

Pre-Colombian Mercury Pollution Associated with the Smelting of Argentiferous Ores in the Bolivian Andes

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Abstract The development of the mercury (Hg) amalgamation process in the mid-sixteenth century triggered the onset of large-scale Hg mining in both the Old and New Worlds. However, ancient Hg emissions associated with amalgamation and earlier mining efforts remain poorly constrained. Using a geochemical time-series generated from lake sediments near Cerro Rico de Potosí, once the world's largest silver deposit, we demonstrate that pre-Colonial smelting of Andean silver ores generated substantial Hg emissions as early as the twelfth century. Peak sediment Hg concentrations and fluxes are associated with smelting and exceed background values by approximately 20-fold and 22-fold, respectively. The sediment inventory of this early Hg pollution more than doubles that associated with extensive amalgamation following Spanish control of the mine (1574–1900 AD). Global measurements of [Hg] from economic ores sampled world-wide indicate that the phenomenon of Hg enrichment in non-ferrous ores is widespread. The results presented here imply that indigenous smelting constitutes a previously unrecognized source of early Hg pollution, given naturally elevated [Hg] in economic silver deposits.

Keywords Mercury · Andes · Smelting · Amalgamation · Colonial

INTRODUCTION

The global mercury (Hg) cycle has been demonstrably impacted by humans. Emissions of Hg are of worldwide concern because of the long atmospheric residence time (6–24 months) of atmospheric elemental Hg (Hg^0), which favors homogenization of atmospheric Hg on a hemispheric scale. Importantly, linkages between inputs of

anthropogenic Hg, especially from the atmosphere, and the formation of monomethylmercury (CH_3Hg) have not been firmly established, and methylated species of Hg can bioaccumulate through food chains to concentrations that are potentially dangerous for top-level consumers. Natural and anthropogenic sources release approximately 5,200 and 2,900 Mg of Hg annually to the atmosphere, though natural emissions include the recycling of some (unknown) amount of Hg that was deposited historically. The most important anthropogenic sources of Hg emissions are thought to include: fossil-fuel consumption ($1,422 \text{ Mg year}^{-1}$), artisanal small-scale gold mining and processing (400 Mg year^{-1}), waste disposal (187 Mg year^{-1}), cement production (236 Mg year^{-1}), and non-ferrous metal manufacturing (310 Mg year^{-1}) (Pirrone et al. 2009), though considerable uncertainty about the absolute magnitude of these emissions exists. Two of these extractive activities, artisanal gold mining and non-ferrous metal production, have long histories predating the industrial revolution, raising the possibility that pre-industrial activities generated large-scale Hg emissions.

Pre-industrial emissions of heavy metals associated with mineral extraction have been convincingly demonstrated in both the New and Old Worlds. In Europe, the earliest indications of atmospheric lead (Pb) pollution date to ~1500 BC. Early Pb emissions were transported atmospherically across the Northern Hemisphere, and are registered within ice cores from Greenland (Hong et al. 1994), lake sediments from Northern Fennoscandia (Brännvall et al. 2001, Renberg et al. 1994), and peat cores from Europe (Martínez-Cortizas et al. 2002; Monna et al. 2004). Similar early pollution signatures have been reported from central China associated with metal production during the early Han Dynasty (206 BC–220 AD) (Lee et al. 2008). In the New World, early metal pollution appears to be limited

to the South American Andes, where argentiferous galena [(Pb, Ag)S] was heavily utilized during silver production (400–1000 AD) (Abbott and Wolfe 2003; Cooke et al. 2007, 2008, 2009b).

Despite this extensive history of Pb pollution, there is no evidence for Hg emissions associated with early smelting of non-ferrous ores. Non-ferrous ores contain Hg as an impurity (Kerfoot et al. 2002; Schwartz 1997), and the smelting of non-ferrous ores today constitutes a major source of atmospheric Hg emissions. The hypothesis, therefore, emerges that, analogous to Pb, artisanal mining and smelting of non-ferrous ores may have been a significant source of Hg to the preindustrial atmosphere. Testing this hypothesis is difficult, however, because (i) the Hg content of non-ferrous ore deposits is poorly constrained, and (ii) many of the world's richest ore deposits were exhausted decades, centuries, or even millennia ago. Here, we address these limitations using lake sediment geochemical archives obtained downwind from Cerro Rico de Potosí in the Bolivian Andes, historically the world's largest silver deposit. By exploiting the environmental archive preserved within lake sediments, we infer a temporally continuous regional history of Hg emissions associated with the smelting of world's richest silver ores. We also present a suite of measurements of [Hg] within global ore deposits, suggesting that Hg occurs as a persistent trace contaminant in massive metal deposits. Collectively, our results indicate that smelting of metal-bearing ores constitute a hitherto unrecognized and potentially significant source of pre-industrial Hg emissions to the global atmosphere.

METHODS AND MATERIALS

Study Site

Cerro Rico de Potosí (Fig. 1) was first exploited by pre-Incan metalsmiths a millennium ago (Abbott and Wolfe 2003). Smelting of argentiferous ores was initially conducted in artisanal wind-drafted kilns called *huyaras* (Fig. 2a, b), culminating with the silver riches of the Incan empire. Between initial Colonial control of the mine in 1545 AD and the introduction of Hg amalgamation in 1574 AD, various phases of metallurgical experimentation occurred, typically involving the enslavement of indigenous miners and metallurgists by the Spanish crown. Potosí became the largest consumer of Hg globally in 1574 AD when Hg amalgamation was adopted at the mine (Fig. 2c), a distinction it retained for the next ~300 years. By the mid seventeenth century, the population of Potosí exceeded 160,000 people, making it one of the largest and most economically important cities in the world. Silver

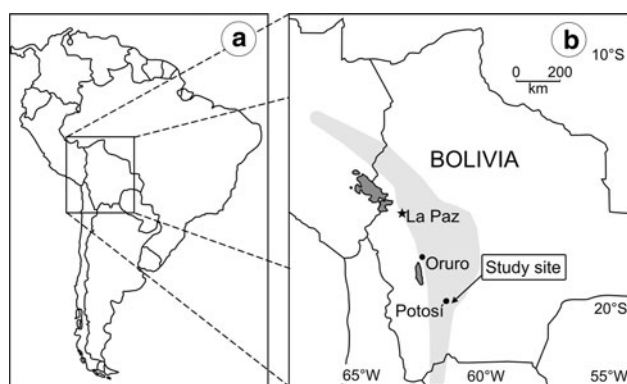


Fig. 1 Maps of **a** South America and **b** Bolivia showing the location of Potosí. The shaded region represents the extent of the Bolivian tin belt

production at Potosí declined until its eventual abandonment in 1930 AD. As the supply of silver progressively declined over the eighteenth and nineteenth centuries, tin production became increasingly important, and peak tin production, driven by heightened demand during WWI, was reached during the early twentieth century. Mining of silver-rich alluvium at the base of Cerro Rico, known as *pallacos* (Bartos 2000), has recently been initiated by the Coeur d'Alene Mines Corporation.

Core Chronology

In order to assess the history of Hg pollution associated with each stage of metallurgical development at Potosí, we exploited the well-dated geochemical record preserved in a nearby lake, Laguna Lobato, situated 6 km east of Cerro Rico. The Laguna Lobato core preserves a continuous record of sedimentation spanning the Holocene, and both the core and the age model used here have been described in detail previously along with geochemical stratigraphies for lead (Pb), silver (Ag), antimony (Sb), bismuth (Bi), and tin (Sn) (Abbott and Wolfe 2003). The chronology for the Laguna Lobato sediment core was developed using ^{210}Pb , ^{137}Cs , and ^{14}C radioisotopes.

Sediment Geochemistry

New measurements of total [Hg] were determined on each interval in which sufficient sediment remained from previous analyses. Sediment Hg burdens were quantified using a DMA80 direct mercury analyzer (Milestone Inc.) at the University of Connecticut, Department of Marine Sciences (EPA 1998). Blank values averaged $0.31 \pm 0.25 \text{ ng g}^{-1}$ ($n = 22$); recoveries of standard reference material MESS-3 (marine sediment) averaged $90 \pm 2 \text{ ng g}^{-1}$ ($n = 18$) and were in agreement with certified values ($91 \pm 9 \text{ ng g}^{-1}$);

Fig. 2 **a** Painting from the Colonial era of smelting operations at Cerro Rico de Potosí using Incan *huyaras* (artist unknown). **b** Model of a clay *huyara* used to smelt argentiferous ores at the time of Colonial contact. The small slots vented the kiln, and the molten metal was retrieved from the large basal opening. Ore was introduced from above, onto the fuel. The model was created by the late Jeanne M. Wolfe (McGill University). **c** A 1584 painting by an unknown artist of Cerro Rico de Potosí, with trains of llamas transporting ore from the mountain to one of the amalgamation facilities built to process the ore. The paintings are courtesy of *The Hispanic Society of America*



and the relative percent difference between duplicate measurements of the same sample averaged $5.30 \pm 0.03\%$ ($n = 19$).

Total Hg pollution burdens for the core were calculated as the product of sediment dry mass (g m^{-2}) and Hg concentration (mg g^{-1}). Core intervals lacking [Hg] data were estimated using linear interpolation between measurements, and intervals within each cultural period (i.e. Colonial, pre-Colonial, and industrial) were summed.

Global Ore Geochemistry

Mercury is known to occur in trace amounts in sulfide ores (e.g., PbS), and can form natural alloys with silver (including arquerite (Ag_{12}Hg), kongspertite [α -(Ag,Hg)], and moschellandsbergite [γ -(Ag,Hg)]). However, direct measurements of Hg content in non-ferrous ores are limited. In order to assess the possible larger implications of

our results, we measured the Hg content in a suite of ore samples collected from mines around the world. Ores were grouped into five broad categories based on primary ore mineralogy: native copper, silver ores, copper-silver ores, zinc ores, and native silver.

For world ore comparisons, samples from the Seaman Mineral Museum (Michigan Technological University) were digested in a Milestone Thos 900 microwave digester, and analyzed for total mercury by the cold vapor technique using a Perkin-Elmer Model 5000 and a Perkin-Elmer MHS-10 mercury-hydride system. For every set of 10 samples, a minimum of two sets of standards were analyzed, in addition to two procedural blanks and one duplicate sample. Natural matrix certified reference materials included: Metals of soil/sediment #4 (Ultra Scientific; SRM 2704a) and Buffalo River sediment (National Bureau of Standards, NIST 1990). Mercury recovery from these reference materials was $96.7 \pm 9.0\%$ ($n = 35$).

RESULTS

Core Chronology

The chronology of the Laguna Lobato sediment core has been published and described previously (Abbott and Wolfe 2003) and, therefore, is only summarized here (Fig. 3a). The upper 23.5 cm of the Laguna Lobato sediment core contained inventories of unsupported ²¹⁰Pb, to which the constant rate of supply (CRS) model was applied. The resultant ²¹⁰Pb age model was verified by matching peak sediment ¹³⁷Cs activity with the CRS model year for 1963 AD. Of the nine calibrated ¹⁴C dates obtained on plant macrofossils at Laguna Lobato only the uppermost two are shown here, as they encapsulate the period of interest (the last ~1000 years). Sedimentation rates for the core were calculated as the product of linear sediment accumulation rates between dated horizons (cm year⁻¹) and dry bulk density (g cm⁻³) (Fig. 3b). We note that while sedimentation rates for this portion of the sediment record are relatively poorly constrained, they are broadly consistent with long-term sedimentation rates over Holocene within Laguna Lobato (Abbott et al. 1997).

Sediment Geochemistry

Laguna Lobato sediment [Hg] rises dramatically above background ~1100 AD, in concert with a similar rise in [Ag], and following the initial rise in [Pb] (~1000 AD; Fig. 4). These features are not artifacts of variable sedimentation, and are expressed whether the data are

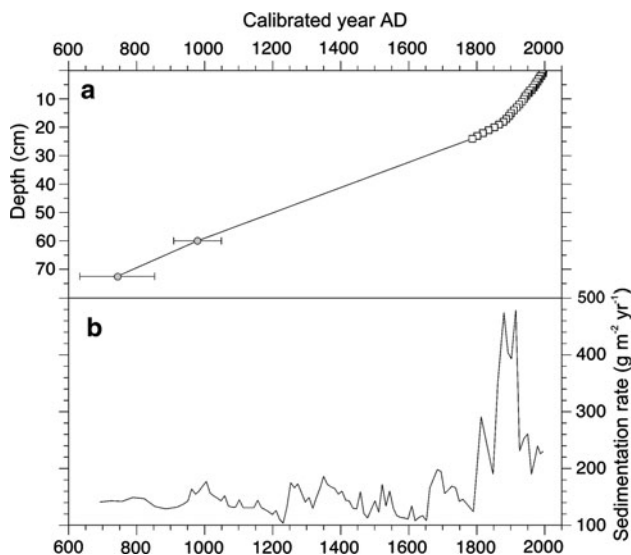


Fig. 3 **a** Composite age depth model for the Laguna Lobato sediment core. Squares represent CRS ²¹⁰Pb dates whereas circles are calibrated AMS ¹⁴C dates with associated 2σ error ranges. **b** Down-core sedimentation rate for the Laguna Lobato sediment core

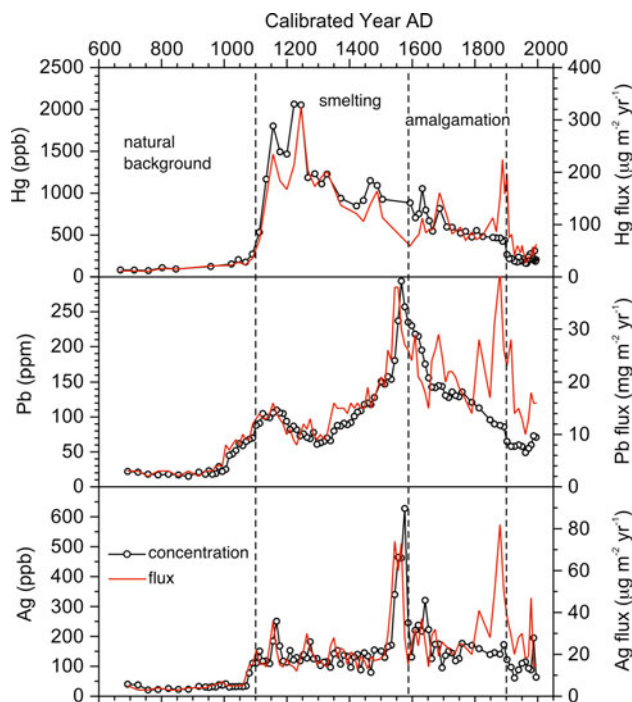


Fig. 4 Stratigraphic profiles of concentrations (circles) and fluxes (red lines) for Hg, Pb, and Ag in Laguna Lobato sediment. Note the different units between Pb (ppm; mg m⁻² year⁻¹) and Ag and Hg (ppb; µg m⁻² year⁻¹). Vertical dashed lines separate background, smelting and amalgamation time periods. (Color figure online)

presented as metal concentrations or fluxes. By 1250 AD, sediment [Hg] and Hg flux attain peak values of 2,000 ppb, and 325 µg m⁻² year⁻¹, respectively. After 1300 AD, and into the Colonial era (1554–1900 AD), Hg steadily decreases, whereas Pb increases and Ag remains relatively constant at ~100 ppb. While both Hg concentration and flux are characterized by a declining trend through the Colonial era, they remain elevated relative to background values ([Hg]: >300 ppb; Hg flux: 80 µg m⁻² year⁻¹).

Flux rates for all three metals experience a brief increase during the late nineteenth century, which is attributable to an increase in sedimentation rates at this time (Fig. 4). During the twentieth century, concentrations and fluxes for all three metals decline to their lowest values since enrichment first appeared ~1000 years before present.

World Ore Geochemistry

Figure 5 and Table 1 summarize the [Hg] results for the 109 ore samples analyzed. There is considerable heterogeneity in [Hg] both between and among the four groups of ores. Native copper ores and silver ores contain the lowest Hg concentrations, but span nearly three orders of magnitude in [Hg]. Native silver ores contain on average the highest concentrations of Hg and are characterized by the greatest variability in [Hg] spanning nearly four orders of

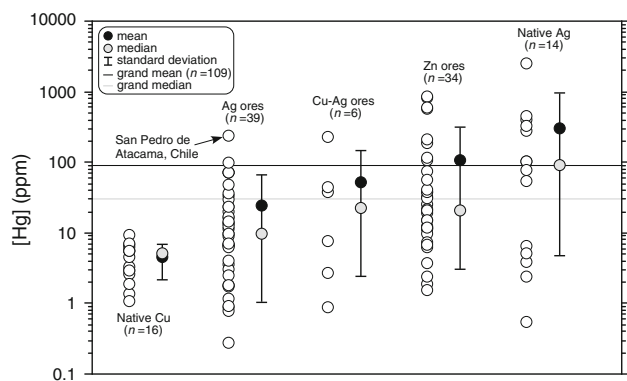


Fig. 5 Comparison of [Hg] for five types of ore deposits indicating both individual measurements and the mean, median, and standard deviation of each group and the grand mean and median for all samples combined

Table 1 Summary statistics of Hg concentrations (ppm) within worldwide ore samples

Ore type	<i>n</i>	Max	Min	Mean	S.D.	Median
Native Ag	14	2548.0	0.6	314.5	662.8	93.3
Zn ores	34	872.2	1.6	119.9	235.1	21.4
All ores	109	2548.0	0.3	90.4	11.9	283.3
Cu-Ag ores	6	230.1	0.9	54.2	88.2	22.9
Ag ores	39	244.3	0.3	25.0	43.4	9.9
Native Cu	16	9.4	1.1	4.6	2.3	5.2

The complete data set is available on request from the authors

magnitude (0.3–2548 ppm). The second highest [Hg] measured was on a Ag-rich ore from San Pedro de Atacama, Chile, which is located <400 km from Potosí. While we lacked ore from Potosí or even Bolivia, the high [Hg] noted from northern Chile may suggest regional enrichment of Hg in silver ores from the Andean *altiplano*.

DISCUSSION

Pre-Columbian smelting at Cerro Rico de Potosí was conducted in wind-drafted clay furnaces called *huyaras*, in which galena (PbS) was used as a flux. The first Columbian conquistadors to visit Potosí recorded the use of both *huyaras* and Pb flux by Incan metalsmiths (Bakewell 1984). The legacy of this technology is preserved in lake sediment archives surrounding several metallurgical centers in the Andes (Abbott and Wolfe 2003; Cooke et al. 2007, 2008, 2009b). Pb-based smelting continued to be relied upon to win silver throughout the pre-Colonial era. Surface ores at Potosí were depleted shortly after the Spanish took control of the mine in 1545 AD (Craig 1989), and *huyara*-based smelting was largely replaced by

mercury amalgamation, which facilitated extraction from lower-grade ores recovered from subterranean audits (Nriagu 1994). Mercury amalgamation continued at Potosí until the early twentieth century, when silver mining was largely abandoned.

The stratigraphies of Pb and Ag in Laguna Lobato sediment reflect volatile losses of these metals during the smelting of argentiferous galena (Abbott and Wolfe 2003). However, [Hg] and Hg flux are highest during the pre-Colonial era. Enrichment factors (EF) are unitless ratios in which metal concentrations at each interval are normalized to the average background metal concentration, providing a relative measure of the increase in Hg, Pb, and Ag (Fig. 6). Background concentrations of Hg, Pb, and Ag are 95 ± 19 ppb, 20 ± 4 ppm, and 31 ± 7 ppb, respectively. These background concentrations are comparable to the bulk composition of the upper continental crust (Wedepohl 1995), suggesting little pre-industrial enrichment of these metals in catchment soils surrounding Laguna Lobato, despite its proximity to the world's largest silver deposit. Of the three metals presented here, Hg shows the greatest relative increase, with EF exceeding 15 during the pre-Inca period of 1100–1250 AD (Fig. 6). In contrast, Pb and Ag EF remain tightly coupled remaining between 5 and 15 throughout much of the record, despite the fact that they are characterized by very different absolute concentrations.

The relatively large pre-Colonial increase in Hg occurs despite the fact that Pb, not Hg, was involved in the smelting process. At Huancavelica in central Peru, Cinnabar (HgS) has been mined continuously since ~1400 BC (Cooke et al. 2009a). Indeed, the early onset of mining at Huancavelica suggests cinnabar was one of the first minerals to be exploited in the Andes. While the Inca may have experimented with the heating or retorting of cinnabar, the early use of cinnabar appears to have been limited to its use

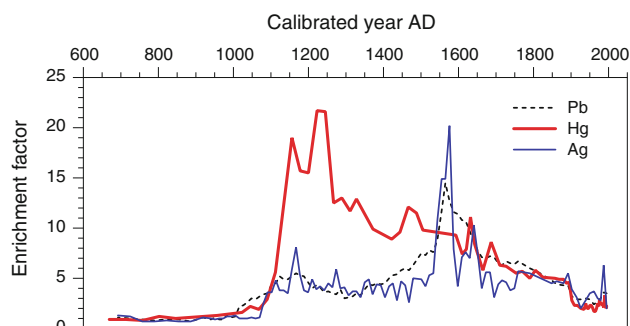


Fig. 6 Temporal evolution of metal enrichment factors (EF) for Ag (blue), Hg (red) and Pb (black). Enrichment factors are unitless ratios calculated by normalizing concentrations from each interval to the average background metal concentration, taken here to be pre-1000 AD. Average background concentrations of Hg, Pb, and Ag are 95 ± 19 ppb, 20 ± 4 ppm, and 31 ± 7 ppb, respectively. (Color figure online)

as a pigment (vermillion). We know of no documentary or archeological evidence to suggest pre-Colonial use of Hg to facilitate silver extraction. Our preferred interpretation is, therefore, that the extensive pre-Colonial Hg pollution present in Laguna Lobato sediment represents native Hg within the silver ore at Potosí. Hg has a high vapor pressure and any Hg present as a trace-constituent in the ore would have been rapidly emitted to the atmosphere during smelting. The highest-grade surface ores may have exceeded 25% Ag (Craig, 1989), and apparently contained large amounts of Hg as well. Moreover, total [Hg] within the ore appears to have changed with time, as Hg EF gradually decreases throughout the pre-Colonial era (Fig. 6).

There is independent support for our suggestion that pre-Colonial smelting released large quantities of Hg to the regional environment. Cerro Rico de Potosí is drained by the Río Pilcomayo, which is the largest river system in southern Bolivia. To estimate the environmental impact of both modern and ancient mining activity on the Río Pilcomayo, Hudson-Edwards et al. (2001) measured the concentration of Pb, Ag, Hg, and other metals in contemporary and buried channel deposits and in modern and ancient terraces down the course of the Río Pilcomayo. Remarkably, these authors found elevated Hg burdens (but not Pb, Ag, or any other metals) in organic-rich terrace deposits that ¹⁴C date to 1220–1435 AD, thus predating the adoption of Hg amalgamation at Potosí. The concentration of Hg in these ancient organic-rich units exceeded 5,000 ppb, and they contained the highest Hg levels measured along the Río Pilcomayo. However, Hudson-Edwards et al. (2001) were unaware of the long pre-Colonial mining history at Potosí and therefore lacked an explanation for the pre-Colonial Hg enrichment. Our new results reconcile these data by suggesting that pre-Colonial mining activities were a vector for both atmospheric Hg emissions and increased Hg supply to the Río Pilcomayo.

The Spanish arrived at Potosí in 1545 AD and immediately took control of mining at Potosí (Bakewell 1984). Soon after silver-rich surface ores were depleted and

mercury amalgamation was adopted as the predominate ore-processing method. Mercury amalgamation was performed in large open-air patios and was thus known as patio amalgamation. The patio process allowed for large amounts of ore, containing as little as 400 g Ag per 1 Mg of ore to be extracted profitably (Nriagu 1994). In modern mercury amalgamation operations, the ratio of mercury lost to silver produced ($R_{\text{Hg/Ag}}$) is commonly between 1.0 and 1.5 (Lacerda 2003; Pfeiffer and Lacerda 1988; van Straaten 2000). In Tanzania and Zimbabwe, 70–80% of the Hg lost is emitted to the atmosphere whereas only 20–30% is lost to tailings, soils, stream sediments and water (van Straaten 2000). Similar results have been reported from Brazil (Lacerda 1997). During the Colonial era, Nriagu (1993, 1994) suggested a similar average $R_{\text{Hg/Ag}}$ of 1.5, and that 60–65% of the mercury lost was released to the atmosphere. This suggests that New World amalgamation activities released ~156,000 Mg of mercury to the atmosphere and in excess of 250,000 Mg of mercury to the environment Nriagu (1993, 1994). During the Colonial era, Potosí accounted for 25–50% of the total silver produced globally (Fisher 1977), and, therefore, likely emitted between 50,000 and 100,000 Mg of mercury to the atmosphere. These estimates remain highly conservative because (i) patio amalgamation likely had a higher $R_{\text{Hg/Ag}}$ than modern-day mining operations and (ii) some of the silver produced during the Colonial era went unregistered.

To estimate atmospheric Hg emissions associated with pre-Colonial smelting, we calculated sediment Hg pollution burdens for pre-Colonial, Colonial, and industrial time periods (Table 2). The excess Hg pollution burden represents the difference between the total inventory of Hg on the lake bottom and the expected natural inventory, if no anthropogenic Hg enrichment had occurred. Approximately 70% of the total Hg pollution inventory in Laguna Lobato sediment predates the adoption of amalgamation. As Hg amalgamation at Cerro Rico generated a minimum of 50,000 Mg of atmospheric mercury emissions, our sedimentary Hg record suggests that at least 125,000 Mg were emitted to the atmosphere during pre-Colonial

Table 2 Average [Hg], Hg enrichment factors (EF), Hg flux, and Hg pollution burdens for different temporal intervals including: Inca and pre-Inca smelting, Colonial amalgamation, and industrial mining

Period	[Hg] (ng g ⁻¹)	Hg EF	Hg flux (µg m ⁻² year ⁻¹)	Hg pollution burdens (mg cm ⁻²)	n
Pre-pollution (pre-1100 AD)	95	1	14	-	6
Inca & pre-Inca (1100–1550 AD)	1049	11	143	69	21
Colonial amalgamation (1575–1900 AD)	613	6	104	27	20
Industrial (post-1900)	214	2	55	4	24

smelting. While this estimate possesses several caveats, the largest being that Hg pollution burdens within Laguna Lobato sediment can be directly related to mercury emissions at Potosí through time, it remains a conservative estimate because a greater fraction of ore-hosted mercury would have been emitted relative to amalgamation, where some mercury was recaptured.

Mercury in Global Ores

Measurements of [Hg] within ores suggest that Hg enrichment in non-ferrous ores is widespread (Table 1; Fig. 5). Hg concentrations in the sampled ores ($n = 109$) average 90.4 ± 11.9 ppm, which is $\sim 1,500$ times the lithospheric average of 0.06 ppm (Wedepohl 1995). Hg is a chalcophile element and the small difference between the radii of Hg, copper, silver, lead, and other heavy metals, makes it possible for Hg to replace these metals within mineral structures. However, considerable heterogeneity in the [Hg] of ores exists both within and among ore types, because [Hg] is frequently controlled by mineralogical variability or local depositional conditions. In a detailed study of the Hg content of Zn deposits, Schwartz (1997) suggested that the Hg content of Zn ores also depends on ore type and age. For example, sphalerites (ZnS) from Proterozoic exhalative deposits contain more Hg than those from Phanerozoic deposits. However, concentrations of Hg are high in many types of ore (Fig. 5), and Hg occurrences in copper, silver, and gold ores are only beginning to be fully appreciated (Kerfoot et al. 2004, 2009; Schwartz 1997). Nonetheless, the existing data are sufficient to identify a number of coherent trends, such as the consistently elevated [Hg] of native Ag deposits relative to other ore types (Table 1). The results of our analysis [Hg] in global ores suggest that non-ferrous metal smelters may serve as important point sources for Hg emissions that have, until now, been severely underestimated in both pre- and post-industrial contexts.

CONCLUSIONS

The sediment record from Laguna Lobato near Potosí demonstrates a long history of New World metal pollution extending back over 1000 years. Most previous studies have focused on lead, largely because of its immobility in lake, peat, and ice core deposits, and the utility of lead stable isotopes for fingerprinting anthropogenic emissions. However, a growing body of evidence suggests significant and widespread mercury pollution beginning as early as $\sim 1,400$ BC in the New World (Cooke et al. 2009a) and 500 BC in the Old World (Martínez-Cortizas et al. 1999). Early mercury pollution resulted from both the mining of

cinnabar (Cooke et al. 2009a; Martínez-Cortizas et al. 1999) and the use of mercury in amalgamation (Cooke et al. 2009b). The results from this study demonstrate that pre-Colonial silver smelting was potentially a major source of Hg pollution in the Andes. If these results apply to early silver, copper, and gold extraction elsewhere, as is suggested by elevated [Hg] in many economic ore types, extensive pre-industrial mercury pollution may be similarly encountered elsewhere, for example in association with the Roman Empire in Europe. Consequently, the possibility exists that pre-industrial anthropogenic mercury pollution inventories have been grossly and systematically underestimated.

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