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A Millennium of Metallurgy Recorded by Lake Sediments from Morococha, Peruvian Andes

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To date, information concerning pre-Colonial metallurgy in South America has largely been limited to the archaeological record of artifacts. Here, we reconstruct a millennium of smelting activity in the Peruvian Andes using the lake-sediment stratigraphy of atmospherically derived metals (Pb, Zn, Cu, Ag, Sb, Bi, and Ti) and lead isotopic ratios (^{206}Pb/^{207}Pb) associated with smelting from the Morococha mining region in the central Peruvian Andes. The earliest evidence for metallurgy occurs ca. 1000 A.D., coinciding with the fall of the Wari Empire and decentralization of local populations. Smelting during this interval appears to have been aimed at copper and copper alloys, because of large increases in Zn and Cu relative to Pb. A subsequent switch to silver metallurgy under Inca control (ca. 1450 to conquest, 1533 A.D.) is indicated by increases in Pb, Sb, and Bi, a conclusion supported by further increases of these metals during Colonial mining, which targeted silver extraction. Rapid development of the central Andes during the 20th century raised metal burdens by an order of magnitude above previous levels. Our results represent the first evidence for pre-Colonial smelting in the central Peruvian Andes, and corroborate the sensitivity of lake sediments to pre-Colonial metallurgical activity suggested by earlier findings from Bolivia.

Introduction

Natural records of pre-industrial metal pollution have been recovered from ice cores (*1*, *2*), lake sediments (*3*), and peat cores (*4*), which collectively archive nearly three thousand years of metal pollution in the northern hemisphere. These archives demonstrate a legacy of metal pollution associated with pre-industrial metallurgical activities such as early cupellation and coinage. However, despite the fact that the South American Andes were the cradle of New World metallurgy, efforts aimed at reconstructing the history of metal pollution in South America have been limited (*5*). This is despite a rich archaeological record of metallurgical activity, and the potential for natural archives to elucidate questions regarding the development of metallurgy. Here, we combine a lake sediment record of pre-historic metal pollution from the Morococha region of the central Peruvian Andes, with the archaeologically reconstructed regional culture history, to provide a more complete picture of metallurgical development in the central Peruvian Andes.

Having been subject to four decades of extensive archaeological research, the cultural development of the central Peruvian Andes is well described (*6*–*9*). The earliest metal artifacts (of copper-arsenic bronze) post-date the Wari Empire, and are attributed to the Wanka cultural phases (1000–1450 A.D.). However, thus far, findings associated with metallurgy are limited to the late stages of metal production (*10*). It therefore remains uncertain whether ores were smelted locally amid the rich mineral deposits of the region, or if metal-rich ores were imported and traded from outside the central Andean region, as has been suggested for smelting conducted along Peru's north coast (*11*).

To assess the timing and magnitude of smelting at Morococha, Peru, we measured the concentrations of six metals: copper, lead, zinc, antimony, bismuth, and silver (Cu, Pb, Zn, Sb, Bi, and Ag), all of which are associated with the composition of local intrusive ores, and titanium (Ti), which originates from local crustal rocks. Of these metals, Pb forms the basis for our interpretations for three reasons. First, Pb is not appreciably affected by postdepositional mobility in lake sediments (*12*, *13*). Second, Pb stable isotopic ratios can be used to trace ore provenance (*13*, *14*). Third, Incan smelting technologies relied upon the use of galena [(PbS); locally known as *soroche*] as a flux during smelting of silver bearing ores, which was conducted in charcoal-fired, wind-drafted furnaces known as *huayras* (*15*).

Study Sites. The Morococha mining region is located in the Junín district of the western Cordillera of central Peru (Figure 1). Morococha was reportedly discovered during the 17th century by Colonial metallurgists (*16*), and is situated over replacement bodies, such as mantos, chimneys, and skarns (*17*). In addition to native silver, the ores contain combinations of bournonite ($CuPbSbS_3$), arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), emplectite ($CuBiS_2$), enargite (Cu_3AsS_4), argentiferous galena [(Pb, Ag) S)], matildite ($AgBiS_2$), proustite ($Ag_3As_3S_3$), sphalerite [(Zn, Fe)S], stromeyerite (AgCuS), and tennantite ($Cu_{12}As_4S_{13}$) (*18*, *19*). During the 1990s, over 2.8 million tons of ore were mined at Morococha, with an average silver grade of 260 g t^{-1} (M. Steinmann, personal communication).

Located 11 km northeast of modern silver mining operations at Morococha, Laguna Pirhuacocha (11° 31′ S, 76° 04′ W; 4520 m asl; Figure 1) occupies Cretaceous terrain composed of igneous, metamorphic, and carbonate rocks. There is no hydrological connection between the lake and any mining activity. The lake is small (0.05 km^2), occupies a nonglacial, undisturbed catchment of 3.14 km^2, and is 18 m deep. Laguna Pirhuacocha drains to the east during the wet season (December to March) through a small creek, and a shallow littoral bench sits at the mouth of this creek. Surface winds driven by daytime heating blow predominantly from the west rising up the valleys and sinking back down the valleys at night. Situated up-valley from Morococha, Laguna Pirhuacocha is strategically located to record local atmospheric deposition of metals volatilized during smelting.

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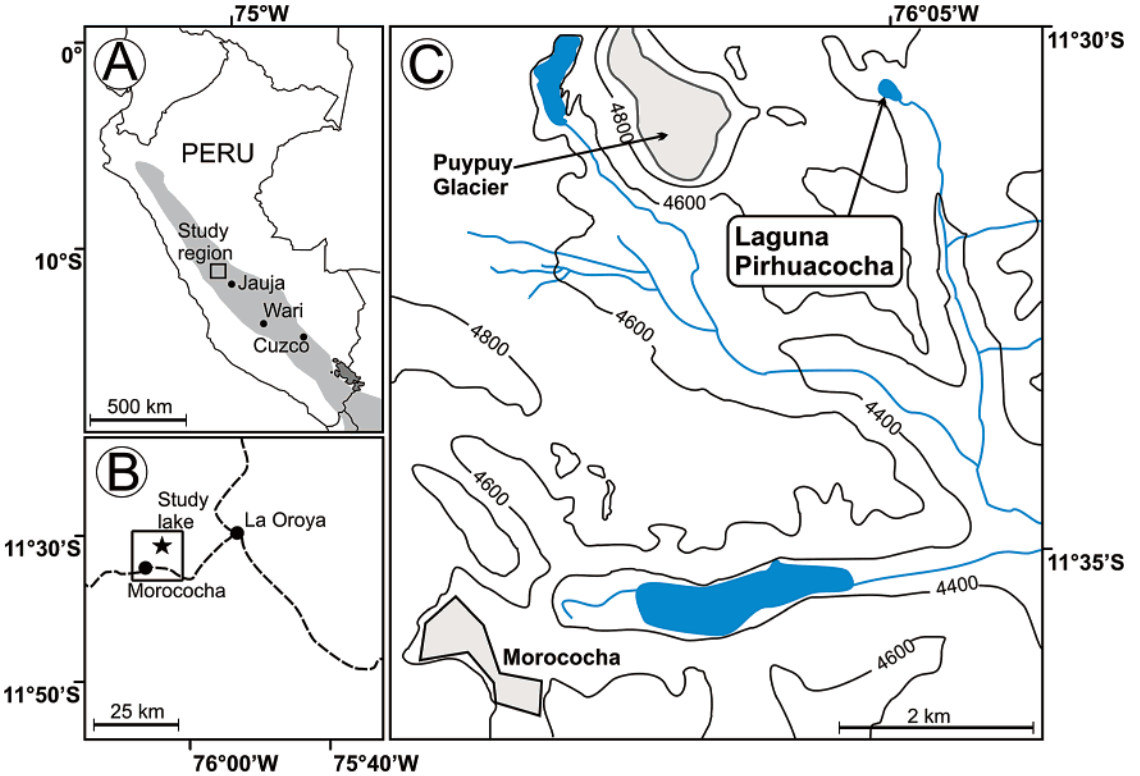

FIGURE 1. (a) Map of Peru showing study area and location of sites mentioned in text; (b) magnification of the central Andean region; and (c) base map of the Morococha mining region, Laguna Pirhuacocha, and the nearby Puypuy glacier, which lies outside of the Laguna Pirhuacocha catchment.

TABLE 1. Peak and Background Concentrations (μg g^{-1}), Enrichment Factors (Peak to Background Ratios), and the CIC Age of Peak Metal Concentration within Laguna Pirhuacocha Sediment

	Zn	Ti	Pb	Cu	Ag	Sb	Bi
peak concentration (μg g^{-1})	835	56	2512	170	1.52	14	72
background concentration (μg g^{-1})	45	46	14	26	0.02	0.02	0.02
enrichment factor (peak/background ratio)	19	1	185	7	75	600	3863
CIC age of peak enrichment	2005	1957	1974	1974	2005	2005	1974

Methods

Core Collection and Chronology. A 62-cm sediment core was collected from the deepest point of Laguna Pirhuacocha using a slide hammer corer fitted with a 7-cm diameter polycarbonate tube (*20*). The core contained an intact sediment−water interface, with no visible disturbance to the sediment column. The upper 15-cm of the core was extruded in the field into continuous 0.5-cm increments to eliminate potential disturbance. The upper sediments were dated using ^{210}Pb activities ($t_{1/2} = 22.3$ years) measured by α-spectroscopy. The lower core was dated using accelerator mass spectrometry (AMS) ^{14}C age determinations obtained from aquatic plant macrofossils and charcoal.

Geochemical Characterization. Every 0.5-cm from 0 to 60 cm and every 2.5-cm from 60 to 87.5 cm was sampled and freeze-dried. Samples (0.1−0.5 g dry mass) were leached using 10 mL of 1.6 M HNO_3 (Optima grade, Fisher Scientific) at room temperature for 24 h. This procedure targets weakly bound elements adsorbed to organic and inorganic surfaces, and not those hosted in the lattice sites of detrital silicate minerals (*21*). Inductively coupled plasma−atomic emission spectroscopy (ICP−AES) was used to quantify Cu, Pb, Ti, and Zn concentrations, while Sb, Bi, and Ag were quantified on a single collector inductively coupled plasma−mass spectrometer (ICP−MS Element 1). Concentrations were verified against the certified multi-element standard, SPEX ICP−MS-2. Analytical error was <10% for every element run. Duplicates were run every 10th sample and were consistently within 8% of each other. A minimum of 6 blanks or 10% of the number of samples (whichever was greater) was carried through the entire procedure with each batch of samples (*22*). Blanks were consistently below the method detection limit for each element.

Data Preparation. Although elemental concentration data are often directly employed to reconstruct historical metal fluxes, such data must be considered with care. Trace metals are delivered to lakes by both atmospheric deposition and edaphic processes including podogenesis and sorption to soil organic matter (*22, 23*). The natural (edaphic) component may fluctuate through time due to local catchment evolution or climatic change. To remove the influence of variable natural contributions, trace metal concentrations were normalized to that of the refractory lithophilic element Ti, which is principally derived from the drainage basin (*24*). Our use of Ti as a reference element is supported by the observation that modern sediment is not significantly enriched in Ti relative to background, suggesting that the natural geochemical cycle of Ti is completely decoupled from

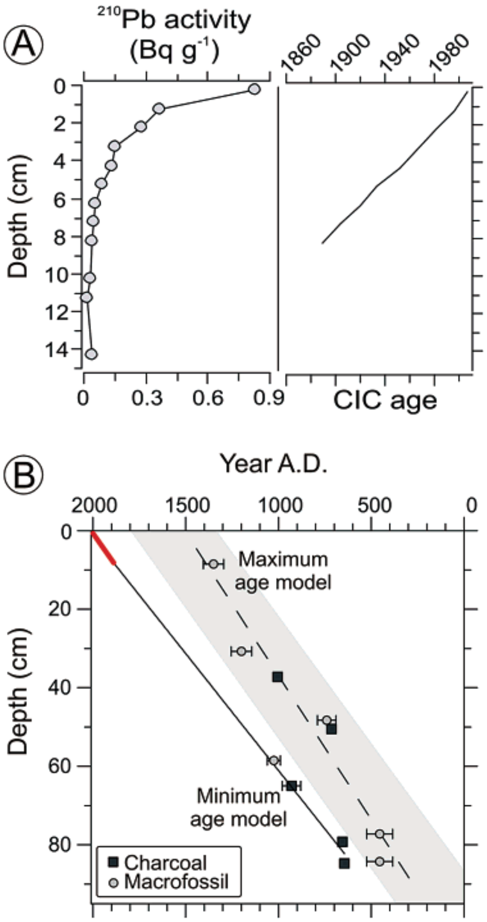

FIGURE 2. (a) Down-core sediment ^{210}Pb activities and corresponding CIC ages for the uppermost 8 cm of the Laguna Pirhuacocha core. (b) Composite age-depth model integrating ^{210}Pb and ^{14}C derived results used to constrain sediment ages beyond the limit of ^{210}Pb dating. The ^{14}C results are subdivided into maximum and minimum age models fitted with linear functions of similar slope. The minimum age model intersects the base of the ^{210}Pb chronology, and thus represents the most conservative interpretation of the AMS ^{14}C data. Dates within shaded region are suspected to have incorporated old carbon from catchment geological sources. The reservoir effect is in the order of 200−600 cal. years. Our interpretations of the geochemical record are based upon the minimum age model for the core. Error bars represent the 2σ range on dates.

local mining activities (Table 1). The excess or anthropogenic portion of the trace element inventory is thereby calculated by subtracting natural from the total concentrations of a given metal at each sediment interval using the formula

$$\mathrm{M}_{\mathrm{anthro}} = \mathrm{M}_{\mathrm{sample}} - \mathrm{Ti}_{\mathrm{sample}} \bullet (\mathrm{M/Ti})_{\mathrm{natural}} \qquad (1)$$

where $\mathrm{M}_{\mathrm{anthro}}$ represents the anthropogenic metal content, $\mathrm{M}_{\mathrm{sample}}$ and $\mathrm{Ti}_{\mathrm{sample}}$, respectively, are the total metal and titanium concentrations, and $(\mathrm{M/Ti})_{\mathrm{natural}}$ is the natural ratio, which is assumed to be constant (*22*, *25*, *26*). The value of $(\mathrm{M/Ti})_{\mathrm{natural}}$ was approximated by the 10 lowermost samples (>64 cm, older than ca. 900 A.D.), which predate any potential anthropogenic contribution. The $(\mathrm{M/Ti})_{\mathrm{natural}}$ values obtained are 0.29 ± 0.02, 0.97 ± 0.16, 0.56 ± 0.15, 0.0004 ± 0.0001, 0.0005 ± 0.0001, and 0.0004 ± 0.0001 for Pb, Zn, Cu, Ag, Sb, and Bi, respectively.

Lead Isotopes. Lead isotopic ratios were measured using a single collector ICP−MS, and ratios were corrected for instrumental mass-bias by bracketing unknowns with measurements of NIST 981 Lead Isotopic Reference Standard. Instrument parameters were based on Townsend and Snape (*27*). The relative standard deviation was less than 0.3% for all Pb isotopic measurements.

Results and Discussion

Core Chronology. Total ^{210}Pb activity declines without reversal from a surface value of 0.80 Bq g^{-1} to a relatively steady supported background of 0.03 Bq g^{-1} at depths below 8.5 cm (Table S1 in the Supporting Information; Figure 2a). The behavior of ^{210}Pb therefore indicates constant sedimentation down-core and the undisturbed character of the Laguna Pirhuacocha core. This is despite a 3-fold decrease in Ti concentrations during this period (Figure 3), suggesting that, while important for trace metal accumulation, the erosion of catchment soils has exercised little influence over lake-sedimentation rates. Because sedimentation rates are nearly constant (0.007 ± 0.0003 g cm^{-2} yr^{-1}; Table S1), the constant initial concentration (CIC) dating model was applied to calculate sediment ages (*28*). Dating uncertainty based on this model is less than ±5 years for the entire inventory of unsupported ^{210}Pb (i.e., the last 130 years).

To estimate sediment age beyond the limit of ^{210}Pb dating, 11 AMS ^{14}C dates were obtained on charcoal and emergent plant macrofossils (Table S2). All AMS ^{14}C dates were calibrated using Calib 5.0 (*29*) and are reported as calibrated years A.D. The calibrated ^{14}C results produce two distinct groupings that can be fitted with linear functions of similar slope (Figure 2b). When extrapolated, the linear fit through the first group of dates, composed of one macrofossil and three charcoal samples, intersects the base of the ^{210}Pb chronology at 8 cm, implying near-constant sedimentation along the length of the entire core. This age model is the minimum age model for the core, and the most conservative interpretation of the AMS ^{14}C data. The second group of dates comprises two charcoal and five macrofossil samples that are systematically 200−600 years older than the first group, yet with similar slope. The uppermost date in the second group overlaps with the base of the CIC ^{210}Pb chronology, but is 500 years too old. We therefore suggest that the second group of dates has suffered a reservoir effect due to the uptake of old carbon, noting that Laguna Pirhuacocha contains abundant carbonate lithologies in its catchment. Interestingly, susceptibility to the reservoir effect does not appear consistently related to sample type, which further complicates the matter of securing reliable ^{14}C dating targets. Although charcoal is normally considered a reliable material for lake-sediment ^{14}C dating (e.g., *30*), we have observed other instances of misleadingly old charcoal dates in the Peruvian Andes, suggesting that the problem is not unique to Laguna Pirhuacocha (*31*). While there are other ways that these dates could be interpreted and alternative age-depth profiles drawn, we interpret our sediment record using the most conservative age model possible, and thus present the minimum ages for the sediment. By incorporating some of the older ^{14}C dates, sediment ages become systematically older.

Sediment Geochemistry. Late 20th-century Pb concentrations in Laguna Pirhuacocha exceed 2500 μg g^{-1}, representing massive enrichments associated with extensive local mining activity (Figure 3; Table 1). This Pb enrichment is accompanied by sediment ^{206}Pb/^{207}Pb isotopic ratios that closely parallel those of Morococha ores (*17*, *32*). Because we know of no natural process capable of inducing this level of Pb enrichment and isotopic depletion, and given Laguna Pirhuacocha's proximity to two major sources of metal pollution (the Morococha mine and La Oroya smelter; Figure 1), we associate both geochemical signatures to the intensity of local smelting activity. In this context, the recent trends become a template for inferences concerning earlier smelting episodes.

Indeed, sediment ^{206}Pb/^{207}Pb has been within the range of Morococha ore since 1400 A.D., and began to decline as

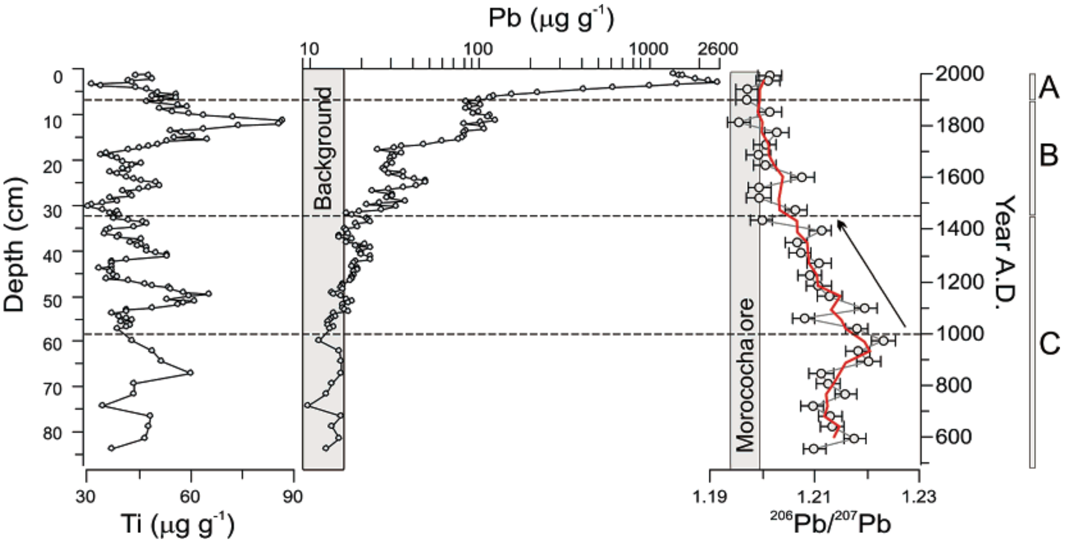

FIGURE 3. Stratigraphy for Ti, Pb, and $^{206}Pb/^{207}Pb$ with a 3-point smooth on the $^{206}Pb/^{207}Pb$ data (red line). Note that Pb concentration is plotted on a log-scale. Error bars represent the 1σ range on $^{206}Pb/^{207}Pb$ measurements. The isotopic ratio for Morococha ore is shaded (*18*, *33*).

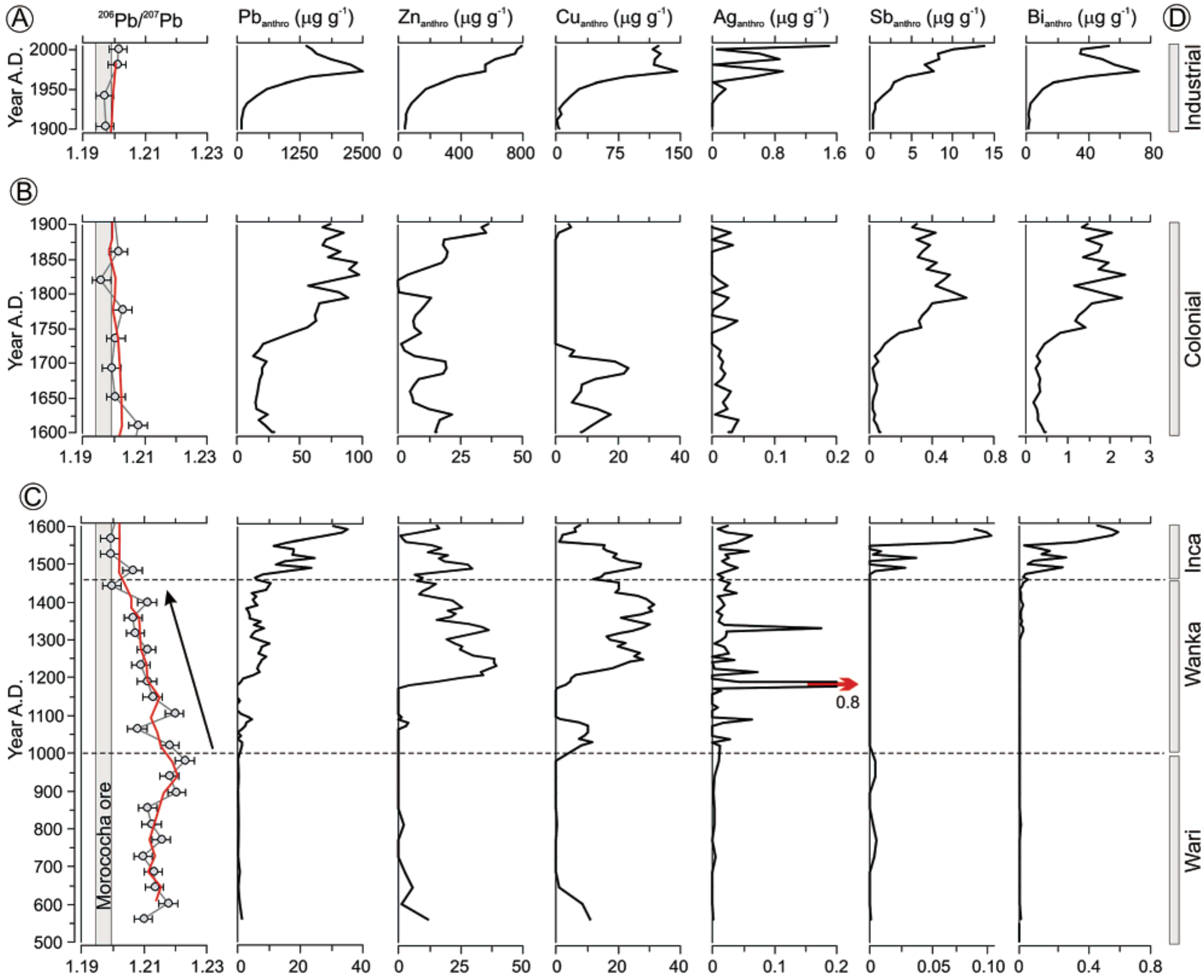

FIGURE 4. Stratigraphies for $^{206}Pb/^{207}Pb$, Pb_{anthro}, Zn_{anthro}, Cu_{anthro}, Ag_{anthro}, Sb_{anthro}, and Bi_{anthro}. Anthropogenic metal burdens were calculated using Ti-normalization to account for variable natural contributions (e.g., edaphic processes; see text). The record has been subdivided temporally into pre-Colonial (a), Colonial (b), and Industrial (c) to accommodate large-scale changes. Regional culture history (d) (*6*−*11*) is shown alongside the Laguna Pirhuacocha sediment record for comparison.

early as 1000 A.D. (Figure 3). The initial Pb stable isotopic inflection is closely matched by increases in concentrations of both Pb_{total} (Figure 3) and Pb_{anthro} (Figure 4c), which first rise above background between 1000 and 1200 A.D. Therefore, we place the onset of smelting at Morococha to between 1000 and 1200 A.D., that is, after the fall of Wari civilization, but well before the rise of the Inca. Increases of Cu_{anthro}, Zn_{anthro}, and Ag_{anthro} support the contention of such early initial metallurgy (Figure 4c).

By 1200 A.D., both Cu_{anthro} and Zn_{anthro} display large and sustained increases relative to Pb_{anthro} (Figure 4c). We suggest this reflects a predominance of copper-based metallurgy at this time, with the ultimate goal of bronze production for which there is a substantial archaeological record (*10*). Relatively low amounts of Pb pollution may reflect that lead was not used as a flux during copper smelting, as it was subsequently during Inca silver production (*5*, *15*). We surmised that Wanka metallurgy at Morococha was aimed primarily at copper and copper alloys.

After 1450 A.D., intensification of smelting activity at Morococha is indicated by a marked rise in concentrations of Pb_{anthro} and Pb_{total}, and concomitant increases of Sb and Bi in Laguna Pirhuacocha sediment (Figures 3 and 4c). It is also after 1450 A.D. that $^{206}Pb/^{207}Pb$ ratios have declined sufficiently as to be indistinguishable from those of Morococha ore. The increase in Pb, Sb, and Bi, and the decrease in $^{206}Pb/^{207}Pb$, suggests either a shift in smelting techniques, or the exploitation of new mineral deposits containing significant amounts of antimony and bismuth. We attribute these changes to the rise of Incan metallurgy at Morococha, which lasted until Spanish conquest. In all likelihood, silver was being exploited at this time, given its symbolic ceremonial status among the Inca.

Colonial mining at Morococha began shortly after 1600 A.D., driven largely by the European demand for silver. The geochemical signature of this period in Laguna Pirhuacocha sediment is larger increases of Pb, Zn, Sb, and Bi, a decline of Cu, and sustained low $^{206}Pb/^{207}Pb$ ratios (Figure 4b). Both official and clandestine Colonial mining operations were active in the area (*16*), the latter using traditional *huayara* technology to win silver in wind-drafted kilns using a Pb-based flux, a technology known to produce significant Pb pollution (*5*). It is likely for this reason that the geochemical signatures of Inca and Colonial mining activities at Morococha are reflected by similar elemental suites in the sediments of Laguna Pirhuacocha.

With construction of the central Peruvian railway in the early 20th century, the central Andes were rapidly developed. Rapid increases in all metal concentrations began shortly after 1925 A.D. (Figure 4a), co-incident with the opening of the La Oroya smelting complex (Figure 1). Peak metal enrichments were reached either in 1974 (Pb, Cu, and Bi) or in 2005 (Zn, Ag, and Sb), demonstrating an overwhelming disturbance to the natural biogeochemical cycling of metals within the lake environment (Table 1). While the deposition of Pb, Cu, and Bi has declined in recent decades, all metals remain well above their background levels.

Archaeological Implications. The inferred onset of smelting at Morococha occurs during the transition between the Middle Horizon (500 to 1000 A.D.) and the Late Intermediate (1000 to 1450 A.D.) cultural periods. The Middle Horizon witnessed growth and expansion of the largest pre-Incan Peruvian culture, the Wari, whereas the Late Intermediate Period was characterized by decentralized and often-warring regional chiefdoms. Because the onset of smelting at 1000 A.D. coincides broadly with the fall of the Wari Empire, a late expansion of Wari cannot be responsible for the initiation of metallurgy to central Peru. Owen (*33*) suggested that the end of the Middle Horizon in Bolivia triggered a large-scale diaspora, leading to the dissemination of ideas and technology. If this had occurred in Peru as well, it may explain the coeval rise of metallurgy at Morococha and collapse of the Wari Empire.

During the Inca hegemony, several changes pertaining to the production of metal objects were initiated across the Andes. The Inca began incorporating tin into all copper and bronze alloys (*34*), and they deliberately targeted Bi-rich ores (*35*). Furthermore, the Inca extracted silver objects from local populations as a tribute tax (*10*). Based on the gradual decrease of Cu_{anthro} and contemporaneous increase of Pb_{anthro} in Laguna Pirhuacocha during the Inca regime, we suggest a shift occurred away from copper toward silver production at Morococha, partially in order to supply this tribute tax. This notion is supported by attendant increases in Sb and Bi during both Inca and subsequent Colonial eras (Figure 4), the latter of which is historically known to have targeted solely extraction of silver.

The results from Laguna Pirhuacocha imply a millennium of metal smelting in the central Peruvian Andes. While historical records indicate Morococha was discovered by Spanish metalsmiths during the 17th century, our data suggest that the ores of this site were known and exploited for copper production as early as the Late Intermediate Period. Simple calculation of anthropogenic metal burdens using Ti-normalization suggests that, as early as 1400 A.D., 30−50% of sediment Pb was derived from atmospheric deposition. The anthropogenic Pb fraction increased to >80% during the Colonial era, and >99% post-1950 A.D. Given that no intact pre-Colonial smelting facilities have survived in the archaeological record of the central Peruvian Andes, the lake-sediment record of metallurgical pollution is of considerable value in reconstructing ancient smelting histories.

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Supporting Information Available

A full table of ^{210}Pb and radiocarbon data. This material is available free of charge via the Internet at http://pubs.acs.org.

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