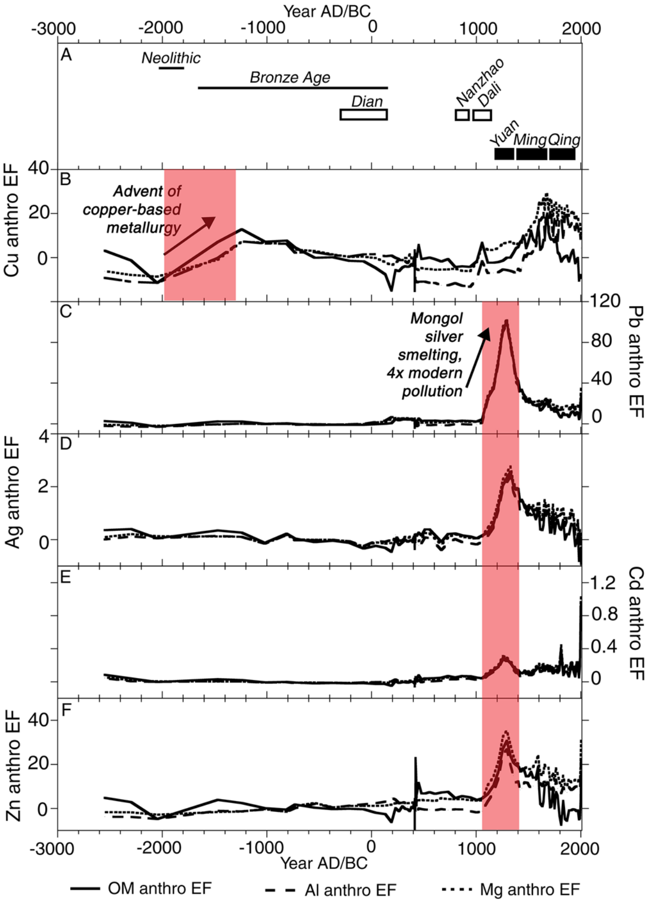


Figure 4. (A) Archaeological periods, Yunnan cultural periods in white boxes, and Chinese dynasties in black boxes. Anthropogenic EFs for organic matter (solid line), aluminum (dashed line), and magnesium (dotted line) for (B) copper (Cu), (C) lead (Pb), (D) silver (Ag), (E) cadmium (Cd), and (F) zinc (Zn) from Cores C-12. Shading from 1100 to 1400 AD corresponds to the increased concentrations of Pb, Ag, Cd, and Zn during the time period of the Yuan Dynasty (the Mongols).

Peak in Lead Pollution. The Pb anthro EF increases after 1100 AD, reaches a peak of 100 ± 2 at 1300 AD, and declines to 30 ± 2 by 1420 AD (Figure 4). Anthro EFs of Ag, Cd, and Zn follow similar trends (Figure 4). Argentiferous galena is a common ore in Yunnan, and there are a number of such ore bodies close to Erhai[17,18] (Figure 1B). The Baiyangchang ore body, 75 km northwest of Erhai, has rich deposits of silver with impurities of lead and zinc[67] and mining and exploitation of this deposit is a possible source of the observed increases in metals. Geochemical data that would allow us to confidently attribute this increase in metals to a particular ore body currently do not exist; however, this is a direction of future research. The peak of this enrichment corresponds to the Yuan Dynasty (1271−1368

AD), the Mongols, within the limits of the age uncertainty (±30 years).

The Mongols established the first government operated silver mine in Yunnan in 1290 AD, and by 1328 AD, taxes from silver production in Yunnan accounted for 47% of national tax revenue.[68] The process of purifying ores relied on cupellation,[68] where the ores would be roasted in low temperature fires in a furnace that ensures sufficient oxygen flow.[69] As wood is combusted, lead monoxide and other metal oxides form from ore impurities and are volatized into ash, which is then deposited on the land and water via wet and dry deposition. Since this metallurgical procedure requires large amounts of wood, it is reasonable to expect that deforestation occurred in the lake catchment. We see no sedimentological evidence of this; however, a previous study by Dearing et al.[31] found a decrease in arboreal pollen coincident with the rise in lead. The sudden decline in lead pollution at Erhai is likely related to the end of the Mongol Dynasty in 1368 AD. Since silver mining was restricted during the beginning of the subsequent Ming Dynasty,[70] this contributed to the decline in lead emissions.

Our hypothesis is that these metals were primarily deposited in the lake via atmospheric transport. There is no accompanying change in the concentration of organic matter (Figure 3) or bulk density of the sediments (constant at 0.6–0.7 g/cm^3). Additionally, since metals such as Pb and Zn are generally not subject to remobilization from oxidation/reduction changes during diagenesis,[71] we do not believe that the increases are the result of variations in water chemistry. In a lake such as Erhai that has a large surface area and catchment, it is possible that sediment storage on floodplains and hillslopes can occur over several hundred years[72] and that the remobilization of contaminated sediment can create peaks in metal concentration.[73] However, the narrow, high gradient fluvial systems in Erhai's catchment, especially on the western side near sites A-09 and C-12 (Figure 1C), limit the potential for floodplain sediment storage. Furthermore, there is no change in sediment stratigraphy or mineralogical composition during this interval. While we cannot definitively reject the possibility of floodplain sediment storage, the geochemical signal in the lake sediments seems more likely influenced by atmospheric deposition than remobilization of stored, contaminated sediments.

Lee et al.[16] measured metal concentrations in lake sediments in central China and found an increase in lead from 1370 to 1470 AD, attributed to increased warfare and demand for manufacturing of weapons associated with the beginning of the Ming Dynasty.[16] Yunnan has some of the largest zinc deposits in the world, and the Ming Dynasty established at least 20 zinc smelting operations in southwestern China.[74] However, most of these activities took place in the latter half of the Ming Dynasty (~1500 AD), and many of the zinc smelters are 1000 km east of Erhai.[74] Moreover, we can confidently attribute the pollution to the Mongols as we have a radiocarbon date on a terrestrial macrofossil directly at the increase (Table S1, Supporting Information). Whatever zinc distillation activities may have impacted the lake, they were not as large as the silver smelting that was taking place during the time of the Mongols.

Our study differs significantly from previous work by Dearing et al.[31] whose study found increases in Cu at 400 BC from 12 to 14 μg/g and Pb increases of 4 to 14 μg/g from 550 to 950 AD (Figure S5, Supporting Information). In the previous study, the copper rise is 1000 years later and the lead rise is 700 years earlier. These differences in timing are significant, because the lead increase in the Dearing et al.[31] study is incorrectly attributed to the Nanzhao and Dali kingdoms. Our results provide a more accurate chronology allowing us to attribute the pollution to the Mongols, as well as pinpoint a specific process (silver smelting), that was responsible for the observed increases in metal concentrations. Since it is our hypothesis that these increases are due to atmospheric emissions, this implies that deposition and metal loading also took place on the surrounding landscape. As deforestation and land use change has already led to soil loss within Erhai's catchment,[75] the mobility of this soil, likely high in concentrations of lead, silver, zinc, and cadmium, may lead to further contamination problems.

Another discrepancy between this study and the previous work by Dearing et al.[31] is the magnitude of the copper and lead increases in the sediments. An increase of 2 μg/g of copper in the previous study is within the range of natural variability (Figure S5, Supporting Information). The increase of 10 μg/g of lead is ten times less than the observed increase in this study. This is due to differing extraction techniques; however, the details of the extraction methods were not documented in the Dearing et al.[31] study, and it is unknown what strength and type of acid was used to measure the metals weakly sorbed to the sediments. Our work shows that the increases in metal concentrations were actually much more substantial. According to consensus-based sediment quality guidelines, the concentrations of lead at 1300 AD (120 μg/g) approached the probable effect concentration of 128 μg/g, above which harmful effects are likely to be observed in freshwater organisms.[76] A study of Idaho wetlands documented that the persistence of lead in sediments impacted organisms several centuries after mining activity was reduced.[77] Similarly, we suggest that the elevated concentrations of lead due to the environmental legacy of Mongol silver mining have impacted the lake for several centuries.

Modern Pollution. Lead anthro EF declines from 30 ± 2 in 1420 AD to 9 ± 5 in 1980 AD (Figure 4). The Pb anthro EF in the uppermost sediments deposited in the last 20 years increases to 30 ± 4. Silver and Zn anthro EFs follow similar trends of slowly declining at 1400 AD and increasing slightly after 1980 AD. It is only the Cd anthro EF that displays values five to six times higher in modern day sediments than the past. Modern industrial activities near the lake include nickel, copper, and platinum mining.[20] While these activities may contribute to the observed present-day decline of sediment quality in the lake, the magnitude of these activities is small in comparison to the historical ones: the Pb anthro EF at 1300 AD is almost four times greater than modern pollution. This may be due to the larger scale of metallurgical operations in the historical period or the low efficiency of metallurgical procedures, which caused greater amounts of impurities to be volatized and delivered to the lake. Copper anthro EF reaches a peak of 25 in 1670 AD, during the Qing Dynasty (Figure 4). This corresponds to the surge in Yunnan copper production associated with the Qing Dynasty's increase in the demand of copper for coinage.[10] Notably, the 20th and 21st century Cu anthro EF averages 8, despite copper mining currently occurring within the lake's watershed.

Our findings are unique: while preindustrial pollution has been detected in lake sediments over many time periods and regions of the world, only a few studies have found preindustrial pollution levels to be greater than modern day levels[50,78] and none of these have been in China. The long slow decline of lead concentrations to present day values may in part be influenced by the persistence of the historical lead pollution being reworked from lake sediments or remobilization of stored legacy sediments. Therefore, we suggest that modern pollution issues rest on a long history of decline in sediment quality at Erhai. This environmental legacy of silver smelting creates complications in accurately attributing the accumulation of heavy metals to specific modern day processes as well as developing mitigation strategies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Five figures and three tables describing the Dearing et al.[31] previous age model, sediment core collection details, lead concentrations by depth, age uncertainty analysis, comparison with the Dearing et al.[31] previous study, radiocarbon and ^{210}Pb ages, and correlation coefficients. 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 David Pompeani, Matthew Finkenbinder, Colin Cooke, and Ellen Fehrs for useful feedback and ChunLiang Gao and Jordan Abbott for assistance with fieldwork. Four anonymous reviewers provided feedback that improved the quality of this paper. We thank the financial support of the Geological Society of America Graduate Student Grants, the National Natural Science Foundation of China (NSFC grants 40571173, 40871008, and 41171171), and the US National Science Foundation (EAR/IF grant 0948366).

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