

# Late-Holocene atmospheric lead deposition in the Peruvian and Bolivian Andes

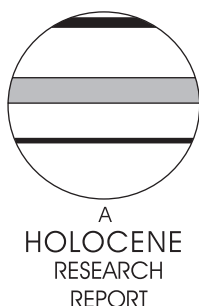
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**Abstract:** The analysis of lead (Pb) in lake-sediment cores is a useful method to reconstruct local histories of Pb pollution. Here, we use Pb concentration profiles from lake sediments to reconstruct local trajectories of pre-Colonial smelting from three metallurgical centres in the South American Andes: the Morococha mining district, Peru; the Bolivian *Altiplano* around Lake Titicaca; and the silver-mining centre of Potosí, Bolivia. The earliest evidence for Pb enrichment from smelting is on the *Altiplano* beginning ~AD 400, coincident with the rise of the pre-Incan Tiwanaku and Wari Empires. Coeval with the collapse of these Empires ~AD 1000, there is a dramatic decrease in Pb pollution on the *Altiplano*, suggesting metallurgical activity was closely tied to the Tiwanaku state. In contrast, metallurgy at Morococha, Peru and Potosí, Bolivia began ~AD 1000–1200, likely as the result of the diaspora generated by the collapses of Tiwanaku and Wari. The independent chronologies of these records suggest asynchronous metallurgical activity between mining centres, and local-scale control of mineral resources. Following Inca conquest of the Andes ~AD 1450, strong increases in Pb are noted at all three study sites, suggesting an increase in silver production to meet Inca imperial demand. Following Hispanic conquest (AD 1532), large increases in Pb pollution are noted at Morococha and Potosí, only to be superseded by industrial development. The records presented here have implications for the reconstruction of Andean prehistory, and demonstrate the sensitivity of lake sediment geochemistry to pre-Colonial smelting activity. The technique has much potential for exploring the timing and magnitude of pre-industrial metallurgy in the New World.

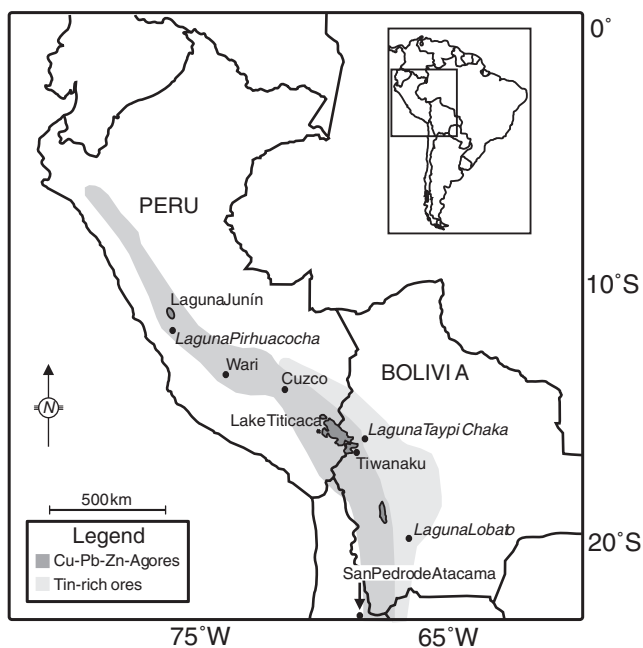
**Key words:** Atmospheric lead deposition, Pb, Andes, lake sediments, metallurgy, pollution, geoarchaeology, late Holocene, Peru, Bolivia.

## Introduction

Natural archives can be used to document the timing and relative magnitude of atmospheric lead (Pb) pollution. Such archives include ice cores (Rosman *et al.*, 1994; Hong *et al.*, 1996), peatlands (Shotyk *et al.*, 1996; Martinez Cortizas *et al.*, 2002), marine sediments (Gobeil *et al.*, 2001), lichens (Doucet and Carignan, 2001; Carignan *et al.*, 2002) and lake sediments (Bindler *et al.*, 2001; Renberg *et al.*, 2002). Such natural archives are sufficiently sensitive to chronicle pre-industrial Pb pollution associated with metallurgical activity at local to regional scales (eg, Monna *et al.*, 2004; Baron *et al.*, 2005). Despite a rich history of metallurgical development prior to Hispanic conquest (Lechtman, 1980), this approach is only beginning to be applied to the Andean region (Abbott and Wolfe, 2003; Cooke *et al.*, 2007).

To reconstruct local to regional histories of anthropogenic Pb pollution in the Andes, we measured weakly bound Pb in three lake cores located along a north–south transect through Peru and Bolivia. The flux of Pb to lake sediment can be used as a proxy for smelting intensity because there is both historical and archeological evidence for the use of argentiferous galena ((Pb, Ag)S; locally known as *soroché*) during the smelting of silver-rich ores, which was conducted in clay-lined, wind-drafted furnaces called *huayaras* (Bakewell, 1984). In addition, Pb has the advantage of not suffering from diagenetic overprinting in lake sediments (Brännvall *et al.*, 2001; Gallon *et al.*, 2004). Here, we present three middle- to late-Holocene histories of Pb pollution due to smelting from the Peruvian and Bolivian Andes. We combine the previously published Pb records from Laguna Lobato, Cerro Rico de Potosí, Bolivia (Abbott and Wolfe, 2003) and Laguna Pirhuacocha, Peru (Cooke *et al.*, 2007) with a new geochemical record from Laguna Taypi Chaka, Bolivia.

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**Figure 1** Map of study area showing locations of the cored lakes (in italics) as well as archaeological sites and towns discussed in the text. Arsenic-rich polymetallic ore bodies as well as tin-rich ore deposits are noted on the map

## Study sites

Because Pb is delivered to lakes by both atmospheric deposition and soil erosion (Norton, 1986; Boyle, 2001), lakes with simple bathymetric profiles and small catchments were deliberately selected in an attempt to maximize lake-sediment sensitivity to atmospheric deposition. Laguna Pirhuacocha ( $11^{\circ}31'S$ ,  $76^{\circ}04'W$ ; 4520 m; Figure 1) is situated in the Morococha mining region in the Junín district of the western Cordillera. The mining area sits in the Río Puará river valley and is situated over an assortment of hydrothermal replacement bodies (Gunnesch *et al.*, 1990). In addition to native silver, the richest ores at Morococha contain combinations of anhydrite ( $\text{CaSO}_4$ ), barite ( $\text{BaSO}_4$ ), bournonite ( $\text{CuPbSbS}_3$ ), arsenopyrite ( $\text{AsFeS}$ ), chalcocopyrite ( $\text{CuFeS}_2$ ), emplectite ( $\text{CuBiS}_2$ ), enargite ( $\text{Cu}_3\text{AsS}_4$ ), galena (PbS), matildite ( $\text{AgBiS}_2$ ), proustite ( $\text{Ag}_3\text{As}_3\text{S}_3$ ), sphalerite, stromeyerite ( $\text{AgCuS}$ ) and tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ) (Ward, 1961; Einaudi, 1977). The first European documentation of Morococha metal resources is from seventeenth-century Colonial prospectors (Purser, 1971).

Located 11 km northeast of modern silver mining operations at Morococha, Laguna Pirhuacocha occupies Cretaceous terrain composed of igneous, metamorphic and carbonate bedrock. The lake itself lies within a cirque at the head of a small valley located perpendicular to the Río Puará river valley. The lake is circumneutral ( $\text{pH} = 7.5$ ) and is 18 m deep. Laguna Pirhuacocha is small ( $0.05 \text{ km}^2$ ) and occupies a non-glacial catchment of  $3.1 \text{ km}^2$ . Laguna Pirhuacocha drains to the east during the wet season (December to March) through a small creek. Surface winds driven by daytime heating blow up the valley during the day and sink back down the valley at night.

In Bolivia, Laguna Taypi Chaka ( $6^{\circ}13'S$ ,  $68^{\circ}21'W$ ; 4300 m) is currently a glacially fed lake situated in the Río Palcoco valley on the western side of the Cordillera Real, in the Lake Titicaca drainage (Abbott *et al.*, 1997b). The lake covers an area of  $1.3 \text{ km}^2$  within a large catchment of  $83.3 \text{ km}^2$ . It is circumneutral ( $\text{pH} = 7.5$ ) and is 12 m deep. Though Laguna Taypi Chaka is not located near any modern mining activities, it was included in this study because it lies ~40 km northeast of the Tiwanaku archaeological

zone, which was an important area of cultural development during Andean pre-history (Kolata, 1993, 2003; Stanish, 2002).

The final site, Laguna Lobato ( $19^{\circ}38'S$ ,  $65^{\circ}41'W$ ; 4640 m), covers an area of  $0.2 \text{ km}^2$  within a non-glacial catchment of  $3.9 \text{ km}^2$ . It is circumneutral and is 11 m deep. Laguna Lobato sits 6 km east of Cerro Rico de Potosí, the largest silver deposit of the Bolivian tin belt. Cerro Rico lies within a zone of xenothermal mineralization related to mid-Tertiary intrusions. In addition to native silver, the richest ores contain combinations of acanthite ( $\text{Ag}_2\text{S}$ ), andorite ( $\text{PbAgSb}_3\text{S}_6$ ), chlorargyrite ( $\text{AgCl}$ ), matildite, miargyrite ( $\text{AgSbS}_2$ ), pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ) and tetrahedrite ( $(\text{Ag}, \text{Cu}, \text{Fe}, \text{Zn})_{12}\text{Sb}_4\text{S}_{13}$ ) (Abbott and Wolfe, 2003).

## Methods

### Core collection and chronology

Lake sediment cores were recovered from the deepest points of the lakes using coring devices that preserve an intact sediment–water interface (Glew *et al.*, 2001). A minimum of 15 cm of the uppermost sediment from each core was extruded in the field at 0.5 cm resolution to eliminate disturbance of the uppermost sediments. The upper sections of Lagunas Pirhuacocha and Lobato were dated using unsupported  $^{210}\text{Pb}$  activities measured by  $\alpha$ -spectroscopy (Appleby, 2001). To constrain sediment ages beyond the limit of  $^{210}\text{Pb}$  dating (~100 years), Accelerator Mass Spectrometry (AMS)  $^{14}\text{C}$  dates were obtained on macrofossils and charcoal. Radiocarbon dates were converted to calendar years AD using the program Calib 5.0 based on the IntCal04 data set (Reimer *et al.*, 2004).

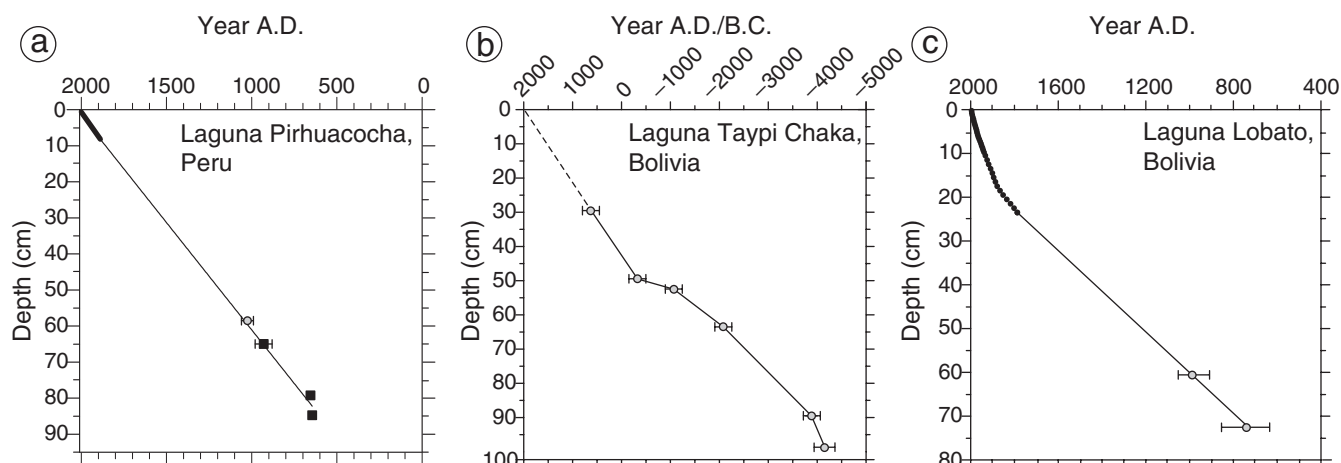
### Sediment geochemistry

Cores were subsampled at 0.5 cm, 1 cm and 2 cm intervals for Lagunas Pirhuacocha, Lobato and Taypi Chaka, respectively. Sediment Pb was extracted from 0.1 to 1.0 g (dry mass) of precisely weighed, homogenized and freeze-dried sediment using 10 ml 1.6 M  $\text{HNO}_3$  (Optima grade, Fisher Scientific) at room temperature for 24 h. This weak extraction procedure deliberately targets weakly bound Pb adsorbed to organic and inorganic surfaces, and not Pb hosted in the lattice sites of detrital silicate minerals (Shirahata *et al.*, 1980; Ng and Patterson, 1982; Hamelin *et al.*, 1990; Kober *et al.*, 1999). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES Spectroflame-EOS) was used to quantify Pb in samples from Lagunas Pirhuacocha and Taypi Chaka, while a Perkin-Elmer Sciex Elan 6000 inductively coupled plasma-mass spectrometer (ICP-MS) was used for Laguna Lobato. Concentrations were verified against the certified multi-element standard, SPEX ICP-MS-2. Duplicates were run every tenth sample and were consistently within 8% of each other. Method detection limits for Pb reflect both initial sample size and instrument sensitivity, and range from 1 to  $5 \mu\text{g/g}$  (ICP-AES) and  $0.0005 \mu\text{g/g}$  (ICP-MS).

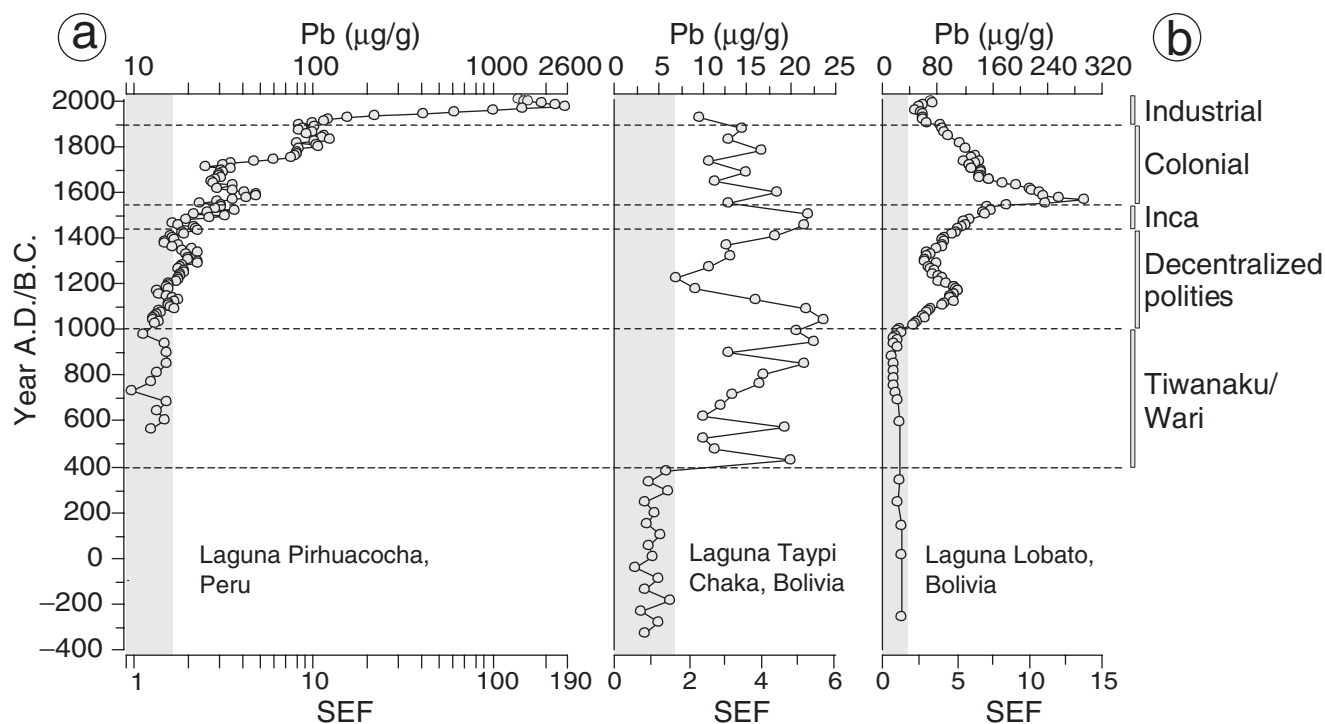
## Results

### Core chronology

Chronologies for each of the cores have been described elsewhere (Abbott *et al.*, 1997b; Wolfe *et al.*, 2001a,b; Abbott and Wolfe, 2003; Cooke *et al.*, 2007), and are therefore only briefly summarized here. At Laguna Pirhuacocha, excess  $^{210}\text{Pb}$  activity was confined to the uppermost 8 cm and sedimentation rates are nearly constant ( $0.007 \pm 0.0003 \text{ g/cm}^2$  per yr) along the length of the core (Figure 2a). Therefore, the constant initial concentration (CIC) model was applied to calculate sediment ages. Four AMS  $^{14}\text{C}$  dates constrain the chronology below the limit of  $^{210}\text{Pb}$ , representing the subset of measurements that do not appear to suffer from a hard-water reservoir effect (Cooke *et al.*, 2007). A best-fit line between



**Figure 2** Age models for (a) Laguna Pirhuacocha, (b) Laguna Taypi Chaka and (c) Laguna Lobato. Solid circles represent  $^{210}\text{Pb}$ -derived ages, grey circles represent AMS  $^{14}\text{C}$  dates on macrofossils and solid boxes represent  $^{14}\text{C}$  dates on charcoal. Error bars on ages represent the  $2\sigma$  error range



**Figure 3** (a) Stratigraphic profiles of Pb concentrations for the three study lakes, shown alongside (b) generalized Andean archaeological history. Shading indicates range of background Pb concentration

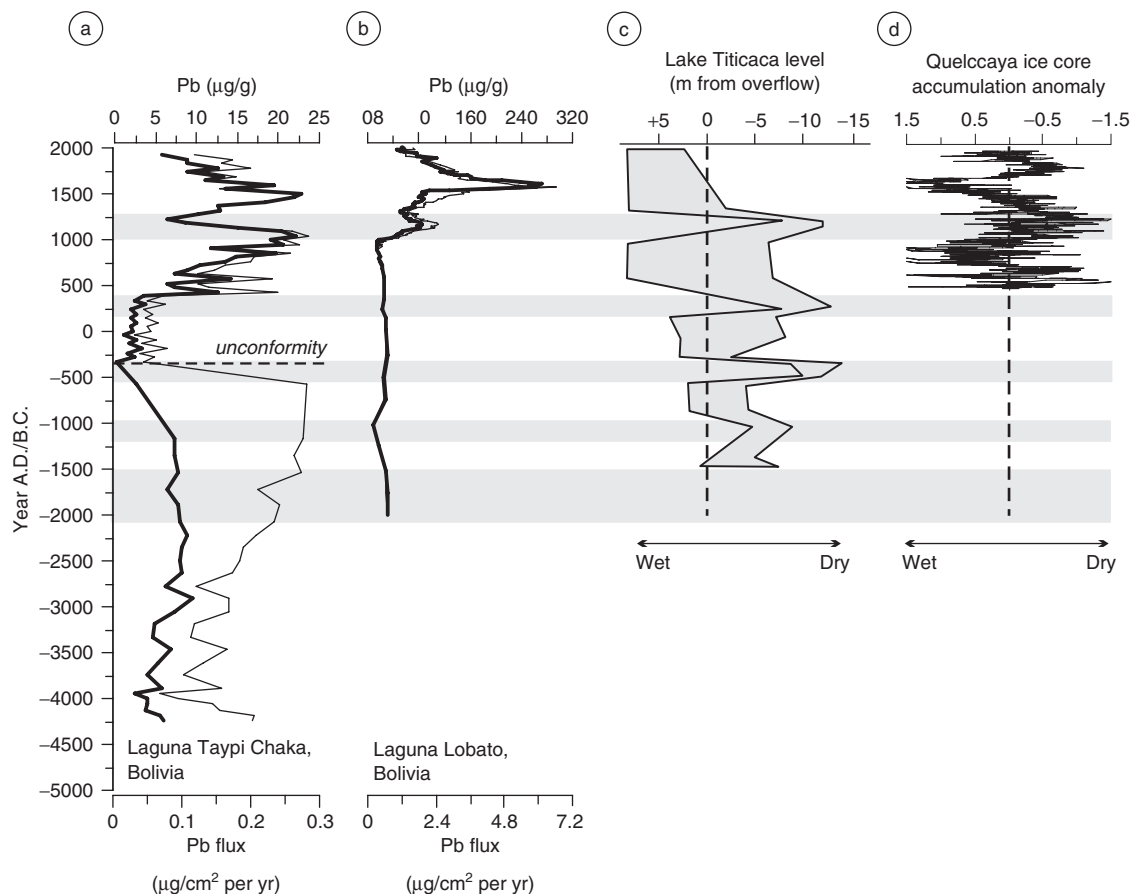
the base of the  $^{210}\text{Pb}$  chronology and the  $^{14}\text{C}$  dates suggests uniform sedimentation downcore, largely reflecting the undisturbed nature of the Laguna Pirhuacocha catchment.

At Laguna Taypi Chaka, six AMS  $^{14}\text{C}$  dates on *Isoetes* megaspores provide the chronological framework (Figure 2b). These are the only available target material for AMS  $^{14}\text{C}$  dating and, although they are potentially prone to hard-water effects, our observations are that the majority of *Isoetes* are emergent, and thus nonetheless capture atmospheric  $^{14}\text{CO}_2$ . In addition, *Isoetes* remains have not produced a single age reversal (eg, Abbott *et al.*, 1997b). The chronology and lithostratigraphy indicate a depositional hiatus at 50 cm, or  $\sim 1000$  bc (Figure 2b; Abbott *et al.*, 2003). Before  $\sim 400$  bc, Laguna Taypi Chaka was shallow (potentially dry for prolonged periods), seasonally closed, and its watershed was glacier-free. The transition from arid conditions to an overflowing and glacial-fed lake is marked by an unconformity, and marked changes in core lithology and organic matter content.

At Laguna Lobato, the upper 23.5 cm contained inventories of unsupported  $^{210}\text{Pb}$ , to which the constant rate of supply (CRS) model was applied (Abbott and Wolfe, 2003). The resultant  $^{210}\text{Pb}$  age model was verified by matching peak sediment  $^{137}\text{Cs}$  activity with the CRS model year for AD 1963. Of the nine calibrated  $^{14}\text{C}$  dates obtained on plant macrofossils at Laguna Lobato only the uppermost two are shown here, as they encapsulate the period of interest (the last  $\sim 1000$  years). A full chronology for the Laguna Lobato core is published elsewhere (Wolfe *et al.*, 2001a,b). Linear extrapolation from the  $^{14}\text{C}$ -dated levels intersects the base of the  $^{210}\text{Pb}$ -derived chronology, enabling a composite chronological model (Figure 2c).

### Sediment geochemistry

Background Pb concentrations vary between the lakes, averaging  $4\ \mu\text{g/g}$  (Laguna Taypi Chaka),  $15\ \mu\text{g/g}$  (Laguna Pirhuacocha) and  $20\ \mu\text{g/g}$  (Laguna Lobato) (Figure 3a). Between-lake variability of



**Figure 4** Late- to middle-Holocene records of Pb concentration (thin lines) and Pb accumulation rates (thick lines) for (a) Laguna Taypi Chaka and (b) Laguna Lobato. Pb records are shown alongside reconstructed lake level for Lake Titicaca (Abbott *et al.*, 1997a) (c), and a 9-point smooth of the Quelccaya ice core accumulation anomaly record (Thompson *et al.*, 1985)

background Pb is due to differences in the physical, geological, biological and chemical characteristics of each lake and its associated watershed. However, each lake is characterized by a low and stable background flux of non-pollution Pb. In order to explore further what influence (if any) regional climatic and hydrologic change might exert on the Pb records, an additional 26 samples from Laguna Taypi Chaka and 15 samples from Laguna Lobato were analysed extending back into the middle Holocene.

From 200 BC to AD 400 at Laguna Taypi Chaka, concentrations of Pb are stable and low,  $\sim 4 \mu\text{g/g}$  (Figure 3a). Prior to this date, however, Pb concentrations rise to  $\sim 25 \mu\text{g/g}$  before gradually declining down-core. However, Pb concentration is influenced not only by the rate of deposition, but also by sedimentation rates and core compaction (ie, sediment bulk density) (Boyle, 2001). At Laguna Taypi Chaka, the lower portion of the sediment record is a much denser shallow-water facies, reflecting consistently lower lake levels (Abbott *et al.*, 1997b). To compensate for changing sediment lithology, and to provide a more complete picture of atmospheric Pb deposition, concentrations have been converted to fluxes (accumulation rate ( $\mu\text{g/cm}^2$  per yr)), calculated as the product of Pb concentration ( $\mu\text{g/g}$ ), sedimentation rate ( $\text{cm/yr}$ ) and bulk density ( $\text{g/cm}^3$ ). The result is a stable and low flux of Pb to Laguna Taypi Chaka between  $\sim$ AD 400 and 4000 BC (Figure 4a). This is despite dramatic shifts in lake level during the Holocene, and ample proxy evidence for severe periods of aridity and pronounced hydrologic change (Thompson *et al.*, 2006) (Figure 4c, d). A parallel situation is apparent at Laguna Lobato, where both Pb concentration and flux data indicate the stable accumulation of non-pollution Pb with time. Therefore, we suggest that the accumulation of non-pollution Pb in Bolivia has remained stable through time.

Given that natural fluxes of Pb to these lakes have remained relatively constant, then enrichments above these background levels

represent excess Pb deposition of anthropogenic origin. Supporting this assertion is the observation that Pb enrichment began at different times and is of varying magnitudes between lakes (Figure 3). We thus associate the magnitude of Pb enrichment with the intensity of ore smelting at local metallurgical centres, but use sediment enrichment factors (SEF), defined by  $[\text{Pb}]_{\text{sample}}/[\text{Pb}]_{\text{background}}$ , for comparisons between sites. Such a normalization strategy minimizes the influence of both within- (Yang *et al.*, 2002; Bindler *et al.*, 2004) and between-lake (Engstrom *et al.*, 1994) variations of sediment Pb.

The earliest increase in Pb above background levels occurs *c.* AD 400 at Laguna Taypi Chaka. Between AD 400 and 1000, Pb in Laguna Taypi Chaka sediment gradually increases, peaking  $\sim$ AD 1040 (Figure 3a). Concentrations of Pb during this time reach  $25 \mu\text{g/g}$ , a six-fold increase above background levels. While the Pb pollution inventory is quite small, the relative enrichment represents a substantial shift in Pb delivery to the lake. Both the Pb concentration and flux data preserve this increase. Because we know of no natural mechanism capable of inducing such a shift after  $\sim$ 4000 years of stability, and given the lake's location near the major archaeological site of Tiwanaku, we attribute the rise in Pb to the onset of Tiwanaku smelting activity on the Bolivian *Altiplano* or in the adjacent Cordillera. The earliest metal artefacts recovered in the area also date to this time period (Lechtman, 2002).

After  $\sim$ AD 1040, the concentration of Pb in the sediments of Laguna Taypi Chaka steadily decline, reaching background levels by  $\sim$ AD 1200. The decrease in Pb is coeval with the collapse of the Tiwanaku culture, and the first appearance of Pb enrichment at Laguna Lobato. At Laguna Lobato, Pb concentrations rise steadily, reaching a first peak between AD 1130 and 1150 (Figure 3a). Concentrations of Pb during this interval reach  $100 \mu\text{g/g}$ , a five-fold

increase above background levels. As observed at Laguna Taypi Chaka, Pb concentrations at Laguna Lobato decrease between AD 1150 and 1300, though not returning to background levels.

While Pb concentrations declined at Lagunas Taypi Chaka and Lobato in the AD 1150–1300 interval, to the north at Laguna Pirhuacocha they increased at this time. While still low, concentrations of Pb at this time exceed background levels, rising to 30 µg/g by AD 1300 (~2.5-fold above background; Figure 3a). Pb stable isotopes confirm that this burden is anthropogenic in origin (Cooke *et al.*, 2007).

High levels of Pb pollution occur in all three of the lake records following Inca conquest of the Peruvian and Bolivian Andes *c.* AD 1450 (Figure 3). Immediately following Hispanic conquest of the Inca (AD 1532), Colonial mining activities were focused on Cerro Rico de Potosí, which at the time was considered the world's largest silver deposit. The Laguna Lobato sediment record faithfully records this historically known intensification of smelting at Potosí, as Pb concentrations exceed 300 µg/g immediately following Spanish arrival in AD 1545. In contrast, concentrations of Pb in Laguna Taypi Chaka sediment gradually decline reflecting a general decline in metallurgical activity on the Bolivian *Altiplano* and the focus on Potosí. At Laguna Pirhuacocha, Pb concentration remains stable until ~AD 1700, after which it rapidly increases to ~100 µg/g, a ten-fold increase above background (Figure 3a).

During the early twentieth century, Pb concentration in Laguna Pirhuacocha sediment rapidly increased (Figure 3a). By ~AD 1974, concentrations of Pb exceed 2600 µg/g, nearly 200-times background, demonstrating an overwhelming disturbance to the natural biogeochemical cycling of Pb at Laguna Pirhuacocha. At Laguna Lobato during the industrial era, Pb concentration gradually declines, becoming stable at ~70 µg/g. Because of a lack of surface sediment from the Laguna Taypi Chaka core, no parallel industrial era data are available for the Bolivian *Altiplano*.

## Discussion

The first appearance of Pb pollution ~AD 400 at Laguna Taypi Chaka coincides with the onset of the Andean Middle Horizon (AD 400–1000) and the rise of Tiwanaku and Wari cultures in Bolivia and Peru, respectively. The Tiwanaku were centred on the southern shores of Lake Titicaca, but engaged in trade as far south as San Pedro de Atacama, Chile (Figure 1) (Kolata, 1993; Moseley, 2001; Rodman, 1992; Stanish, 2002). An array of bronze artefacts have been recovered during archaeological excavations within the Titicaca basin, suggesting a copper-based metallurgical industry of considerable scope (Lechtman, 2002). The Laguna Taypi Chaka sediment record faithfully records this metallurgical activity. The relatively low amount of Pb pollution observed during this time within Laguna Taypi Chaka sediment may be due, in part, to the fact that lead was not involved in the copper smelting and alloying process as it was for silver.

After ~AD 1040, Pb levels in Laguna Taypi Chaka sediment rapidly decrease to background levels. This coincides with the collapse of the Tiwanaku culture on the *Altiplano*, and the first appearance of smelting at Laguna Lobato. The collapse of the Tiwanaku has been linked to pervasive drought, which forced the abandonment of raised field agriculture (Kolata, 1993; Binford *et al.*, 1997), a hypothesis that remains controversial (Callaway, 2005; Isbell, 2004; Williams, 2002). The lake level of Titicaca dropped by as much as 6 m between AD 1100 and 1250 (Abbott *et al.*, 1997a), when precipitation declined as recorded by the Quelccaya ice core (Thompson *et al.*, 2006). Concentrations of Pb in Laguna Taypi Chaka sediment decline steadily after AD 1040, eventually dropping to background levels by AD 1200. Therefore, assuming that metal production was under the direct control of the Tiwanaku state, these data would support a collapse of the Tiwanaku culture beginning *c.* AD 1040. The subsequent

decline of Pb concentrations likely reflects a decline in regional population and hence a decrease in demand for metals.

Just as metallurgy was in decline in the Titicaca basin, activity was gaining momentum at both Cerro Rico de Potosí in southern Bolivia and Morococha in central Peru (Figure 3). Initial Pb pollution at Potosí and Morococha occurred during the Late Intermediate Period, which lasted until the start of the Inca Empire ~AD 1450. The Late Intermediate Period separates Tiwanaku (Bolivia) and Wari (Peru) Empires from the Inca, and was a time of decentralized polities across the Bolivian and the central Peruvian Andes (D'Altroy, 1997; Bauer and Stanish, 2001). The onset of metallurgy at Potosí and Morococha thus appears to have occurred in the absence of a large imperial state. While Abbott and Wolfe (2003) suggested previously that metallurgy was brought to Cerro Rico de Potosí during final expansion of the Tiwanaku, there is little evidence for such an exodus, especially to somewhere as distant and remote as Potosí. On the contrary, many Tiwanaku (Owen, 2005) and Wari (Glowacki, 2005; Moseley *et al.*, 2005) colonies were abandoned ~AD 1000, implying that neither the Tiwanaku (in Bolivia) nor the Wari (in Peru) were responsible for the Late Intermediate Period expansion of metallurgy suggested by our data. We propose instead that an expansion of peoples with metallurgical knowledge occurred sometime after AD 1000, bringing smelting technology to new cultural groups and previously undeveloped mineral deposits. This expansion may have been triggered by the very breakup of the Tiwanaku and Wari Empires, thus generating a 'victim/refugee' diaspora (Owen, 2005). This diaspora would have dispersed Tiwanaku peoples, culture and technologies including smelting over a wide geographical area following the collapse of the Tiwanaku and Wari Empires. Archaeological evidence for a westward dispersal of Tiwanaku peoples has been summarized by Owen (2005), and includes: (1) the appearance of new mortuary practices; (2) an influx of Tiwanaku-style artefacts including wooden spoons, textiles and ceramics; and (3) bioanthropological evidence for the immigration of intrusive populations. Based on our sediment records, we propose that the Late Intermediate Period expansion of metallurgical knowledge into central Peru and southern Bolivia occurred as part of a large, post-Middle Horizon (post-AD 1000) diaspora initiated by the collapse of the Tiwanaku and Wari Empires.

During the Late Intermediate Period, increases in Pb concentration are noted beginning ~AD 1300 at Lagunas Taypi Chaka and Lobato (Figure 3). This renewed intensification of metallurgy precedes the rise of the Inca Empire by ~150 years. Increased metal production at this time was likely driven by regional population increases and attendant demand for metal as regional climate ameliorated. With the conquest of Peru and Bolivia by the Inca Empire *c.* AD 1450, Pb concentrations at all three study lakes meet or exceed any previous levels of Pb pollution (Figure 3).

Following Hispanic conquest of Peru and Bolivia beginning in AD 1532, Incan mines and metallurgical centres were placed under Colonial control. Potosí was the first metallurgical centre in the Andes to be developed following Spanish arrival in AD 1545. Early Colonial smelting at Potosí utilized bellows Castilian stone furnaces, which repeatedly failed (Bakewell, 1984). Because of the failure of these furnaces, smelting at Potosí was placed in the hands of Incan metallurgists, who retained traditional *huayara* technology that elevated Pb emissions, consequently driving Pb concentrations in Laguna Lobato sediment to nearly 300 µg/g (Figure 3a). Atmospheric fluxes to Laguna Lobato sediment progressively declined following the introduction of mercury amalgamation as the primary extractive technique at Potosí in AD 1572 (Abbott and Wolfe, 2003).

With the exhaustion of silver-rich surface ores at Potosí, a new search for silver deposits began and new mines were developed. Colonial mining at Morococha began shortly after AD 1600, driven largely by the European demand for silver. Both official and clandestine Colonial mining operations were active in the area, the

latter using a Pb flux and traditional *huayara* technology. Their collective emissions elevate Pb in Laguna Pirhuacocha sediment to over 100 µg/g, representing a ten-fold increase above background levels (Figure 3a).

With construction of the central Peruvian railway in the early twentieth century, the central Andes were rapidly developed. The industrial era increase in Pb at Laguna Pirhuacocha is coincident with the opening of the La Oroya smelting complex, which is located ~15 km east of the lake. Conversely, the low amount of industrial-era Pb pollution at Laguna Lobato represents a switch to tin-based metallurgy, for which Pb was not involved in the extraction process, following the abandonment of silver extraction in AD 1930 (Abbott and Wolfe, 2003).

## Conclusion

The results from this study reveal a long and rich history of pre-Colonial, Colonial and industrial Pb pollution in the Andes extending as far back as AD 400. The timing of both initial and peak smelting was asynchronous between different mining centres, suggesting that each had a unique history of development. Within the Titicaca basin, periods of peak metallurgical activity coincide with the climaxes of the Tiwanaku and Inca Empires. In the central Peruvian and southern Bolivian Andes, metallurgy developed somewhat later and apparently independently of state control. Instead, metallurgical activity appears to be coupled to local culture, and may have been imported via a pan-Andean diaspora following the collapse of major pre-Incan empires.

The records presented here demonstrate the contribution that natural archives can offer to the archaeological record. Because pre-Inca Andean smelting technologies were likely similar to the *huayaras* described by conquistadors at the time of contact, they are unlikely to produce much of an archaeological record (Van Buren and Mills, 2005). Lakes are common across the Andean landscape and therefore offer an independent method for local-scale reconstructions of ancient metallurgical activities, thereby enriching our knowledge of pre-industrial resource utilization and its relationship to culture.

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