Seven Thousand Years of Records on the Mining and Utilisation of Metals from Lake Sediments in Central China

CELINE S. L. LEE,[†] SHI-HUA QI,[‡] GAN ZHANG,[§] CHUN-LING LUO,[†] LU Y. L. ZHAO,[†] AND XIANG-DONG LI [†*]

Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, Faculty of Geosciences, China University of Geosciences, Wuhan 430074, China, State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

A 268 cm section of sediment core from Liangzhi Lake in Hubei province in central China was used to assess the use and accumulation of metals in the lake in the past 7,000 years. The concentrations of trace metals, including Cu, Pb, Ni and Zn, and major elements, Ca, Fe and Mg, in a ^{14}C- dated segment of sediment core were analysed. Historical trends on the input of metals to Liangzhi Lake from around 5000 BC to the present were recorded in the sediments, representing about 7,000 years of history on the mining and utilisation of metals in central China. The concentrations of Cu, Ni, Pb and Zn increased gradually from about 3000±328 BC, indicating the start of the Bronze Age in ancient China. During the period 467±257 – 215±221 AD, there was a rapid increase in the concentrations of these metals in the sediments, indicating enormous inputs of these metals at that time. This era corresponded to China's

Warring States Period (475 - 221 BC) and the early Han dynasty (206 BC – 220 AD), during which copper and lead were extensively used in making bronze articles such as vessels, tools and weapons. From 1880±35 AD to the early 1900s, there was also a significant increase in the concentrations of metals such as Cu, Ni, and Pb, which probably reflected the metal emissions and utilisation during the early period of industrial development and weapon manufacture during the wars in China. The Pb isotopic analysis showed that the surface and subsurface sediments had lower ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios than the deeper layers, reflecting the additional input of Pb from mining activities that took place during the Bronze Age era and in modern times. This study provides direct evidence of the environmental impact of the mining and utilisation of metals in the last 7,000 years in one of the important regions of Chinese civilisation.

Introduction

Humans have a long history of utilising metals since the discovery of techniques for their mining and recovery thousands of years ago. Metals are released into the atmosphere from various activities, such as coal and oil combustion, mining, the pyrometallurgical production of iron and non-ferrous metals, and other human activities (*1, 2, 3*). Copper was first used about 7,000 years ago, and has been produced in substantial amounts since the Bronze Age (4000- 5,000 years ago) (*4*, *5*). During the period of the Roman Empire, large quantities of metals were produced, especially Pb (80,000 to 100,000 metric tons per year), Cu (15,000 tons/year), Zn (10,000 tons/year), and Hg (>2 tons/year) (*6*, *7*), to meet a significant increase in demand for metals for military and civilian purposes, such as for tools and coinage. However, Roman-era mines were small-scale operations. It was not until the Industrial Revolution in the eighteenth century, when industrial production increased on a massive scale, that the demand for metals grew exponentially, as did the intensity of metal emissions with the use of large furnaces with tall smokestacks (*8, 9, 10*).

Sedimentary records are widely used to reconstruct the historical inputs of metals and other pollutants in the environment. Lakes and their sediments change rapidly in response to the sedimentation process in the drainage basin, which provide a detailed record of the transformation of the terrestrial environment (*11*). The study of sediment cores allows historical inputs of many pollutants in the ecosystem to be determined, and provides an estimate of the variability of the natural climate (*12, 13*, *14*). Metals can enter the drainage system through atmospheric deposition and be conserved in the sediment bed. If the sediment accumulation rate is known, the depth profiles of trace metals in the sediments may be used to evaluate the rate of influx of metals in the past. Previous studies have demonstrated that a record of past depositions of metal can be obtained from lake sediments (*15-21*). The history of atmospheric lead pollution in Europe has been constructed by studying lead concentrations and lead isotopic ratios in lake sediments and peat deposits (*22-25*). Renberg et al. (*25*) showed that the first indication of the atmospheric deposition of lead pollution dates to between 2000 and 1500 BC. The concentration profiles of lead in the lake sediments and peat cores were found to follow the pattern of the history of world lead production: an initial increase at about 2000 BC; an early peak during the Greco-Roman period at around 0 AD; an increase from about 1000 AD; a decline sometime between 1300 and 1700 AD; an increase during the Industrial Revolution; a peak in the 1970s; and a decline thereafter (*3, 23, 25*).

Some studies have been conducted using lake sediments to investigate the human impact on lakes in China. Heavy metals, nutrients and spheroidal carbonaceous particles in several lakes in the Jianghan Plain and the Taihu region of China were analysed (*17, 26*). These studies have shown that the sediment cores were significantly enriched in heavy metals with fossil fuel-derived carbonaceous particles due to the influence of urbanisation and industrial development in the surrounding region in the past few decades. However, high resolution studies have been limited to the recent one hundred years of sedimentary records.

For the present study, in order to determine the historical record on the utilisation of metals in ancient China, a sediment core of about 268 cm long in depth was collected from Liangzhi Lake in Hubei province in central China. There is a long history of human habitation in the area around Liangzhi Lake, an important region in the development of Chinese civilisation. Liangzhi Lake is relatively undisturbed from known local discharges of wastewater; hence it is an ideal site to study ecological changes and the impact of past human activities, such as mining and the uses of metals (including the manufacturing of various tools and weapons during the Bronze Age), on the aquatic ecosystem in ancient China. This is probably the first study on 7,000 years of sedimentary records of metals in China.

Experimental Section

Study Area. Liangzhi Lake is located at 30^{o}14’60”N and 114^{o}29’01E [see Figure S1 in supporting information (S.I)]. The lake is situated at the middle reaches of the Yangtze River. It is a permanent freshwater lake, covering an area of approximately

230 km^2 and with an average water depth of 2.8 meters. Liangzhi Lake is one of the many lakes within the Jianghan Plain. Thousands of years ago, the Jianghan Plain was a huge area of marshland known as the Yunmengze (Yunmeng marsh). However, the marshland gradually shrank and was replaced by a fluvial area studded with thousands of lakes and small marshes (*27*). Liangzhi Lake has a great ecological value, as it is the habitat of many lacustrine species, such as fish and crabs. The water quality in Liangzhi Lake has been deemed to be of a Grade 2 or 3 levels, according to the standards set up by the State Environmental Protection Agency of China (GB3838-2002). This means that the water in Liangzhi Lake is low in nutrients and toxic pollutants (*28*). Compared to other lakes in the alluvial plain, there has been relatively less influence on this lake from local human activities in the last few decades.

Sampling Description. A sediment core with a depth of 268 cm was collected at the centre (the deepest part) of Liangzhi Lake in June 2002 using a piston coring device. The diameter of the core was 6 cm. The sediment core was sectioned at 1 cm intervals *in situ*, which were immediately stored in pre-washed polyathylen bags. The samples were then transported to the laboratory and stored at 4 - 6 °C prior to analysis.

Radiocarbon Dating. The sediment chronologies used in this study were determined at the China Seismological Bureau based on conventional ^{14}C dating method using Accelerator Mass Spectrometry. The ^{14}C ages were then calibrated using the calibration programme CALIB-4.3 (*29*). All of the dates described in this paper were obtained by interpolation (polynomial) based on the calibrated radiocarbon age, and the bulk radiocarbon and calibrated ages by depth are given in Table S1 and Figure S2 in the supporting information (S.I.).

Heavy Metal Analysis. The sediment samples were oven dried at 60 °C for 24 h, and subsequently ground to fine particles. They were digested using the strong acid digestion method (see ref. *30* for details.). The concentrations of metals were determined using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; Perkin Elmer Optima 3300DV). Reagent blanks, replicates and standard reference material (NIST SRM 1646a Estuarine Sediment) were used as the QA/QC protocols in the analysis. The precision and bias assessed by the reagent blanks and replicate samples were <5 % of the mean analyte concentrations for all of the elements in the analysis. The recovery rates in the standard reference material (NIST SRM 1646a) for all of the measured elements were around 80% - 105%.

Analysis of Pb Stable Isotopic Compositions. The Pb isotopic compositions of 25 selected sediment samples were determined to study the natural and anthropogenic origins of Pb in the lake sediments. The Pb isotopic ratios (^{204}Pb/^{207}Pb, ^{206}Pb/^{207}Pb, and ^{208}Pb/^{207}Pb) of the sediments were measured using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Perkin Elmer Elan 6100DRC^{plus}) (*30*). The Pb counts of the procedural blanks were <0.5% of that of the samples, and the precisions (%RSD) of the Pb isotopic ratios were <0.5%. International standard reference material (NIST SRM 981 Common Pb Isotopic Standard) was used for quality control. The measured ^{204}Pb/^{207}Pb, ^{206}Pb/^{207}Pb, and ^{208}Pb/^{207}Pb ratios of NIST SRM 981 were 0.0645±0.0001, 1.0936±0.0008, and 2.3703±0.0021, which were in good agreement with the standard reference values of 0.0646, 1.0933, and 2.3704, respectively.

Results

Metal Concentrations in the Sediment Profile. The vertical profiles of major elements, including Ca, Fe, and Mg, and trace metals, including Cu, Ni, Pb, and Zn in the sediment core are shown in Figure 1, 2 and 3. The concentrations of metals in different historical times are summarised in Table 1. In general, the concentrations of these metals decreased with depth. Before 3000±328 BC, the concentrations of Cu, Ni, Pb and Zn in the sediments were relatively low and constant (see Figure 2). From about 3000 – 2700 BC, these elements showed a gradual increase in concentration. There was a rapid increase of elements such as Cu, Ni, and Zn in 76±237 BC, and Pb in 467±257 BC, reflecting an abrupt input of these metals into the sediments. Subsequently, the concentrations of Cu, Ni, Pb, and Zn were relatively constant, with some occasional variations. The Ca concentrations were observed to peak at about 1500±102 AD, and to decrease gradually towards modern times. The concentrations of Fe in the sediment profile exhibited a highly varied pattern and those of Mg concentrations showed a general trend of increasing towards the surface.

Pb Isotope Compositions in the Sediment Profile. The results of detailed stable Pb isotope compositions in the Liangzhi Lake sediments are given in Table S1 in the supporting information (S.I.). The vertical profiles of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios, and the concentrations of Pb are shown in Figure 4. The concentrations of Pb increased towards recent times, while decreasing trends were observed in the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios from 4940±347 BC to 1040±280 BC, the $^{208}Pb/^{207}Pb$ ratio in the last 2000 years (see Figure 4).

Discussion

Chronology of Metal Inputs in the Sediments. The literature indicates that the Bronze Age emerged in China at around 2000 BC, during the Xia dynasty (*31*). For the chronology of Chinese dynasties, the systems described by Ma (*31*) were used in the present study (see Table S3 in S.I.). Bronze was widely used for tools, weapons, and ritual vessels in China since about 2000 BC until the Han dynasty (206 BC - 220 AD). The enrichment of Cu, Pb, Ni, and Zn in the Liangzhi Lake sediments is illustrated in Figure 2. These patterns may be attributed to the use of these metals in central China in ancient times. As shown in Figure 2 and the enrichment factor chart (Figure S3 in S.I.), there were two noticeable increases in the concentrations of Pb, Ni, and Zn, in 3000 (± 328) - 2700 (± 323) BC, and later in 467 (± 257) – 76 (±237) BC The increase in concentration of these metals possibly marks important changes, in mining practices and in the use of these metals that occurred during these periods. The distribution of metals differed in the sediment core which led to its division into discrete stratigraphic phases (see Figure 2). The following discussion will focus on primarily on the anthropogenic metals, including Cu, Pb, Ni, and Zn, which are important indicators of past metal pollution from various human activities. The distribution patterns of these metals along the sediment core were observed to fall into the following five phases, 1) Phase I – the pre-mining phase (before 3000±328 BC); 2) Phase II – the early Bronze Age (2890±326 to 549±260 BC); 3) Phase III – the late Bronze Age (467±257 BC to 168±224 AD); 4) Phase IV – the post-Bronze Age (215± 221 – 1360±122 AD); and 5) Phase V – the modern period in China (after 1370 ±120 AD)

Pre-mining Phase (Phase I). Before 3000±328 BC, the concentrations of Cu, Pb, Ni, and Zn were at their lowest and were generally constant in the whole profile, which had average values of 16.8, 15.7, 34.1, and 46.7 mg/kg, respectively (Table 1 and Figure 2). These values may represent the natural background concentrations of metals from the parent bedrocks in the surrounding area. This period probably represented the time before large-scale human activities began to take place in this region.

Early Bronze Age in China (Phase II). There was a gradual increase in the concentrations of Cu, Ni, and Zn starting at around 3000±328 BC (Figure 2). The concentrations of Cu, Ni, and Zn increased from background values of 16.8, 34.1, and 46.7 mg/kg to 18.3, 39.4, and 58.0 mg/kg in 2520±319 BC (increased by 9.0%, 16%, and 24%, respectively). The concentration of Pb increased gradually from a background value of 15.7 mg/kg to 20.3 mg/kg in 2720±260 BC (an increase of 29%). The increase in the concentrations of these metals in the sediments probably indicates an increase in the mining and utilisation of these metals in China during the early Bronze Age. Several copper mining sites which can be traced back to 1310 BC have been reported in the east Hubei province (*32*).

Late Bronze Age in China (Phase III). From 467±257 BC to 168±224 AD, there was a rapid increase in the concentrations of Cu, Ni, and Zn in the sediments, to 36.7, 59.0, and 98.2 mg/kg (increased by 120%, 73%, and 110% from background values of 16.8, 34.1, and 46.7 mg/kg, respectively) (see Figure 2). This period corresponded to the Warring States (475-221 BC) and Han dynasty (206 BC – 220 AD) A nearby ancient copper mining site, Tonglushan, which is located in Daye in Hubei province, had been in operation from the Spring and Autumn Period and throughout the Han Dynasty (about 770 BC – 220 AD) (*31*). It is estimated that about 10,000 tons Cu were produced in this site (*33*). The enrichment of Cu, Ni, and Zn in the sediments can perhaps be attributed to the mining activities that occurred in this region since the early Bronze Age, and which subsequently peaked during the Han dynasty (206 BC - 220 AD)

The concentration of Pb increased rapidly from 467±257 BC to 168±224 AD to about 28.5 mg/kg (increased by 82% from a background value of 15.7 mg/kg) (see Figure 2). In ancient China (3000 BC to 200 AD), copper was alloyed with lead to make various bronze articles (*31*). The input of Pb to sediment was found to increase gradually since the start of the early Bronze Age until about the Warring States Period (475 - 221 BC) in China. After that, a rapid increase was observed in the use of Pb until the Han dynasty (206 BC – 220 AD)

Moreover, during the Han dynasty (206 BC – 220 AD), there was an expansion in agricultural activities due to a rapid increase in population (*34*). The government introduced the "tai-tian" method in 85 BC, which involved growing crops in well-regulated alignments to achieve optimum space-saving conditions and good irrigation methods. At that time, better tools made of iron came into use, such as the weeding hoe, ox-drawn plough, and a seed box attached to a light oxen-drawn plough, which increased crop yields. The intensive agricultural activities that took place during the Han dynasty caused a large-scale exploitation of uncultivated land. This may have also led to an increase in the leaching and accumulation of trace metals, such as Cu, Ni, Pb, and Zn, and some major elements (Fe, Mg and Ca) in the sediments as a result of intensive agricultural practices (see Figure 1 and 2).

Post-Bronze Age in China (Phase IV). At the end of Eastern Han dynasty (25 - 220 AD), ceramics played a more important role than before, and iron tools and vessels began to be used in place of bronze ones (*35*). The sediment records show that there was a decrease in the concentrations of Cu, Ni, and Zn after a peak in 215±221 AD (Figure 2). The decrease in the concentrations of these metals coincided with the end of the Bronze Age in China. After 215±221 AD, the concentration of Pb continued to increase at a lower rate, indicating that after the Bronze Age the mining and use of Pb in China was still increasing, particularly in the Jianghan Plain region.

Modern Period in China (Phase V). The concentrations of Cu, Ni, Pb, and Zn from 1300 – 1900 AD (Phase V) are shown in Figure 3. During the period

1370±120 – 1470±106 AD, there was an increase in the concentrations of Cu, Pb, and Zn in the sediments (see Figure 3). This period coincided with the end of the Yuan dynasty and with the early Ming dynasty. During this period (1334 – 1487 AD), there was social instability across the country due to famine, adverse climatic conditions, and poverty, which eventually led to peasant rebellions (*36*). There was an average of 2.15 – 3.46 instances of warfare per year in the country. These wars may have led to an increase in the utilisation of metals for the manufacturing of weapons and tools. Thereafter, the concentration of Zn remained relatively constant. The concentrations of Cu and Pb continued to increase from 1370±120 AD, but showed a decreasing trend from about 1600±88 AD (during the Ming Dynasty) until about 1830±46 – 1880±35 AD (the Qing dynasty). There were years of severe drought for about 40 years, from 1601 to 1644 AD, during the Ming dynasty (*37*). The dry climate may have led to a reduction in human activities, which was reflected in a decrease in the concentration of metals in the sediments. From 1830±46 – 1880±35 AD to the early 1900s, there was a significant increase in the concentrations of Cu, Pb, and Ni (see Figure 3). During the 1860s and 1870s, the Qing government promoted a "self-strengthening" movement to utilise Western technology to develop China's industrial and defence systems (*38, 39*). At that time, various railroads, textile factories, arsenals, and a modern army and navy were built, and mining activities (for coal and metals) were initiated to support the manufacturing industry and the army. In subsequent years, several wars broke out in China, such as the first Sino-Japanese War in 1894 and the 1911 Revolution that led to the fall of the Qing Dynasty. According to Zhang et al. (*36*), the frequency of warfare reached a high level of 1.93 times per year during the period 1806 – 1912. The small increase in the concentrations of Cu, Ni, and Pb in the sediments around 1830±46 – 1880±35 AD probably reflects the impact of industrial and military developments and wars during the late 1800s.

From 1930±21 to 1960±14 AD, the concentration of Pb increased significantly from 29.1 mg/kg to 33.1 mg/kg, an increase of 13.6% (see Figure 3). This period corresponded to the second Sino-Japanese War during World War II (1937 – 1945 AD) and to the post-war industrial period (following the establishment of the People's Republic of China in 1949). The noticeable increase in the concentrations of Pb in the surface sediments can be attributed to the massive use of Pb alkyl additives in gasoline (*40*).

Temporal Variations in ^{206}Pb/^{207}Pb, and ^{208}Pb/^{207}Pb Ratios. Before 3000±328 BC, the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios were relatively constant, probably reflecting the background Pb isotopic signatures from natural parent materials. Subsequently, the Pb isotopic ratios decreased, reaching a low at about 978±277 BC when the concentration of Pb reached a maximum. The Pb isotopic ratios then showed a remarkable increase from 978±277 BC to 467±257 BC. This coincided with a corresponding decrease in the concentration of Pb. After 467±257 BC, the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios generally decreased as the concentration of Pb increased in the sediments.

Origins of Pb in the Sediments. To further investigate the possible sources of Pb in the sediments, the Pb isotopic compositions of the sediments were compared to ancient mining ores and bronze materials in China and other environmental samples (see Table S2 and S3 in S.I.).

Figure 5 shows the plot of the ^{206}Pb/^{207}Pb vs ^{208}Pb/^{207}Pb ratios of the sediments, representing the Pb isotopic compositions at different historical periods. Before 3000±328 BC, the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios were at their highest, representing background values during the prehistoric era, with average values of 1.1930 (^{206}Pb/^{207}Pb) and 2.4958 (^{208}Pb/^{207}Pb) (see Figure 5). From 3000±328 to 467±257 BC, the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios decreased, and more closely resembled those of ancient mining materials (at Tonglushan) and bronze articles (at Daye) (the end member A in Figure 5). Copper mining activities at the Tonglushan site took place from the Spring and Autumn Period (770 - 476 BC) and throughout the Han dynasty (306 BC – 220 AD) (*31*), and lead was used in making bronze articles. The changes in the Pb isotopic compositions in the sediments may indicate the influence of mining activities during the early Bronze Age era. After 500±201 AD, the Pb isotopic compositions of the sediments were observed to have shifted indicating the prominence of other regional sources (the end member B in Fig 6), including those mining areas in Hunan, Jiangxi, Yunnan and Guangdong (see Figure S1 in S.I.). The Pb isotopic signatures in this period may indicate that there were inputs of Pb from major mining operations in the south China region.

Acknowledgements

This work was supported by the Research Grants Council (RGC) of the Hong Kong SAR Government (N_PolyU535/05) and the Natural Science Foundation of China (NSFC) (Nos. 40173032 and 40518002).

Supporting Information (SI) Available

The radiocarbon and calibrated ages, Pb isotopic compositions of the sediments and other possible sources, a brief chronology of the dynasties in China are given in Tables S1 – S4 of SI. The sampling location, interpolation line based on the calibrated radiocarbon age, and the enrichment factors of Cu, Ni, Pb and Zn over the background concentrations (the sediments before 3000±328 BC) along the sediment profile are presented in Figures S1 – S3 of SI. This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Nriagu, J. O.; Pacyna, J. M. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* **1988,** 333, 134-139.

(2) Shotyk, W.; Cheburkin, A. K.; Appleby, P. G.; Fankhauser, A.; Kramers, J. D. Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland. *Earth Planet. Sci. Lett.* **1996,** 145, E1-E7.

(3) Kylander, M. E.; Weiss, D. J.; Cortizas, A. M.; Spiro, B.; Garcia-Sanchez, R.; Coles, B. J. Refining the pre-industrial atmospheric Pb isotope evolution curve in Europe using an 8000 year old peat core from NW Spain. *Earth Planet. Sci. Lett.* **2005,** 240, 467-485.

(4) Patterson, C. C. Native copper, silver, and gold accessible to early metallurgists. *American Antiqui.* **1971,** 36, 286-321.

(5) Darling, A. S. Non-ferrous metals. In *An Encyclopaedia of the History of Technology*, McNeil I., ed.; Routledge, London and New York. 1990; 47-145.

(6) Healy, J. F. *Mining and Metallurgy in Greek and Roman World*. Thames and Hudson, London, 1978.

(7) Nriagu, J. O. A history of global metal pollution. *Science* **1996,** 272, 223-224.

(8) Nriagu, J. O. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature* **1979,** 279, 409-411.

(9) Weiss, D.; Shotyk, W.; Appleby, P. G.; Kramers, I. D.; Cheburkin, A. K. Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: Enrichment factors, fluxes, isotopic composition, and sources. *Environ. Sci. Technol.* **1999,** 33, 1340-1352.

(10) Shotyk, W.; Weiss, D.; Heisterkamp, M.; Cheburkin, A. K.; Appleby, P. G.; Adams, F.C. New peat bog record of atmospheric lead pollution in Switzerland: Pb concentrations, enrichment factors, isotopic composition, and organolead species. *Environ. Sci. Technol.* **2002,** 36, 3893-3900.

(11) McLane, M. *Sedimentology*. Oxford University Press, New York, 1995.

(12) Battarbee, R. W.; Thompson, R.; Catalan, J.; Grytnes, J. A.; Birks, H. J. B. Climate variability and ecosystem dynamics of remote alpine and arctic lakes: the MOLAR project. *J. Paleol.* **2002,** 28, 1-6.

(13) Lotter, A. F.; Appleby, P. G.; Bindler, R.; Dearing, J. A.; Grytnes, J. A.; Hofmann, W.; Kamenik, C.; Lami, A.; Livingstone, D. M.; Ohlendorf, C.; Rose, N.; Sturm, M. The sediment record of the past 200 years in a Swiss high-alpine lake: Hagelseewli (2339 m a.s.l.) *J. Paleol.* **2002,** 28, 111-127.

(14) Gallon, C.; Tessier, A.; Gobeil, C.; Beaudin, L. Sources and chronology of atmospheric lead deposition to a Canadian Shield lake: Inferences from Pb isotopes and PAH profiles. *Geochimica et Cosmochimica Acta* **2005,** 69, 3199-3210.

(15) Dominik, J.; Mangini, A.; Prosi, F. Sedimentation rate variations and anthropogenic metal fluxes into Lake Constance sediments. *Environ. Geol.* **1984,** 5, 151-157.

(16) Bollhöfer, A.; Mangini, A.; Lenhard, A.; Wessels, M.; Giovanoli, F.; Schwarz, B. High-resolution ^{210}Pb dating of Lake Constance sediments: stable lead in Lake Constance. *Environ. Geol.* **1994,** 24, 267-274.

(17) Boyle, J. F.; Rose, N. L.; Bennion, H.; Yang, H.; Appleby, P. G. Environmental impacts in the Jianghan Plain: evidence from lake sediments. *Water, Air, Soil Pollut.* **1999,** 112, 21-40.

(18) Kober, B.; Wessels, M.; Bollhöfer, A.; Mangini, A. Pb isotopes in sediments of Lake Constance, Central Europe constrain in the heavy metal pathways and the pollution history of the catchment, the lake and the regional atmosphere. *Geochimica et Cosmochimica Acta* **1999,** 63, 1293-1303.

(19) Åström, M.; Nylund, K. Impact of historical metalworks on the concentrations of major and trace elements in sediments: a case study in Finland. *Appli. Geochem.* **2000,** 15, 807-817.

(20) Mecray, E. L.; King, J. W.; Appleby, P. G.; Hunt, A.S. Historical trace metal accumulation in the sediments of an urbanised region of the Lake Champlain watershed, Burlington, Vermont. *Water, Air, Soil Pollut.* **2001,** 125, 201-230.

(21) Outridge, P.M.; Hermanson, H.H.; Lockhart, W.L. Regional variations in atmospheric deposition and sources of anthropogenic lead in lake sediments across the Canadian Arctic. *Geochimica et Cosmochimica Acta* **2002,** 66, 3521-3531.

(22) Renberg, I.; Wik-Persson, M.; Emteryd, O. Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. *Nature* **1994,** 368, 323-326.

(23) Brännvall, M. L.; Bindler, R.; Emteryd, O.; Nilsson, M.; Renberg, I. Stable isotope and concentration records of atmospheric lead pollution in peat and lake sediments in Sweden. *Water, Air, Soil Pollut.* **1997,** 100, 243-252.

(24) Shotyk, W.; Weiss, D.; Appleby, P. G.; Cheburkin, A. K.; Frei, R.; Gloor, M.; Kramers, J. D; Reese, S.; Van der Knaap, W. O. History of atmospheric lead deposition since 12,370 C-14 yr BP from a peat bog, Jura Mountains, Switzerland. *Science* **1998,** 281, 1635-1640.

(25) Renberg, I.; Brännvall, M. L.; Bindler, R.; Emteryd, O. Atmospheric lead pollution history during four millennia (2000 BC to 2000 AD) in Sweden. *Ambio* **2000,** 29, 150-156.

(26) Rose, N. L; Boyle, J. F.; Du, Y.; Yi, C.; Dai, X.; Appleby, P. G.; Bennion, H.; Cai, S.; Yu, L. Sedimentary evidence for changes in the pollution status of Taihu in the Jiangshu region of eastern China. *J. Paleol.* **2004,** 32, 41-51.

(27) Zhang, J. Environment, market, and peasant choice: the ecological relationships in the Jianghan Plain in the Qing and the Republic. *Modern Chin*a **2006,** 32, 31-63.

(28) Hubei Environmental Protection Department. *Environmental Assessment Report 2004*. 2005.

(29) Stuiver, M.; Reimer, P.J. Extended ^{14}C database and revised CALIB 3.0 ^{14}C age calibration program. *Radiocarbon* **1993,** 35, 215-230.

(30) Ip, C. C. M.; Li, X.D.; Zhang, G.; Wai O.W.H.; Li, Y.S. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. *Environ. Pollut.* **2007**, 147, 311-323.

(31) Ma, C. Y. *Ancient Chinese Bronzes*. Shih H.Y., ed.; Oxford University Press, Hong Kong, 1986.

(32) Li, T.Y. The extension of Chu dynasty to the east and the exploration of ancient copper mining. In *Jianghan Archaeology*. Vol. 2, Wang H.X., ed.; Wuhan, Hubei Province, 1988; 109-114. (in Chinese)

(33) Zhou, B.Q. The productive capacity of ancient Tonglushan copper mining site. In *Jianghan Archaeology*. Vol. 4. Wang H.X., ed.; Wuhan, Hubei Province, 1984; 67-73. (in Chinese)

(34) Hsü, C. Y. Agricultural intensification and marketing agrarianism in the Han dynasty. In *Ancient China: Studies in Early Civilization*. Roy D.T., Tsien T.H., eds.; The Chinese University Press, Hong Kong, 1978; 253-268.

(35) Li X. *The Wonder of Chinese Bronzes*. Foreign Languages Press, Beijing, 1980.

(36) Zhang, D.; Jim, C. Y.; Lin, C. S.; He, Y. Q.; Lee, F. Climate change, social unrest, dynastic transition in ancient China. *Chinese Sci. Bull.* **2005,** 50, 137-144.

(37) Hsu, K. J. Sun, climate, hunger, and mass migration. *Science in China* (Series D) **1998,** 41, 449-472.

(38) Xia, D. Y. *Yang Wu Yun Dong Shi*. Hua Dong Shi Fan Da Xue Chu Ban She, Shanghai, 1992 (in Chinese).

(39) Grasso, J.; Corrin, J.; Kort M. Modernization and revolution in China: from the Opium Wars to world power. M.E. Sharpe, Armonk, New York, 2004.

(40) Nriagu, J. O. The rise and fall of leaded gasoline. *Sci. Total Environ.* **1990,** 92, 13-28.

(41) Peng, Z.; Liu, Y.; Liu, S.; Hua, J. A preliminary study on Shang dynasty bronzes and their Cu-Pb ore sources in Jiangxi, Hubei and Henan Provinces. *Studies History Natural Sci.* **1999,** 18, 241-249 (in Chinese with English abstract).

(42) Zhu, B.Q. The mapping of geochemical provinces in China based on Pb isotopes. *J. Geochem. Explor.* **1995,** 55, 171-181.

TABLE 1. Concentrations (mg/kg) of Heavy Metals and Major Elements in Sediments of Liangzhi Lake.

Time	**Concentrations**	**Cu**	**Ni**	**Pb**	**Zn**	**Ca**	**Fe**	**Mg**
Phase V 1370±120 AD – 1960±14 AD	Min	31.3	49.5	27.5	87.0	2910	37700	5160
	Max	40.2	59.3	34.0	120	11800	49600	7290
	Mean	35.8	53.3	30.3	98.0	4650	42800	6310
	Median	36.1	53.2	30.4	98.0	3910	41800	6290
	Std. Dev.	2.1	2.1	1.8	5.5	1760	2880	5400
Phase IV 215±221 AD – 1360±122 AD	Min	31.7	51.6	25.8	83.5	3070	39300	5130
	Max	37.6	65.4	31.5	102	8440	49100	6590
	Mean	34.0	56.4	27.9	91.8	3980	44100	5750
	Median	33.6	56.9	27.6	92.1	3840	43700	5770
	Std. Dev.	1.5	3.0	1.2	4.2	879	2690	395
Phase III 467±257 BC - 168±224 AD	Min	20.6	39.1	17.6	68.3	3220	36500	3630
	Max	36.7	57.2	28.7	93.8	4810	53500	6060
	Mean	25.5	44.4	24.0	77.5	3950	44800	4380
	Median	24.2	41.9	24.0	73.2	3990	46500	3920
	Std. Dev.	5.0	5.2	3.8	9.8	543	5620	865
Phase II 2890±326 BC – 549±260 BC	Min	14.7	34.6	14.0	54.2	2700	29000	2790
	Max	23.8	45.2	22.3	117	3710	55900	3920
	Mean	18.8	39.0	18.2	68.5	3380	41000	3480
	Median	18.8	38.6	18.3	67.6	3450	41100	3630
	Std. Dev.	2.3	2.2	1.6	11.6	278	6730	379
Phase I 4940±347 BC – 3000±328 BC	Min	15.0	32.2	14.5	42.5	1700	23800	2500
	Max	18.3	37.9	17.3	50.6	2430	33200	2990
	Mean	16.8	34.1	15.7	46.7	2040	28900	2760
	Median	17.0	33.7	15.5	46.1	2070	29300	2760
	Std. Dev.	0.8	1.6	0.8	2.4	203	2700	134

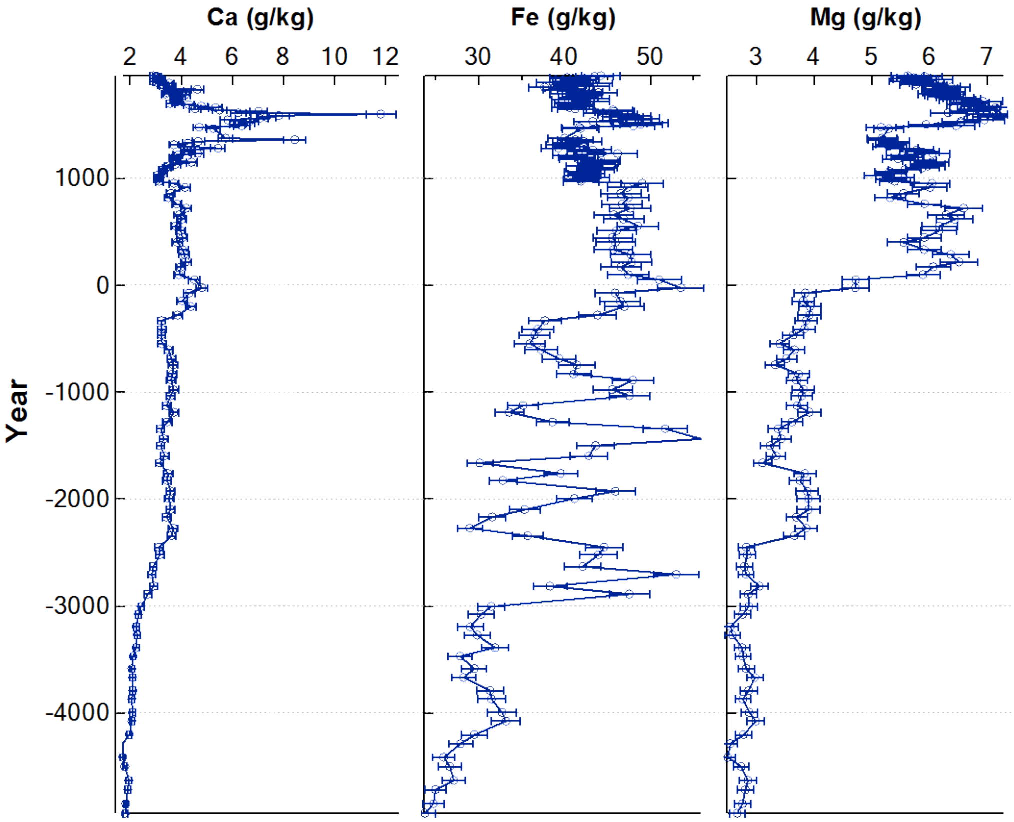
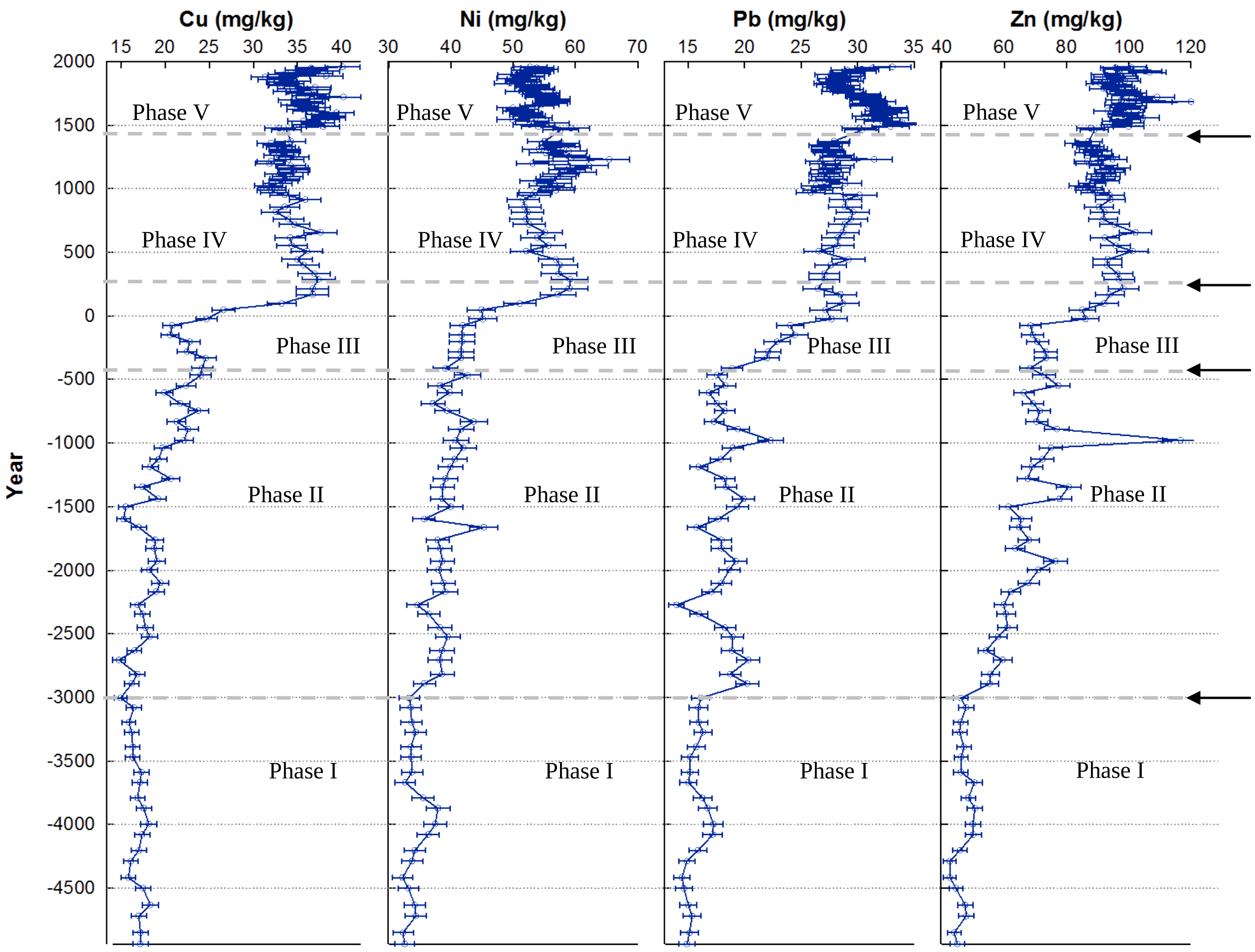


FIGURE 1. The vertical profiles of Ca, Fe, Mg in sediments of Liangzhi Lake.



~ 1372 AD
Increased in Cu, Pb and Zn

~ 215 AD
Decreased in Cu, Ni and Zn

~ 467 BC
Increased in Pb

~ 3000 BC
Increased in Cu, Ni and Zn

FIGURE 2. The distribution of metals in different stratigraphic phases

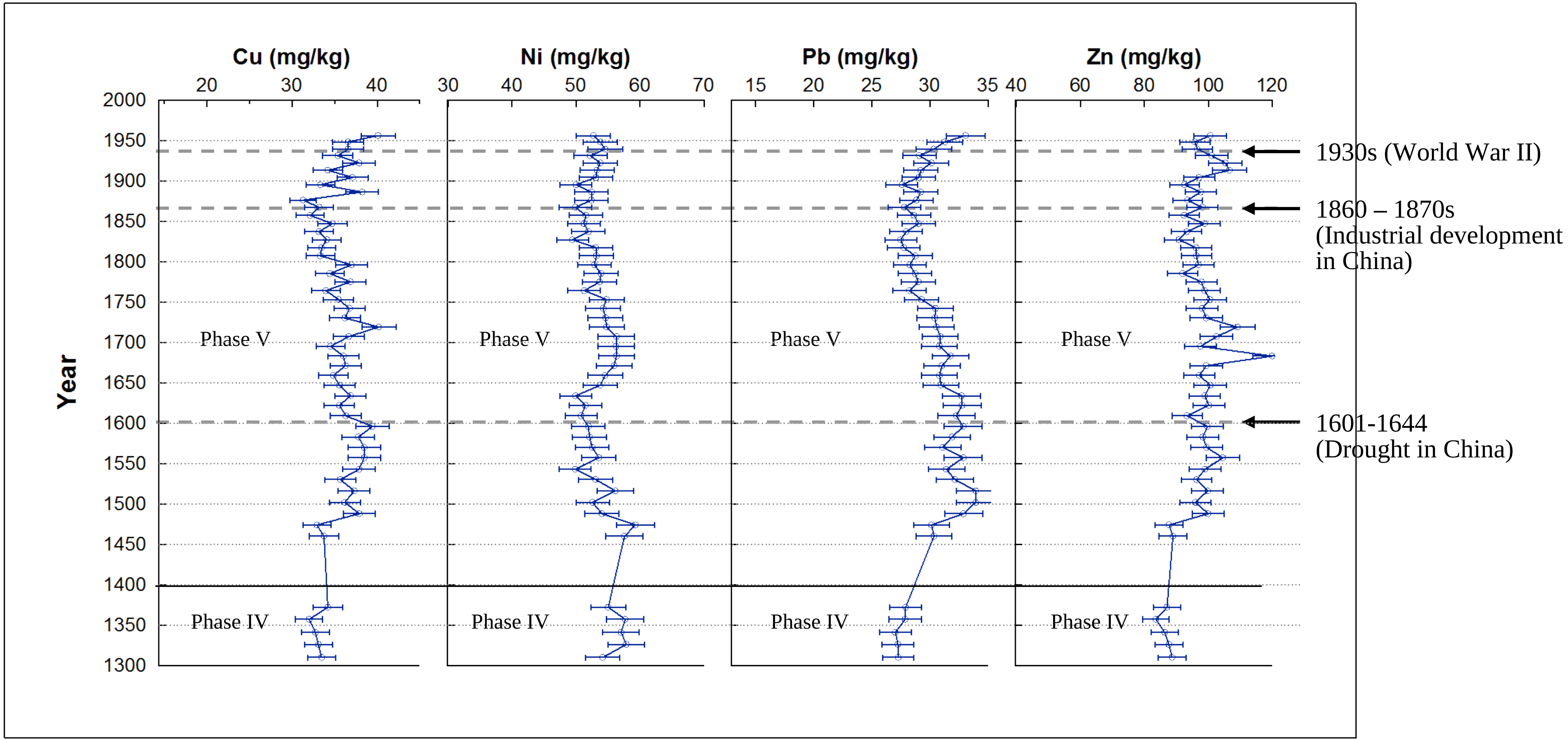


FIGURE 3. The distribution of trace metals during 1300 to 1900s AD (Phase V)

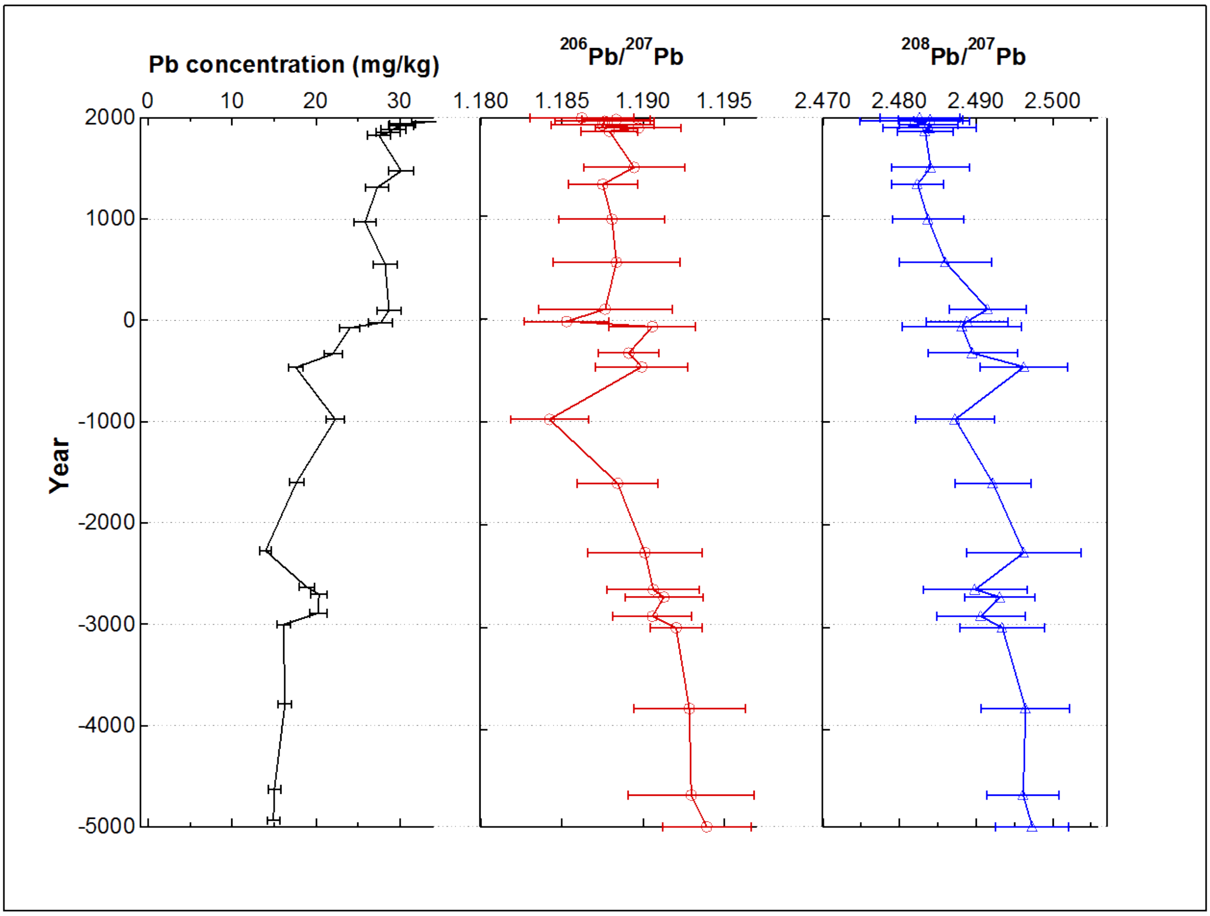


FIGURE 4. The vertical profiles of Pb concentration, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of Liangzhi Lake sediments.

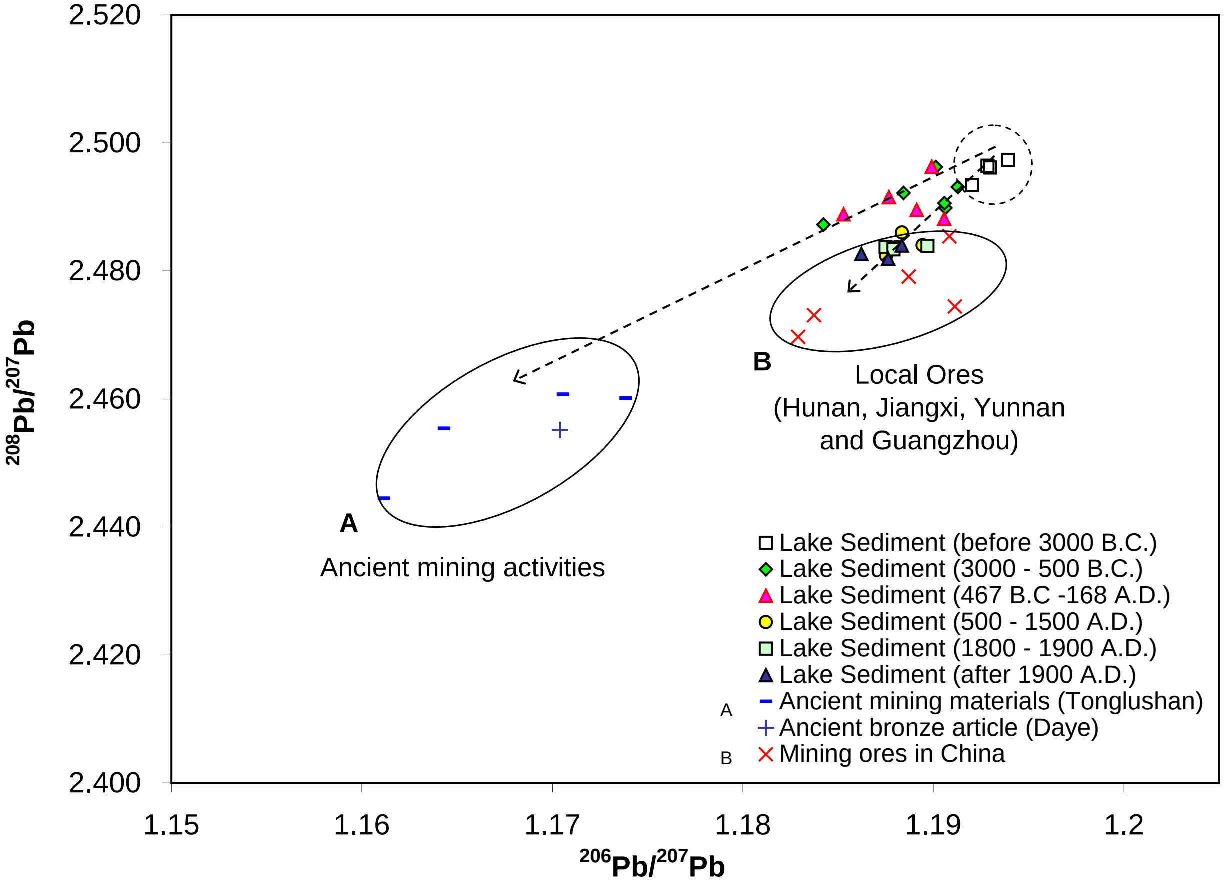


FIGURE 5. Comparison of the Pb isotopic ratios of Liangzhi lake sediments with other known anthropogenic sources ([a]ref. *41*; [b]ref. *42*).

Table of Contents Brief

“The present study provides direct evidence on environmental influences of the mining and utilisation of metals in the last 7,000 years in China”.