Documenting the History of Inca Precious Metal Production Using Geochemical

Techniques from Lake Sediments in the Andahuaylas Region of Peru

by

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The process of studying heavy metal concentrations in lake sediments in order to reconstruct pollution history has been used in a variety of environments and locations. Laguna Pacucha is one in a series of metal pollution studies from Peru and Bolivia, an area with a rich history of metallurgy. Laguna Pacucha lies in the Andahuaylas region of Peru, 145 km west of Cuzco, the Inca capital, and 20 km west of Curamba, a presumed ancient smelting site. The sediment record of Laguna Pacucha reveals a metal record that dates beyond 1225 AD. A major density change ~1225 AD, concurrent with a known period of drought, inhibits the possibility of a reliable age model below this point. Increases in Zn, As, and Cu after ~1225 AD could be indicative of local copper smelting, which supports separate evidence of the Curamba archeological site (near Laguna Pacucha) as a potential copper smelting site. These concentrations drop around the time of the Spanish conquest, and then the concentrations of a number of different metals increase after ~1600 and decrease by ~1850 AD, which could indicate smelting, but more likely indicates a change in land use. Our results provide a complex record of a changing Andean environment, and indicate a need for further study in the Andahuaylas region.

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PREFACE

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1.0 INTRODUCTION

During the Spanish conquest of the Inca Empire in 1532 AD, the Spanish received an entire room full of gold and silver as ransom for Atahualpa, the captured Inca emperor (Hemming, 1993). Additionally, the territories gained by the Spanish conquest were so rich in silver that Spanish America became the world's leading producer of the metal (Garner, 1988). While there are many historical records of mining and metallurgy after the Spanish conquest, our knowledge of pre-colonial mining and smelting remains limited (Garner, 1988). There are no written records of pre-colonial metallurgy, and many of the artifacts have either disappeared due to pervasive looting or were melted down by the Spanish (Abbott and Wolfe, 2003).

Measuring metal concentrations in dated lake sediment cores is a new method used to reconstruct an area's ancient heavy metal pollution and, consequentially, its metallurgical history. This technique has been applied to a number of sites in Peru and Bolivia, and evidence of silver smelting has been found as early as 400 AD (Cooke et al., 2008). Here results from Laguna Pacucha (Peruvian Andes) are discussed and compared with previous work in the region aimed at reconstructing the history of precious metal production.

Laguna Pacucha is an ideal lake to study for a number of reasons, including its physical properties and its location, 145 km west of Cuzco, the Inca capital. No other lake in this area has been studied for the purpose of developing a heavy metal pollution history, so it will be a useful

addition to the geochemical studies of other lakes in Peru and Bolivia (Abbott and Wolfe, 2003; Cooke et al., 2008).

1.1 BACKGROUND

1.1.1 Geochemistry and Pollution History

The use of sediment geochemistry to study heavy metal pollution history has proven to be effective in a number of different situations and locations. In Sweden, Ingemar Renberg and colleagues were among the first to use lake sediments to reconstruct a lead pollution history of much of Europe which saw clear increases in lead concentrations during the Greek and Roman cultures as well as two peaks that match periods of historical metal production in Europe (Renberg et al., 1994). Brannvall (2001) compared ²⁰⁶Pb/²⁰⁷Pb ratios and lead concentration profiles in sediment cores and peat and soil samples to provide evidence that lead enrichment in these sources is caused by anthropogenic lead pollution rather than natural processes (Brannvall et al., 2001). In Greenland, heavy metal concentrations and ²⁰⁶Pb/²⁰⁷Pb ratios were used to determine the sources of the lead pollution in ice cores (Rosman et al., 1994).

The method of using element concentrations in lake sediments to interpret past metal pollution has recently been applied to lakes from multiple locations in Peru and Bolivia. These studies, which build upon each other, have revealed a more comprehensive record of historical South American smelting (Abbott and Wolfe, 2003; Cooke et al., 2008). Here, we are looking specifically at element concentrations in Laguna Pacucha lake sediments in order to reconstruct the area's heavy metal pollution history.

1.1.2 South American Metallurgy History

The earliest well-dated copper and gold artifacts are hammered foils and gilded copper from Mina Perdida, Peru, which date from 1410 to 1090 BC. (Burger and Gordon, 1998). The practice of sheet-metal working continued to be used through the Early Intermediate Period (200 BC- 600 AD) and the Middle Horizon (600-1000 AD). Shultze and colleagues determined that the tradition of silverworking was established further south in the Lake Titicaca basin by the first century AD. The researchers studied and dated a stratigraphic sequence of metalworking remains and concluded that high-temperature silver purification began before the establishment of the Tiwanaku state, and continued after its collapse and throughout the Inca and Spanish Empires (Shultze et al., 2009). Geochemical evidence for silver smelting has been found as early as 400 AD at Laguna Taypi Chaka in Bolivia (Abbott and Wolfe, 2003; Cooke et al., 2008). Large-scale copper and bronze smelting is seen on the northern Peruvian coast by 1000 AD, and during the Late Intermediate Period intensive copper working spread through the Bolivian altiplano (Abbott and Wolfe, 2003). Demand for smelted gold and silver in order to show rank and power increased during the Inca reign, and increased even further after the Spanish conquest (Lechtman, 1984; Abbott and Wolfe, 2003).

| Horizons/Periods | Culture | Approx. Calendar Years | |
|-------------------|----------|---------------------------|--|
| Late Horizon | -Inca- | AD 1400 - 1530 | |
| Late Intermediate | -Chanka- | AD 1000 - 1400 | |
| Middle Horizon | -Wari- | AD 600 - 1000 | |

Table 1. Culture, Historical Periods, and Ages (Lechtman, 1984, Bauer, 2010)

1.1.3 South American Metal Pollution

In South America, smelting was the primary source of pre-industrial heavy metal pollution. Smelting is a process of removing a metal from its ore and involves heat and a chemical reducing agent. During the process, volatiles are released into the atmosphere and deposited onto the environment, including lakes, through wet or dry deposition (fig. 1). The Inca generally used charcoal-fired, wind-drafted clay kilns (known as *huyaras*) for smelting, and were historically known to use argentiferous galena [or *soroche*, (Pb, Ag)S] as a flux during the smelting process (Cooke et al., 2008). The use of *soroche* as a flux causes excessive volatilization of lead, and the high concentrations of the element—along with lead's relative immobility once deposited in sediments—makes it an ideal proxy to study the intensity of sliver production occuring during the time of deposition (Abbott and Wolfe, 2003). Increases in copper, zinc, and arsenic can be indicative of copper-based metallurgy; and the ultimate goal of such metallurgy would be bronze production (Cooke et al., 2007; Brooks, 2010).

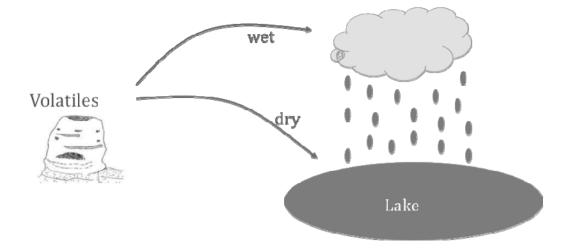


Figure 1. Wet and dry deposition of volatiles from smelting into local lakes

1.2 STUDY SITE

1.2.1 Laguna Pacucha

Laguna Pacucha (13°36′26″S, 73°19′10″W) is a large, 7.5 km² lake with a maximum depth of 30 m and a 121.1 km² catchment (fig. 2).

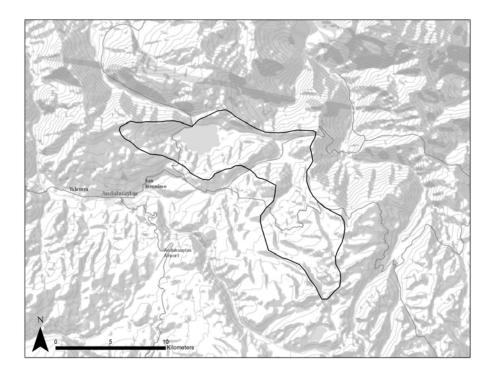


Figure 2. Catchment map of Laguna Pacucha. The black outline represents the catchment area of the lake

Laguna Pacucha, an alpine lake, is found at an elevation of 3100 m and is surrounded by glaciers that terminate in nearby valleys (Hillyer et al, 2008). A small stream drains into the eastern end of the lake and there is a small outflow on the northern shore, though these streams are relatively insignificant when compared with the size of the lake (Hillyer et al., 2008). The lake's high elevation and little connection to other surface waters helps to ensure that much of the metals are deposited into the lake from the atmosphere as wet or dry fallout. Laguna Pacucha

is a thermally stratified lake with oxygenated bottom waters and a slightly basic pH of around 8.4 (fig. 3).

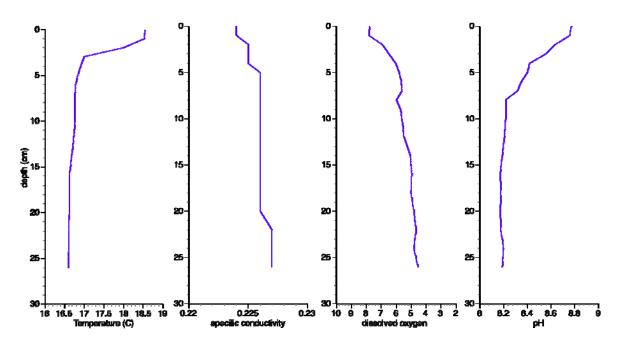


Figure 3. Hydrolab data including temperature, specific conductivity, dissolved oxygen, and pH

1.2.2 Area Resources

Laguna Pacucha lies directly on the Andahuaylas-Yauri belt, which is associated with significant copper, gold and molybdenum mineralizations (Perello et al., 2003). The area surrounding the lake is especially rich in copper, lead, zinc and silver ores. Native silver ores in Peru were often found in altered zones called "iron hat," which were caused by a reaction of meteoric water with the sulfides from the silver veins. This type of secondary mineralization, which is very common in the Andes, made silver ores relatively easy for Peruvian miners to find and extract (Petersen, 2010). Lead ores are economically important, and were often mined for their silver content. Galena (PbS), a common lead ore, was also referred to as *soroche* by the Inca. Copper, primarily

the As-Cu sulfide Enargite, was widely used and of great importance to the ancient Peruvians, and its use dates to approximately 600 BC. Native copper was difficult to find in outcrop, and ancient miners only had access to the deeper zones where it formed if erosion had removed some of the overburden (Petersen, 2010).

1.2.3 Area Culture

The area surrounding Laguna Pacucha has a rich cultural history. The lake lies on the Peruvian Altiplano in the Adahuaylas province. The area was primarily controlled by the Wari, the largest pre-Inca empire in the Andes, during the Early Intermediate and Middle horizon (Stanish, 2001). Records from Llamacocha, a lake in central Peru have shown increases in regional Pb pollution around A.D. 600, which is thought to record increased smelting activity coinciding with the expansion of the Wari Empire (Cooke et al., 2009). Additionally, there is evidence of mining by the Wari State at Mina Primavera, a mine located in southern Peru (Eerkens et al., 2009).

Shifts in the settlement locations in the Andahuaylas region around AD 1000 coincide with the decline of Wari influence as well as prolonged dry periods in Peru and Bolivia (Bauer, 2010; Binford et al., 1997). At this time, the Chanka shifted from raised-field agriculture toward a more mixed economy with an increased role of pastoralism, and situated themselves primarily in hilltop settlements rather than valleys. Bauer and Kellett (2010) note that the Chanka developed as a "uniquely powerful ethnic group" during the time of Inca expansion. The site of Luisinayoc, a known Chanka site, sits directly above the town of Pacucha (Bauer, 2010). While there are a number of references to Chanka ceramics, there are few records of Chanka metal artifacts (Bauer, 2010). The Chanka and the Inca developed as traditional rivals, and in 1438 AD

the Chanka launched the conquest of Cuzco, but the Inca in the Cuzco region united to score a decisive military victory over the Chanka (Bauer, 2002).

Laguna Pacucha lies 145 km west of Cusco, the Inca capital city. During the Inca reign, gold and silver was in high demand in order to show rank and power (Lechtman, 1984). Metal production increased drastically during this time. Demand for gold and silver rose even further after the Spanish Conquest in 1545, and has generally increased through time (Abbott and Wolfe, 2003).

Chepstow-Lusty et al. (2009) conducted a study on lake sediments from Marcacocha (72°12'W, 13°13'S), 12 km north of the major Inca settlement of Ollantaytambo and 130 km northeast of Laguna Pacucha. They found that the inhabitants of the area, much like the Chanka, responded to the ~1000 AD drought by exploiting higher elevations and switching to a systems of agro-forestry and agro-pastoralism. The Marcacocha charcoal record suggests an increase in anthropogenic activity in the area ca. 1150 AD, likely caused by a migration of populations from lower elevations. The warmer temperatures allowed for the exploitation of higher elevations because melting glaciers allowed for glacial-fed irrigation of agricultural terraces. Sharp increases in mite abundances in the mid 1400s are suggestive of a population of large herbivores, probably llamas, using the pasture for grazing purposes. Mite frequencies drop after 1500 AD, around the time of the collapse of the Inca Empire, and then undergo a final increase around 1600 AD, likely due to the introduction of large herbivores from the Old World (Chepstow-Lusty, 2009). The use of the pasture as grazing at this time is supported by evidence of significant burning events (possibly for clearing purposes). A hiatus in burning activity after the 17th century coincides with the collapse of livestock populations, and also a recorded epidemic

(probably smallpox) that wiped out many of the indigenous people in the valley (Chepstow-Lusty et al., 2009).

1.2.4 Curamba Archeological Site

Laguna Pacucha is 20 km west of Curamba (73°8'W, 13°3720"S), an important yet controversial archeological site that lies on the royal Inca road that runs north to the coast (fig. 4). The area was most likely in Chanka possession until the Inca takeover in 1438 (Lechtman, 1976). Curamba has generally been accepted as an ancient smelting site because of the hundreds of fire-reddened strips of earth that may once have been wind-driven furnaces lining the terraces. Upon excavation of the site, Lechtman found that the fire-reddened strips are the remains of rectangular channels that were open at the top, lined with limestone, and covered with a thick layer of mud-plaster to protect the structure from heat. The clay that built up the terraces was brought from somewhere else, probably for its good thermal properties (Lechtman, 1976). All of the channels were built parallel in order to take advantage of the area's strong wind conditions. While there is some evidence of the structures originally being built up, the weaker construction materials do not hold up to weathering and would probably not be preserved in the archeological record (Lechtman, 1976). A lack of colonial sherds or architecture around the terraces makes it likely that the installations were originally Incaic or pre-Incaic (Lechtman, 1976).

Although explorers initially believed these structures to be furnaces, there is some evidence that this scenario is unlikely. No metallurgical slags or ash were found associated with any of the terraces. This could be from the regular occurrence of removal and re-melting of slag from past mining sites, but given Curamba's difficult and remote access, this is unlikely. The construction of an open-pit channel is unusual, but not unheard of, and could be used for roasting ore rather than smelting (Lechtman, 1976). Carbonized maize cobs were found with kernels still intact, which seems unusual if the maize was used as a fuel, because the kernels would likely have been removed first and used for other purposes (Lechtman, 1976).

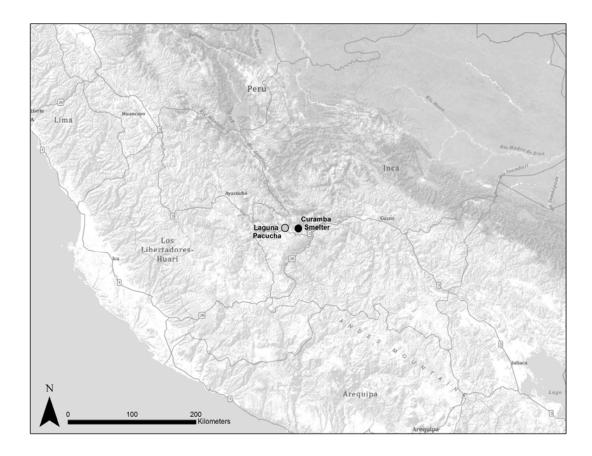


Figure 4. Regional area map with specific markers at Laguna Pacucha and the Curamba smelter.

A study by Parodi et al. (2008) used X-ray diffraction and Mossbauer spectroscopy to study the composition of the existing slag and ore and the maximum temperatures achieved by the furnaces. Samples from two different furnaces showed no evidence of silver ore as part of its composition, but there was some evidence of copper. Additionally, the highest temperature the furnaces could have reached was ($800\pm50^{\circ}$ C). This temperature is not high enough to melt silver, which has a melting point of 960° C, but it may have been hot enough to melt copper with

a 779° C fusion temperature. Lechtman notes that while ores are abundant within 18 km, the ores are typically copper rather than silver (Lechtman, 1976). An increase in lead concentrations in Laguna Pacucha could be indicative of silver smelting in Curamba, while increases in copper, zinc and arsenic would suggest copper smelting, and could help to explain the history of the Curamba site (Cooke et al., 2007; Petersen, 2010).



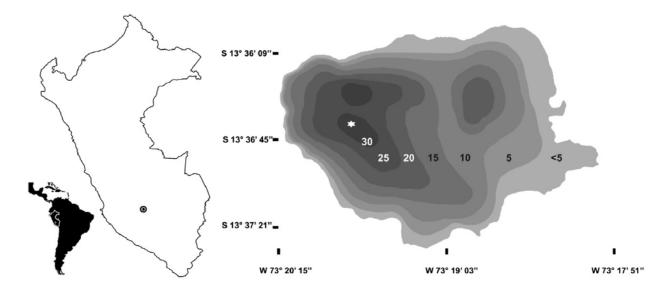


Figure 5. Laguna Pacucha location and bathymetry. From Hillyer et al. 2008. The star indicates the approximate location of coring.

2.1 CORE COLLECTION AND CHRONOLOGY

Lake sediments were collected from Laguna Pacucha in 2008 from the deepest part of the lake (~30 m) using a piston corer designed to recover undisturbed sediments with an intact sedimentwater interface (fig. 5). We recovered 294 cm total, and the upper 50 cm of the core were extruded into sample bags in the field at continuous 0.5-cm increments to eliminate possible disturbance during transport. Sediment characteristics were also described and photographed in the field to ensure accuracy.

Laguna Pacucha was dated using two Accelerator Mass Spectroscopy (AMS) ¹⁴C dates from plant material and charcoal at 101-102 cm and 247-250 cm, respectively. Samples were prepared for radiocarbon dating by soaking in 0.1 M HNO₃ for 30 minutes, 0.1 M KOH for 60 minutes, and then 0.1 M HNO₃ for another 30 minutes. The samples were neutralized by rinsing with deionized water before and after each acid or base. Radiocarbon dates were calibrated to calendar years BP using the Calib radiocarbon calibration program and IntCal09 calibration Curve (Stuiver and Reimer, 1993; Reimer et al., 2009).

2.2 SEDIMENT PROPERTIES

Samples were measured for loss-on-ignition (LOI) at 5-cm intervals. 1-cc samples were weighed, heated to 105°C overnight in ceramic crucibles, and then weighed dry in order to calculate dry density. Samples were then heated to 550°C and 1000°C to calculate percent organic matter and percent calcium carbonate, respectively (Heiri et al., 2001).

2.3 SEDIMENT GEOCHEMISTRY

The core was sub-sampled at 5-cm intervals and then processed and analyzed for elemental concentrations from each level extruded in the field. Metals were extracted from 0.5 g freezedried sediment with 1 M HNO₃ at room temperature overnight. This weak extraction procedure deliberately targets loosely bound metals absorbed to organic and inorganic surfaces, rather than those associated with the mineralogy of inorganic constituents of sediments (Graney et al., 1995). Metal concentrations for 23 metals in the samples were determined using the inductively coupled plasma mass spectrometer (ICP-MS) at the University of Alberta, Canada. Principal component analysis was executed using Canoco version 4.5 software (ter Braak and Šmilauer, 1998).

3.0 RESULTS

3.1 CORE CHRONOLOGY

The age model was built with two calibrated AMS ¹⁴C dates and is reported as calibrated years AD (fig. 6). In addition, we assumed that the top of the core dated to 2008, the year the lake was cored. The first date came from plant material at 101.5 cm (averaged) and dates to 1768 AD. The second was from charcoal at 248.5 cm (averaged) and dates to 1227 AD. Laguna Pacucha is a carbonate rich lake and subject to a hardwater effect, but in order to circumvent this issue we targeted only macrofossils and charcoal, which are not likely to be subject to the effect (Abbott and Stafford, 1996). Sediment accumulation rates for the two segments of the calibration curve are 0.42 cm/yr since 1768 and 0.27 cm/yr before 1768.

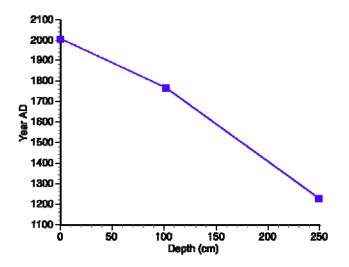


Figure 6. ¹⁴C dates and age-depth model.

3.2 SEDIMENT PROPERTIES

There appears to be a significant increase in the density of the core $(+ 0.5 \text{ g/cm}^3)$ below 250 cm. This could indicate a change in sedimentation rate, a change in sedimentology, a low lake stand, or a change in land use.

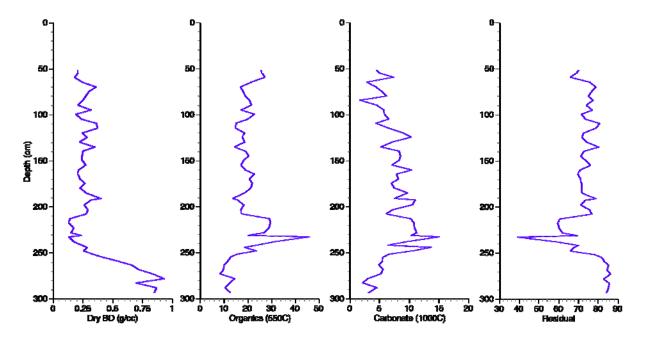
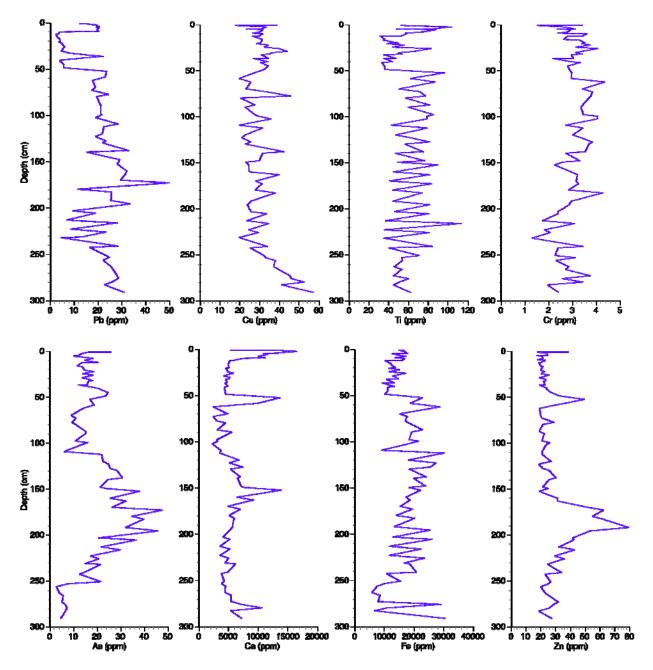


Figure 7. L.O.I. graphs vs. depth including calculated bulk density, % organics, % carbonate, and % residual

Below ~ 250 cm, the sediments become very clay rich, as indicated by the high residual percentage. There is also a noticeable texture change in the sediments—they become much heavier and stickier below ~ 250 cm.

3.3 SEDIMENT GEOCHEMISTRY

Many of the elements, including Pb, Cu, Ca, Ni, Cr and K have higher concentrations near the bottom of the core, which is likely caused by the change in sediment character. It also does not appear that background concentrations of any of the elements were reached, as there are no sustained low concentrations at the bottom of the core, especially for Pb, Cu, Ni and K.



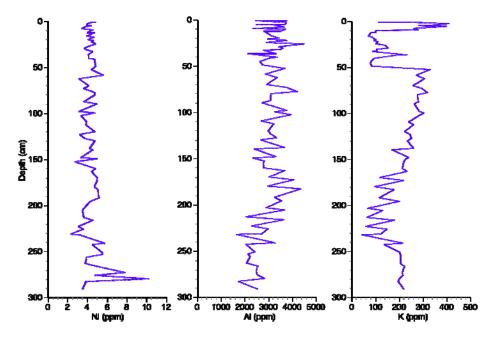


Figure 8. Metal Concentration vs. Depth

Arsenic concentrations increase in the lower density sediments, at a depth of 250 cm. Arsenic reaches a peak of ~50 ppm around 175 cm, and then steadily drops until ~100 cm, where it averages 20 ppm for the rest of the core. Fe and Zn concentrations also start rise at ~250 cm. Iron increases markedly by 240 cm, and sustains this increase until 50 cm when the concentration drops by almost 5,000 ppm. Zinc peaks at 191.5 cm with 80 ppm, and then steadily decreases until 150 cm at which point it remains around 25 ppm with a slight increase at 50 cm. Pb, Cr, and K also see increased concentrations above ~ 200 cm. Lead concentrations peak at 175 cm and then decline for the remainder of the core, until 50 cm when the concentrations drop. Chromium has a very slow rise and fall through the core, peaking at ~4 ppm. Potassium rises steadily above ~200 cm, peaking at 331 ppm, before quickly dropping to 84 ppm at 50 cm depth. Nickel concentrations remain around 4 ppm, with the exception of the bottom of the core (below 250 cm).

It should be noted that the concentrations of a number of the elements (especially Pb, Ti, Ca, Fe, and K) fall drastically at 50 cm, which marks the switch from the intact core samples to

the extruded sediments. This may indicate that the change has to do with a difference in how the sediments were packaged and stored, or sediment focusing, rather than the concentrations of metals in the lake at that time.

In the results from principle component analysis (PCA), many of the elements known to be from weathering (Ti, K, Na) covary in quadrant II, along with Pb. This may imply that the changes in lead concentrations are primarily due to weathering. Additionally, elements in quadrant III (including Zn and As) are decoupled from the weathering elements in quadrant II, meaning that the changes in concentrations of these elements are likely due to something other than weathering, such as metallurgy.

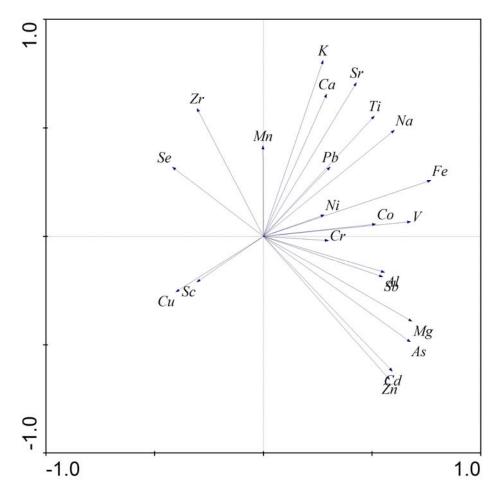


Figure 9. Principle component analysis results.

4.0 **DISCUSSION**

4.1 LAGUNA PACUCHA

4.1.1 Sediment Properties

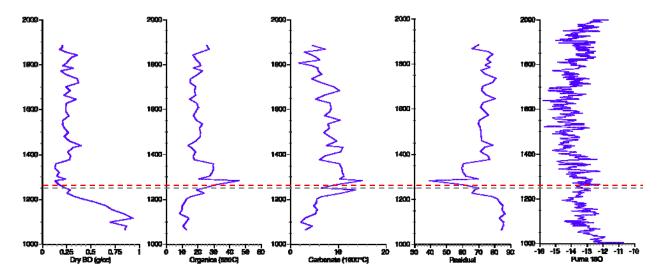


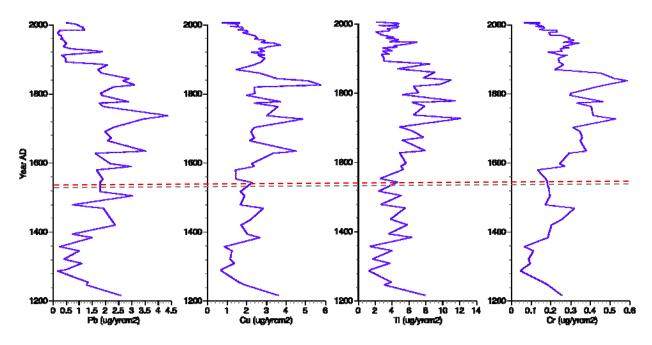
Figure 10. L.O.I. graphs including calculated bulk density, % organics, % carbonate, and % residual. Far right graph is Pumachocha δ^{18} O levels (Bird et al. 2010). Higher δ^{18} O levels indicate drier periods (Bird et al. 2010). The dashed line represents a notable density change as well as the approximate oldest determined age.

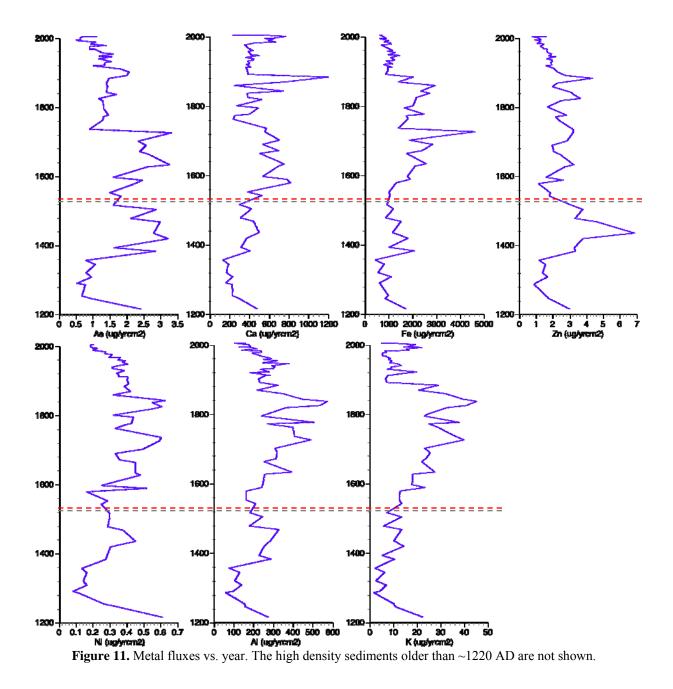
The change in density around 1225 AD could be due to a number of causes including a low lake stand, or changes in land use (sediment supply/ sedimentation sources). Abbott et al. (1997) found that water levels in Lake Titicaca drastically decreased during severe periods of drought from 1040-1490 AD, with the lowest period around 1250 AD. Additionally, a study by Bird et al.

(2010) noted peaks in δ^{18} O from AD 900- 1100, which indicates a weakened South American Summer Monsoon (SASM) rainfall (Bird et al. 2010). This could indicate that the increased density at the bottom of the core is due to a low stand in the lake from drier environments during the medieval climate anomaly. The deepest section of the lake is not far from the land, and one possibility is that during the lowstand, there was a slump of sediments into deeper parts of the lake, explaining the high clay matter (% residual) and high density.

4.1.2 Sediment Geochemistry

Element concentrations were converted to fluxes (accumulation rate μ g/cm² per year) and were calculated using the metal concentration (μ g/g), bulk density (g/cm³), and sedimentation rate (cm/yr). Sedimentation rate was derived using the ¹⁴C age model. The density of the sediments distinctly increases below 1225 AD, which also marks the lowest date on our age model. For this reason, metal fluxes below 1227 AD will not be discussed, as the density changes below this point indicate extrapolation of the age model is not appropriate.





The first major increases in element fluxes outside of the high-density sediments can be seen in As, Zn, Ni, Al, and to a lesser extent Cu, around 1350 AD. Increases in Zn, As, and Cu can be indicative of copper smelting (Cooke et al., 2007; Petersen, 2010). This increase occurs slightly before the rise of the Inca Empire, and while the Inca were primarily known for silver metallurgy, copper smelting in this area is supported by two studies from the Curamba archeological site, which is only ~20 km away from Laguna Pacucha (Lechtman, 1976; Parodi et al., 2008). Copper constitutes a majority of the local ores, and the copper ores in the area are often high in arsenic (Lechtman, 1976; Petersen, 2010). Additionally, the PCA results suggest that the changes in As and Zn are decoupled from the changes in the concentrations of the elements related to weathering, so it is likely Zn and As concentrations are due to something other than weathering, such as smelting. Copper-based metallurgy typically has an ultimate goal of bronze production, and there are significant records of bronze and copper Inca artifacts (Petersen, 2010). As and Zn noticeably drop around 1450 AD, hitting a low point during the Spanish conquest. This could be caused by the abandonment of regional metal production.

Pb, Cu, Ti, Cr, Fe, Ni, Al, and K all reach their highest fluxes roughly between 1650 AD and 1850 AD. This period contrasts with many of the other studies in the area, which see high lead fluxes during the Inca and Early Colonial periods (1400 AD -1650 AD), (Abbott and Wolfe, 2003; Cooke et al, 2007, Cooke et al., 2008).

One explanation for this phenomenon is an incorrect age model. Our current age model is made up of only two dates, which may simply not be enough information to form a reliable age model. The late increases in metal fluxes could also be from late colonial smelting in the area. However, if there was late colonial smelting, it was most likely not at Curamba, as luminescence techniques date the last use of the furnaces to around 1550 AD (Parodi et al., 2008).

It is notable that almost all of the elements, including elements not typically associated with smelting pollution, have similar profiles. This suggests that the changes in flux, at least from ~1600-1900 AD, may have to do with some other factor, such as erosion, rather than smelting. Additionally, the PCA results show Pb covarying with elements that are typically related to weathering. Heather Lechtman specifically mentions that there is considerable

evidence that Curamba may not have been a site of metal smelting at all, and that interpretation may in fact be a complete misunderstanding of the purpose of the site (Lechtman, 1976). If this is the case, then the lack of a distinct metal record in Laguna Pacucha could certainly support this theory. Areas near Laguna Pacucha saw population increases during the low lake levels because of the warmer temperatures and the ability to take advantage of higher elevations for agriculture (Chepstow-Lusty et al., 2009). Sediment records from Laguna Marcacocha, 130 km northeast of Laguna Pacucha, indicate a move towards agro-pastoralism and a number of major burning events near the lake. There are also increases, decreases and changes in land use based on the political climate at the time (Chepstow-Lusty et al., 2009). While this particular record may not necessarily hold true for the area around Laguna Pacucha, it does indicate that there were major changes in land use in the Peruvian altiplano during the time span of the core, and these changes could help to explain the metal concentrations. More analysis of the core should be done in order to test this theory.

4.2 OTHER RECORDS IN THE REGION

There have been a number of other studies done on this subject in various areas of Peru and Bolivia. All of the lakes have been described in detail in previous papers (Abbott and Wolfe, 2003; Cooke et al., 2007; Cooke et al., 2008; Cooke et al., 2009) so there will be only a short discussion of them here.

4.2.1 Laguna Lobato, Bolivia. (Abbott and Wolfe, 2003)

Laguna Lobato is located 6 km from Cerro Rico de Potosi, which was the largest silver deposit in the world (Abbott and Wolfe, 2003). Metal concentrations first increased shortly after 1000 AD, reaching a peak around 1140 AD, which coincides with the late Tiwanaku. A decrease after 1140 AD occured contemporaneously with the fall of the Tiwanaku state, suggesting that the smelting at Cerro Rico was attached to the Tiwanaku polity. The next significant increase occurs after 1400 AD, with the rise of Inca metallurgy. The arrival of the Spanish in 1545 AD brings about the highest peak in lead, as well as increases in Ag, Bi, and Sn because of less effective smelting techniques. The depletion of surface ores saw a switch to the process of mercury amalgamation, until Cerro Rico was abandoned in 1930 AD.

4.2.2 Laguna Pirhuacocha, Peru. (Cooke et al., 2007)

Laguna Pirhuacocha is situated in close proximity to the Morococha mining region, which makes it a good location to record metal deposition from past smelting activity. The first rise in lead, and the likely onset of smelting at Morococha, occurs between 1000 AD and 1200 AD, which is after the fall of the Wari but significantly before the rise of the Inca civilization. Increases in Cu and Zn relative to Pb around 1200 AD suggest that copper-based metallurgy is predominant, until Pb levels start to increase during the rise of Inca metallurgy. Increases in Pb, Sb, and Bi after 1600 AD are attributed to increases in colonial mining at Morococha. The development of the Andes and the opening of the La Oroya smelting complex are the most likely causes of the significant enrichments in all of the metals after 1925 AD.

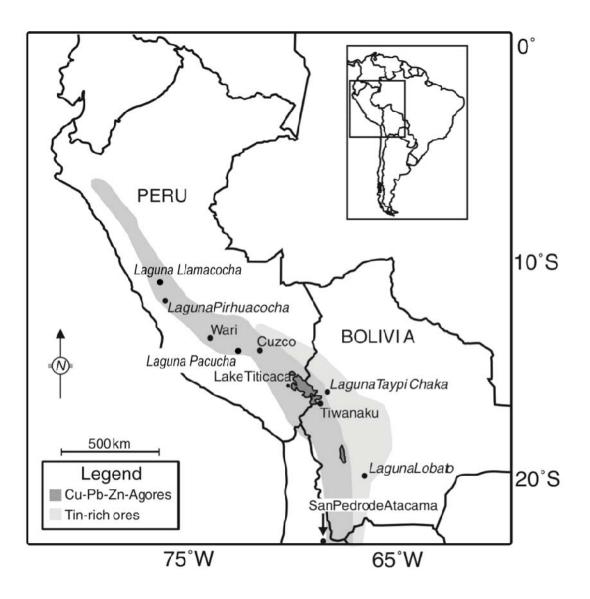


Figure 12. Map of study sites. Re-drawn from Cooke et al., 2009

4.2.3 Laguna Taypi Chaka, Bolivia. (Cooke et al., 2008)

Laguna Taypi Chaka, although not located near any modern mining activities, lies ~40 east of a Tiwanaku archaeological zone. The first major increase in lead concentrations occurs around 400 AD, which coincides with the rise of the Tiwanaku Civilization, suggesting the rise of Tiwanaku smelting activity. Pb concentrations remain high until they start to decrease ~1040 AD,

coincidental with the collapse of the Tiwanaku culture. A large increase in lead concentration occurs during the Inca conquest and the growth of Inca metallurgy, but after the Spanish conquest, mining activities are focused on Cerro Rico and smelting activity falls in the Bolivian Altiplano.

4.2.4 Laguna Llamacocha, Peru. (Cooke et al., 2009)

Situated in the Peruvian Andes, Laguna Llamacocha lies ~60 km southeast of Cerro de Pasco, which became the worlds largest producer of silver in the 1700s. The initial increase of lead concentrations around 600 AD can be attributed to the onset smelting during the Wari expansion in Peru. Lead concentrations continue to rise over time, with little to no effect seen during the fall of the Wari Empire and Hg increases significantly after 1600 AD, and especially during Colonial smelting activities. This is most likely due to the switch to mercury amalgamation as the primary metallurgical process. Considerable increases in all metal concentrations are notable during the Industrial period.

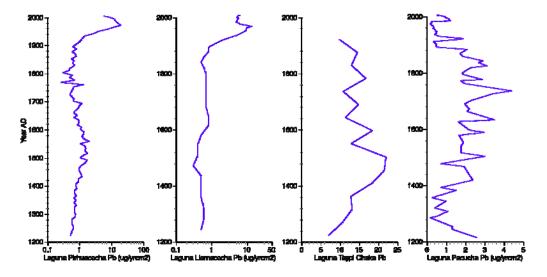


Figure 13. Pb flux vs. Year graphs for Laguna Pirhuacocha (Cooke et al., 2007), Laguna Llamacocha (Cooke et al., 2009), Laguna Taypi Chaka (Cooke et al., 2008), and Laguna Pacucha.

5.0 CONCLUSION

The sediment record from Laguna Pacucha reveals a nearly 1000 year long metal record from the Andahuaylas region of Peru. The sediments indicate a major density change around 1225 AD, which coincides with a regional drought (Bird et al., 2010). The changes in element concentrations through the core provide the groundwork for a compelling story of the area. Increases in zinc, arsenic, and copper around 1225 AD are indicative of copper smelting, and could support the possibility that the Curamba archeological site was used primarily for smelting copper, rather than silver. The similar profiles of a majority of the elements between 1550 and 1850 may indicate that some of the metal concentrations have less to do with smelting than another explanation, such as land use change.

Laguna Pacucha is one in a series of studies that use metal concentrations in lake sediments to reconstruct pollution history in Peru and Bolivia, an area where is a historical legacy of metallurgy but little archeological work. While Laguna Pacucha does not necessarily provide a definitive metal pollution record, it does show evidence of likely copper smelting and, with future research, could certainly provide an interesting record of land use change and the relationship of the indigenous people to the Andahuaylas region of Peru.

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BIBLIOGRAPHY

- Abbott, M.B., and Stafford, T.W. (1996). Radiocarbon geochemistry of modern and ancient arctic lake systems, Baffin Island, Canada. *Quaternary Research* **45**, 300-311.
- Abbott, M.B. and Wolfe, A.P. (2003). Intensive pre-Incan metallurgy recorded by lake sediments from the Bolivian Andes. *Science* **301**, 1893–1895.
- Abbott, M.B., Binford, M.W., Brenner, M., Kelts, K.R. (1997). A 3500 14-C yr High-Resolution Record of Water-Level Changes in Lake Titicaca, Bolivia/Peru. *Quaternary Research* 47, 169-180.
- Appleby, P., and F. Oldfield. (1978). The calculation of lead-210 dates assuming a constant rate of supply of unsupported ²¹⁰Pb to the sediment. *Catena* **5**, 1-8.
- Bird et al. 2010. In review. A 2300-year-long annually resolved record of the South American summer monsoon from the Peruvian Andes. *PNAS*.
- Bauer, B. S. and Covey, R. A. (2002). Processes of State Formation in the Inca Heartland (Cuzco, Peru). *American Anthropologist* **104**, 846–864.
- Bauer, B.S., and Kellett, L.C.. (2010). Cultural transformations of the Chanka homeland (andahuaylas, Peru) during the late intermediate period (A.D. 1000-1400). *Latin American Antiquity* 21.1 87 (25)
- Branvall, M.L., Kurkkio, H., Bindler, R., Emteryd, O., and Renberg, I. (2001). The role of pollution versus natural geological sources for lead enrichment in recent lake sediments and surface forest soils. *Environmental Geology* 40, 1057-1065

- Burger, R.L. and Gordon, R.B. (1998). Early Central Andean Metalworking from Mina Perdida, Peru. *Science* **282** (5391), 1108-1111.
- Chepstow-Lusty, A.J., Frogley, M.R., Bauer, B.S., Leng, M.J., Boessenkool, K.P., Carcaillet, C., Ali, A.A., and Gioda, A. (2009). Putting the rise of the Inca Empire within a climatic and land management context. *Climate Past* 5, 375-388.
- Cooke, C.A., Abbott, M.B., and Wolfe, A.P. (2008). Late-Holocene atmospheric lead deposition in the Peruvian and Bolivian Andes. *The Holocene* **18**, 353–359.
- Cooke, C.A., Abbott, M.B., Wolfe, A.P., and Kittleson, J.L. (2007). A millennium of metallurgy recorded by lake sediments from Morococha, Peruvian Andes. *Environmental Science & Technology* **41**, 3469–3474.
- Cooke, C.A., Wolfe, A.P., and Hobbs, W.O. (2009). Lake-sediment geochemistry reveals 1400 years of evolving extractive metallurgy at Cerro de Pasco, Peruvian Andes. *Geology* **37**(11), 1019-1022.
- Garner, R.L. (1988). Long-Term Silver Mining Trends in Spanish America: A Comparative Analysis of Peru and Mexico. *The American Historical Review* **93** (4).
- Graney, J.R., Halliday, A.N., Keeler, G.J., Nriagu, J.O., Robbins, J.A., and Norton, S.A. (1995). Isotopic record of lead pollution in lake sediments from the northeastern United States. *Geochimica et Cosmochimica Acta* 59, 1715-1728.
- Hemming, John. (1993). The conquest of the Incas. London: Macmillan.Schultze, C.A., Stanish, C., Scott, D.A., Rehren, T., Kuehner, S., and Feathers, J.K. (2009). Direct Evidence of 1,900 years of indigenous silver production in the Lake Titicaca Basin of Southern Peru. PNAS 106 (41). 17280–17283.

- Heiri, O., Lotter, A.F., and Lemcke, G. (2001). Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology* 25, 101–110.
- Hillyer, R., Valencia, B.G., Bush, M.B., Silman, M.R., Stenitz-Kannan, M. (2009). A 24,700-yr paleolimnological history from the Peruvian Andes. *Quaternary Research* **71**, 71-82.
- Lechtman, H. (1976). A metallurgical site survey in the Peruvian Andes. *Journal of Field Archeology* **3** (1), 1-42.
- Lechtman, H. (1984). "Technologies of Power, the Andean Case." From *Configurations of Power* by Henderson, J. and Netherly, P. Cornell University Press. 1984.
- Luisa, V.P., Casagrande, S.P., Yezena, V.H., Fulle, M.M.K. (2008). The Inca Site metallurgical furnaces of Curamba (Peru): A study using XRD, Mossbauer spectroscopy and dating luminescence methods. *Bulletin de l'Institut Français d'Études Andinos* 37 (3), 451-475
- Parodi, L.V., Casagrande, S.P., Vasquez, Y.H., Fulle, M.M.K. (2008). Los hornos metalurgicos del sitio Inca de Curamba (Peru): estudio por DRX, espectroscopia Mossbauer y datacion por metodos de luminiscencia. *Boletin del Instituto Frances de Estudios Andinos* 37.
- Perelló, J., Carlotto, V.,, Zárate, A., Ramos, P., Posso, H., Neyra, C., Caballero, A., Fuster, N., and Muhr. R. (2003). Porphyry-Style Alteration and Mineralization of the Middle Eocene to Early Oligocene Andahuaylas-Yauri Belt, Cuzco Region, Peru. *Economic Geology* 98, 1575 - 1605.
- Petersen, G. (2010). "Mining and Metallurgy in Ancient Peru." trans. Brooks, W.E. *The Geological Society of America*. Special Paper **467**.
- Reimer *et al.* (2009). IntCal09 and Marine09 radiocarbon age calibration curves, 0-50,000 years cal BP. *Radiocarbon* **51**, 1111-1150.

- Renberg, I., Persson, M.W., Emteryd, O. (1994). Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. *Nature* **368**, 323-326.
- Rosman, K.J.R., Chisholm, W., Boutron, C.F., Candelone, J.P. and Hong, S. (1994). Isotopic evidence to account for changes in the concentration of lead in Greenland snow between 1960 and 1988. *Geochimica et Cosmochimica Acta* 58, 3265–69.
- Rosman, K.J.R., Chisholm, W., Hong, S., Candelone, J., and Boutron, C.F. (1997). Lead from
 Carthiaginian and Roman Spanish Mines Isotopically Identified in Greenland Ice Dated from
 600 B.C. to 300 A.D. *Environmental Science and Technology* **31** (12), 3413-3416.
- Stuiver, M. and Reimer, P.J., 1993, Extended ¹⁴C data base and revised CALIB 3.0 ¹⁴C age calibration program, Radiocarbon **35**, 215-230
- ter Braak, C.J.F., and Šmilauer, P., 1998, CANOCO Reference Manual and User's Guide to Canoco for Windows: Software for Canonical Community Ordination (version 4): Ithaca, New York, Microcomputer Power, 352 p.