

Widespread pollution of the South American atmosphere predates the industrial revolution by 240 y

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In the Southern Hemisphere, evidence for preindustrial atmospheric pollution is restricted to a few geological archives of low temporal resolution that record trace element deposition originating from past mining and metallurgical operations in South America. Therefore, the timing and the spatial impact of these activities on the past atmosphere remain poorly constrained. Here we present an annually resolved ice core record (A.D. 793–1989) from the high-altitude drilling site of Quelccaya (Peru) that archives preindustrial and industrial variations in trace elements. During the precolonial period (i.e., pre-A.D. 1532), the deposition of trace elements was mainly dominated by the fallout of aeolian dust and of ash from occasional volcanic eruptions, indicating that metallurgic production during the Inca Empire (A.D. 1438–1532) had a negligible impact on the South American atmosphere. In contrast, a widespread anthropogenic signal is evident after around A.D. 1540, which corresponds with the beginning of colonial mining and metallurgy in Peru and Bolivia, ~240 y before the Industrial Revolution. This shift was due to a major technological transition for silver extraction in South America (A.D. 1572), from lead-based smelting to mercury amalgamation, which precipitated a massive increase in mining activities. However, deposition of toxic trace metals during the Colonial era was still several factors lower than 20th century pollution that was unprecedented over the entirety of human history.

paleoenvironment | ice cores | metallurgy | Colonial period | Anthropocene

Formal recognition of the Anthropocene epoch acknowledges the occurrence of an unprecedented impact of human activities on the Earth system (1). The onset of this period is debated; it is assigned within a wide time range that extends from the beginning of the Holocene (~11 kyBP) to the advent of the nuclear era (A.D. 1945) (2), but is most commonly recognized as the beginning of the Industrial Revolution (1780s to 1830s) (3).

Environmental archives are important recorders of both past natural variability and human activities, especially in regions that have long histories of mining and metallurgy but that lack long-term monitoring data on the emission, cycling, and deposition of trace elements, some of which are toxic at low concentrations. Ice cores from the remote polar ice sheets and high-altitude glaciers receive trace elements exclusively from the atmosphere (4, 5) and can therefore be used to precisely assess the possible large-scale impact of anthropogenic activities through time (6, 7). In this respect, they also offer a unique, global perspective on current efforts to define the onset of the Anthropocene as defined by the International Union of Geological Sciences.

Increases in the concentration of both lead (Pb) and copper (Cu) in ice cores recovered from Greenland (8, 9) and of antimony (Sb), arsenic (As), and bismuth (Bi) in ice cores from the Canadian Arctic (10, 11) caused by anthropogenic activities as early as 500 B.C. have been noted. Preindustrial Pb concentration increases in Greenland have been linked to Pb mining and smelting performed in the Mediterranean region during the Greek, Roman, and Medieval periods (8, 12), indicating the

hemispheric-scale impact of early anthropogenic activities. In contrast, ice cores recovered from midlatitudes provide evidence for anthropogenic aerosol emissions from the late 19th century in the European Alps (13, 14) and from the middle of the 20th century in the Himalaya (6, 15). This suggests an asynchronous postindustrial impact on the atmosphere in various parts of the Northern Hemisphere.

In the Southern Hemisphere, the earliest evidence for anthropogenic trace metal emissions comes from sediment cores recovered from lakes located downwind of major metallurgical centers in Peru and Bolivia (16–18). Exploitation of mineral resources began as early as 1800 B.C. in Peru and Bolivia (19), and approximately 3,000 y later, the Inca Empire (A.D. 1438–1532) disseminated metallurgy across the Andes, which, by this point, included the smelting of a range of nonferrous ores (20). At the time of the Spanish conquest in A.D. 1532, Inca smelting was conducted using a *huyara*, a wind-drafted furnace made of clay (21, 22). The Spanish Conquistadors were primarily concerned with silver (Ag) production, and a technological breakthrough occurred in A.D. 1572 when mercury (Hg) amalgamation was imported from Mexico and adopted at Cerro Rico de Potosí, the world's largest Ag deposit located in southern Bolivia (23) (Fig. 1). Hg amalgamation, which used liquid elemental Hg to extract Ag from low-grade (i.e., waste) ores, triggered an

Significance

An exceptionally detailed ice core from the high-altitude location of Quelccaya (Peru) contains compelling evidence that the well-known metallurgic activities performed during the Inca Empire (A.D. 1438–1532) had a negligible impact on the South American atmosphere. In contrast, atmospheric emissions of a variety of toxic trace elements in South America started to have a widespread environmental impact around A.D. 1540, ~240 y before the industrial revolution when colonial metallurgy began to pollute the Andean atmosphere. 20th century atmospheric pollution levels were the highest on record and remain unprecedented over the entirety of human history.

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the flux and EFC of Pb with the corresponding trends determined in sediment cores extracted in proximity of the past primary mining operations in Peru and Bolivia (16–18) and in the peat record from Tierra del Fuego (25) reveals common long-term temporal patterns with a relative Pb maximum during the Colonial period and with the most prominent feature in Pb deposition during the 20th century (Fig. 3).

The Pre-Inca Period

Trace element concentrations in Quelccaya are generally rather stable and low before around A.D. 1450 (Fig. 2 and Figs. S2 and S3), with some notable exceptions (see below). In addition, trace element EFC values are ~ 1 in most cases (Dataset S1), providing evidence that over this period, trace element input to the ice cap was dominated by the deflation, atmospheric transport, and deposition of aeolian dust from the deglaciated margins of Quelccaya. This is particularly evident for Al, As, Co, Fe, Mn, Rb, Ti, V, and U (see also Fig. S4B). Nevertheless, sporadic increases in some trace element EFC values are apparent in the oldest part of

the ice core record (Fig. 2 and Fig. S2). The earliest of these are brief (5–10 y) increases in the EFC values of elements such as Ag, Bi, Cd, Cr, Cu, Pb, Sb, and Tl, which occur at least 15 times between A.D. 793 and A.D. 1450. These increases in EFC indicate the occasional incorporation of aerosols with elemental compositions different from local dust (Dataset S2) and in most cases can likely be attributed to the fallout of ash injected into the South American atmosphere from the multiple active volcanoes throughout the Andes (SI Text and Dataset S3). During the pre-Inca period (A.D. 793–1450), Ag, Cu, and Mo are the only elements that persistently show deviations from the local crustal composition, as they exhibit median EFC values of 2.0, 3.9, and 5.9, respectively (Dataset S1). While an origin from pre-Inca metallurgic activities (for Cu and Mo) or from volcanic quiescent degassing emissions (for Ag) is possible (SI Text and Fig. S4B), no temporal trend in these trace element concentrations or EFC values can be observed before around A.D. 1450.

Pollution During the Colonial Period

We now examine the time period A.D. 1450–1900, covering the expansion of the Inca Empire (A.D. 1438–1532), the Spanish vice-royal period (A.D. 1532–1833), and the first part of the independence of South America from Spanish domination (A.D. 1833–1900). While the EFC values remain low for the lithogenic elements (Al, Fe, Mn, Rb, Ti, U, and V) and slightly high for Ag and Cu, depositional increases and EFC are noted for many elements that are commonly found to be persistently enriched in snow and ice dating to the industrial era (Fig. 2, Figs. S2 and S3, and Dataset S1). Compared with the pre-Inca period, increases in EFC values over the period A.D. 1450–1900 are noticeable in As (1.6 times), Bi (2.2 times), Cd (2.3 times), Co (1.5 times), Cr (1.5 times), Mo (1.8 times), Pb (1.8 times), and Sb (3.5 times) (Fig. 2 and Fig. S2).

A prolonged increase in the concentration and EFC of Bi is noted beginning at around A.D. 1480 (Fig. 2). This precolonial period also marks the expansion of the Inca Empire. The Inca exploited deposits of this metal in the production of Bi bronze, which has been recovered from the Inca citadel at Machu Picchu (29). Thus, we suggest that the increases in Bi, preserved within the Quelccaya ice core, record the introduction by the Inca of a new bronze alloy across the Andes. Remarkably, no increases of other trace elements are apparent during the Inca Empire period, indicating that their overall metallurgic production was much smaller than during the following centuries (see below). This is in general agreement with the low-resolution Pb peat record from the remote location of Tierra del Fuego (25), whose EFC values do not rise above the natural background until after around A.D. 1500 (Fig. 3). The broadly consistent observations from the pristine locations of Quelccaya and Tierra del Fuego confirm that the prolonged increasing trends in Pb and other trace elements recorded in Peruvian and Bolivian sediment cores during the precolonial period (16–18) (Fig. 3) are more likely representative of the local impact of the adjacent metallurgic activities.

High concentrations and unexpected relative minima of the EFC values of Ag, As, Bi, Cd, Cr, Mo, Pb, and Sb can be observed at about the same time (A.D. 1595–1610) (Fig. 2 and Fig. S2). This can be explained by the well-known volcanic fallout from the A.D. 1600 Huaynaputina ash trace element whose composition closely resembles that of Quelccaya dust that we use as a crustal reference (Dataset S2). This large volcanic fallout must have overwhelmed any other possible trace element enrichment during the A.D. 1595–1610 time period, thus impacting the timing of the EFC changes during the Colonial period.

Immediately after the demise of the Inca Empire (A.D. 1532), the concentrations and the EFC values of various trace elements increased, postdating, in some cases, the Spanish conquest of the Inca by about a decade. Trace element EFC values above the

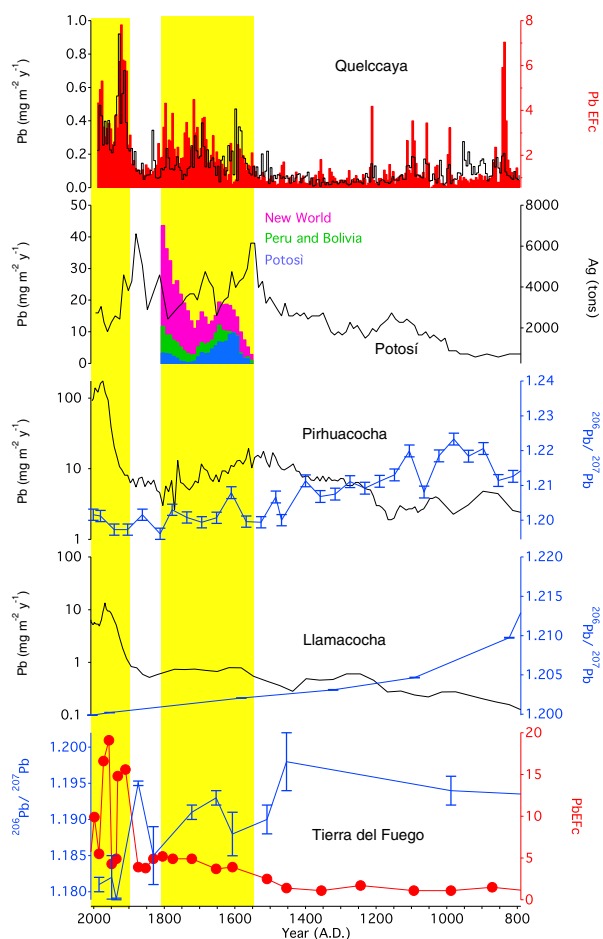


Fig. 3. Pb deposition to South America during the last 1,200 y. Five-year median Pb flux and crustal EFC in the Quelccaya North Dome ice core (this work) are compared with Ag production in Potosí (in blue), Peru–Bolivia (in green), and the New World (in purple; including Peru–Bolivia and Mexico) during the Colonial period (31) and with local Pb fluxes as recorded in sediment lakes in Laguna Potosí (16), Pirhuacochoa (17), and Llamacochoa (18) during the A.D. 793–1989 time period. For Lagunas Pirhuacochoa and Llamacochoa, a low-resolution $^{206}\text{Pb}/^{207}\text{Pb}$ record is also displayed. The Peruvian–Bolivian depositions are compared with the Pb EFC and $^{206}\text{Pb}/^{207}\text{Pb}$ records from the remote site of Tierra del Fuego (25). Vertical yellow bands identify common phases of Pb enrichment in the records. Each record is plotted on its own original timescale.

natural background become detectable at around A.D. 1540 for Cr, Mo, Sb, and Pb. At approximately the same time, step changes in Pb deposition and isotopic composition are recorded in the Peruvian sediment core extracted from Laguna Pirhuacocha (17) and in the peat of the remote location of Tierra del Fuego (25) (Fig. 3). We infer that, when combined with regional and continental evidences, the Quelccaya ice core record of Pb precisely indicates the onset of a widespread impact of colonial metallurgic emission on the South America atmosphere starting at around A.D. 1540 (see discussion below). We note that other EFC changes become detectable in the Quelccaya ice core record but only at around A.D. 1660 for As, Cd, Co, and Cu (Fig. 2 and Fig. S2). We link this apparent two-step EFC increase with the rise of colonial metallurgic emissions combined with the concomitant decade-long interference from the A.D. 1600 Huaynaputina ash fallout.

Compelling evidence for enhanced Ag extraction is provided by the EFC increase in relatively more abundant metals (e.g., Pb), many of which are associated with Ag-bearing minerals. Pb is especially useful in this regard because not only was it used as a flux during smelting by the Inca, but argentiferous galena [(Pb, Ag)S] was an important Ag-bearing mineral exploited historically (20). Starting around A.D. 1540, sustained enrichment of Pb over the natural background (Fig. 3) reflects an increase in mining and Ag production across the Andes (20) that was probably magnified by the adoption of Hg amalgamation (A.D. 1572). While this is a cold process, this new technology most likely resulted in an increased emission of metal-laden dust from extensive milling, which was a fundamental preprocessing step of the amalgamation technique (20).

Variations in Pb EFC and flux to Quelccaya during the Colonial period are also in broad agreement with Ag production in Peru–Bolivia (A.D. 1531–1810) (30, 31) (Fig. 3). The Quelccaya ice core Pb record also resembles Pb fluxes derived from lakes near the main South American Ag mining locations (Fig. 3) (16–18). This supports a Peruvian-Bolivian origin of the Pb excess deposited to the Quelccaya ice cap during the Colonial period. In particular, the Quelccaya Pb record may capture three phases of more intense Ag production in Potosí around A.D. 1600, A.D. 1700, and A.D. 1800 and a pronounced relative minimum at around A.D. 1750 (31) (Fig. 3).

Importantly, a common metallurgic emission and depositional pattern emerges for Pb, Ag, Bi, Cr, Cu, Mo, and Sb during the A.D. 1450–1900 period, indicating a Peruvian-Bolivian metallurgic source for all these trace elements (Fig. S4C). The EFCs of these trace elements increased consistently until around A.D. 1700 and remained at these levels until around A.D. 1830, when they decreased. These EFCs remained low for a large part of the 19th century, tracking an historical crisis in South American mining and metallurgy that began during the Latin American Wars of Independence, which were a series of revolutions that marked the end of the Spanish domination early in the 19th century (A.D. 1833). During the War of Independence, rebel and royalist armies destroyed machinery, killed draft animals, and damaged mines and refineries. In addition, the scarcity of both Hg and labor for amalgamation, lack of transportation infrastructure, dearth of capital, and debilitating fiscal policies all contributed to stagnation in the mining industry during this time (20).

Twentieth Century Atmospheric Pollution

An unprecedented large deposition of trace elements on the Quelccaya ice cap occurred after around A.D. 1900 (Fig. 2 and Figs. S2 and S4D). The Quelccaya EFC records show several-fold increases, compared with the previous 1450–1900 A.D. time period: Ag (2.7 times), As (2.6 times), Bi (7.4 times), Cd (2.5 times), Cr (1.6 times), Cu (2.0 times), Mo (2.2 times), Pb (2.3 times), and Sb (2.3 times) (Dataset S1). In particular, there are three distinct phases in the 20th century record: (i) between A.D.

1900 and around A.D. 1930, when EFC values peak for Ag (8), As (1.7), Bi (3), Cd (13), Cr (6), Cu (15), Mo (20), Pb (8), and Sb (2.5); (ii) between approximately A.D. 1930 and A.D. 1955, when a general EFC relative minimum can be observed for these trace elements; and (iii) between approximately A.D. 1955 and A.D. 1989, when a renewed increasing trend is observed and EFC peaks become apparent for As (1.5), Bi (2.5), Cd (30), Cr (8), Cu (22), Mo (800), Pb (5), and Sb (3) (Fig. 2 and Fig. S2).

The EFC increase between A.D. 1900 and around A.D. 1930 likely reflects larger quantities of low-grade ore that were extracted, pulverized, and refined for profit, increasing metal emission into the South American atmosphere. In fact, by A.D. 1900, South American mining and metal production were stimulated by: (i) the North American and European demand for nonprecious metals [Cu, Pb, and tin (Sn)]; (ii) the use of new technologies (e.g., pneumatic drills) and energy for extraction and grinding (e.g., coal-fired steam power and electricity); (iii) the construction of railroads between the 1870s and the 1890s, which allowed increased exploitation of Cu- and Ag-rich ores in the Peruvian and Bolivian highlands (32); (iv) metallurgical innovations, such as the use of cyanide to extract Ag and gold (Au) and the adoption of the flotation process to refine large quantities of Cu, zinc (Zn), and Pb; and (v) construction of new (but very polluting) smelters such as the one at La Oroya (Peru) (20).

Starting at the beginning of the 20th century, declining Ag prices compelled mining operations in Peru and Chile to focus on Cu extraction, in particular at the Chuquicamata mine (Chile), which alone produced more Cu than any other mine in the world during the 20th century (33). The concomitant twofold increase of Cu levels in Quelccaya ice and in Antarctic snow during the period A.D. 1923–1986 (34) supports the proposition that Cu fallout to Antarctica originated from South American mining and smelting operations.

The use of coal-burning steam locomotives throughout South America at the beginning of the 20th century likely contributed to regional, rather than hemispheric, pollution of both Pb and Cd. This is suggested by the marked concomitant EFC increase of Pb and Cd in the Quelccaya ice core after around A.D. 1905 (Fig. 2 and Fig. S2) but not in Antarctic ice cores (7). In fact, during the period A.D. 1890–1905, the Quelccaya Pb record is distinct from that reported for Antarctica (Fig. 4), particularly the West Antarctic sector that has been argued to be predominantly influenced by aerosol emissions from South America (35). In contrast, our record is consistent with previous findings that the earliest deposition of Pb in Antarctica originated from mining of Ag–Pb ores at Broken Hill and their smelting at Port Pirie (both in southeastern Australia) from A.D. 1889 (7, 36).

Several trace element EFC minima are observed between approximately A.D. 1930 and A.D. 1955 (Fig. 2 and Fig. S2). This reflects both the historical decrease in South American mining activities and metal production during the economic crises of the 1930s, which forced mining companies in South America to lay off many workers thus reducing their mineral output (20), and leading to stagnation in the productivity of metals such as Ag, Cu, Mo, and Pb in South America during World War II (37) (Fig. S5).

Increasing trends and peak EFC values for many trace elements are observed in the Quelccaya record between around A.D. 1955 and A.D. 1989 (Fig. 2 and Fig. S2); in fact, EFC is among or the highest in the entire ice core record for Ag (7), As (1.5), Bi (2), Cd (30), Cr (8), Cu (20), Mo (800), Pb (5), and Sb (3). In Antarctica, a new phase of concentration enhancements for Ag (7 times), Bi (10 times), Cr (2–4 times) after the mid 1940s (38), Pb (3 times) after A.D. 1950 (7), As (5 times), Mo (2 times), and Sb (3 times) after A.D. 1970 (39) are temporally synchronous with the corresponding increments in the Quelccaya ice core record and consistent with an influence of South American anthropogenic emissions on Antarctica during the 20th century (see, for example, Pb in Fig. 4). After World War II, ore extraction in

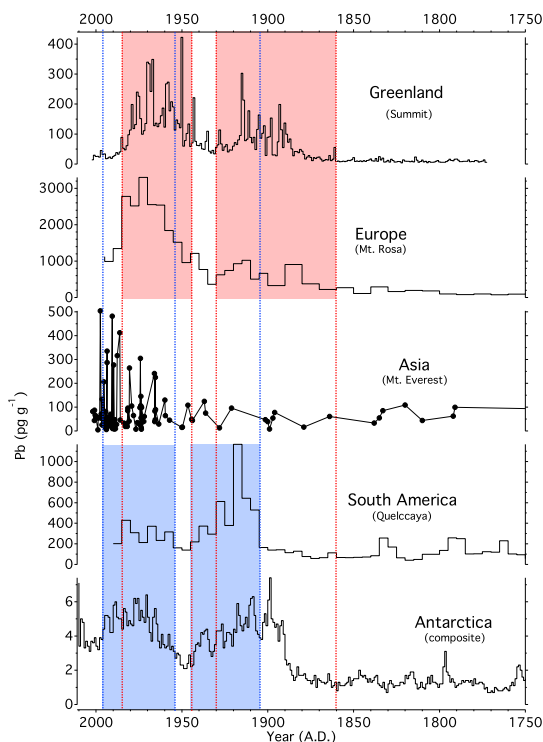


Fig. 4. Pb pollution on different continents during the last 250 y. Pb concentrations as determined in ice cores from Greenland (Summit) (48), Europe (Mt. Rosa) (49), Asia (Mt. Everest) (50), South America (Quelccaya North Dome; 5-y average, this work), and Antarctica (composite of ice core records, mainly from West Antarctica) (7) during the last 250 y. Vertical dotted lines indicate onsets and terminations of the intense Pb atmospheric pollution phases in the different continents. Red and blue areas suggest possible corresponding phases of Pb pollution in the Northern and Southern Hemispheres, respectively.

South America shifted from underground galleries to open pit mines excavated by huge rotary machines (20). These operations likely generated far larger quantities of aeolian metallic dust. In addition, mining in South America started to focus also on the extraction of new metals, including molybdenum (Mo), which was obtained after A.D. 1970 in Toquepala (40), located only 140 km from Quelccaya. These activities could explain at least part of the massive Mo concentration and EFC increases in the 1980s (Fig. 2).

In addition to metallurgy, activities such as fossil fuel combustion likely contributed to the increased trace element deposition on Quelccaya and Antarctica during the second half of the 20th century. An important source of Pb emissions was leaded gasoline, which was introduced in South America and Australia during the 1930s and was not banned until the 1990s (41). In Antarctic firn, corresponding increases in Pb were interpreted to reflect Pb emitted from the continental landmasses of the Southern Hemisphere and possibly also the Northern Hemisphere (36, 42). Long-range transport of atmospheric Pb (and also As, Bi, and Sb) to Quelccaya is consistent with observations of higher EFC during the wet season (EFC = 8) than the dry season (EFC = 4) after the 1950s and might be related to the contribution of humid eastern air masses advected from the inner part of the South American continent. This is in contrast with the beginning of the 20th century when EFC of Pb, As, Bi, and Sb show essentially the same levels during both the dry and the wet seasons, suggesting that intense regional emissions dominated the Pb, As, Bi, and Sb fallout to Quelccaya (*SI Text* and Fig. S6).

Conclusions

The record from the Quelccaya North Dome ice core provides evidence that trace element emissions from mining and metallurgical activities in Peru and Bolivia have been intense enough to be distinguishable from the natural background since around A.D. 1540, shortly after the demise of the Inca Empire (A.D. 1532), at the onset of the Colonial era. This anthropogenic pollution of the South American atmosphere precedes the commencement of the Industrial Revolution by ~240 y. As this is commonly defined also as the onset of the Anthropocene, our record indicates the difficulty in defining an unequivocal commencement of the Anthropocene and suggests that this new epoch emerged discontinuously through space and time during human history. In this context, major 20th century trace element deposition of anthropogenic origin in South America likely started later than in other continents (Fig. 4) but was several times higher than during the Colonial period, which was again several times greater than during the Inca Empire when natural fluxes for the region dominated (Fig. 2 and Fig. S2). This new record complements the growing body of evidence from various continental ice cores, cumulatively suggesting that, today, there are no glaciers on Earth where atmospheric deposition of anthropogenic origin cannot be detected (43).

Materials and Methods

Processing of the Quelccaya North Dome Ice Core (QND) was performed continuously over the lower 105 m of the core. Firn samples that postdate A.D. 1989 were not considered because of recent meltwater percolation that has affected the ice cap during the most recent warm decades only (44). A total of 2,450 QND ice sections of various lengths (2–8 cm; Fig. S1) between 23.23 and 128.49 m depth were cut using a band saw in the cold room laboratory at the Byrd Polar and Climate Research Center of The Ohio State University. In this way, ice core sampling was performed at subannual/annual resolution from A.D. 1383 to A.D. 1989 and multiannual resolution from A.D. 793 to A.D. 1383 (Fig. S1).

The analytical method to determine trace elements in QND is extensively illustrated in two of our recent publications (5, 45). Briefly, the ice sections were decontaminated by triple washing with ultrapure water in a class 100 clean room (46) where they were melted and treated with 2% (vol/vol) HNO₃ simple acidification. Acid leaching was allowed for 30 d at room temperature. Eighteen trace elements (Ag, Al, As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Rb, Sb, Ti, Tl, U, and V) were determined by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS; Element2, Thermo Scientific) (5, 45).

Blanks were significant only for some elements and were subtracted for: Al (143 pg·g⁻¹), Bi (0.04 pg·g⁻¹), Cu (2.2 pg·g⁻¹), Fe (54 pg·g⁻¹), Mn (0.54 pg·g⁻¹) and Pb (1.9 pg·g⁻¹). Concentrations below the limit of detection (LOD) were replaced with the LOD. LOD values were adopted in a few cases for Al, Fe, Mn, and Pb, and in about 1% of the samples for Bi and Cu. LODs were calculated as 3 times the SD of 10 determinations in an Optima grade 2% HNO₃ (Fisher Scientific) ultrapure water solution and ranged from 0.02 pg·g⁻¹ for Bi to 200 pg·g⁻¹ for Al.

Accuracy was assessed by using a certified material solution (TM Rain 95, Environment Canada), which was diluted by a factor of ~20 to obtain concentrations comparable to sample values. This solution was determined with an accuracy within 5–10% for Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sb, Tl, U, and V, 20% for As, and 40% for Bi. Long-term precision was estimated as relative SD of the concentrations determined in the diluted certified material over 1.5 mo and varied from 5% to 10% for Bi, Co, Cd, Cu, Fe, Mn, Mo, Sb, Tl, U, and V to 15% for Cr, Rb, Pb, and Ti. A lower precision was found for Ag, Al, and As (30%).

We take trace element composition as determined in dust collected in the vicinity of the Quelccaya ice cap (using the same methodology as for the ice samples; see *SI Text*) as crustal reference material for our specific study because (i) it incorporates and thus cancels out the possible artifact introduced by differential acid leaching in the melted ice samples (47) and (ii) compared with the mean terrestrial average, trace element composition of Quelccaya dust is a more accurate match of the background crustal composition determined in Quelccaya ice, allowing deviations much smaller than the typical factor of 10 to be taken into consideration to infer a different trace element contribution in the ice.

For these reasons, we calculated the crustal enrichment factor (EFC), defined as $\{[TE]/[Fe]\}_{ice}/\{[TE]/[Fe]\}_{Quelccaya}$, where $\{[TE]/[Fe]\}_{Quelccaya}$ is the mass ratio between trace elements and Fe in dust collected in the vicinity of the Quelccaya ice cap (Dataset S2), while $\{[TE]/[Fe]\}_{ice}$ is the corresponding mass

ratio in the ice. Fe is treated as a crustal element for three reasons: (i) Fe is very precisely and accurately determined, (ii) typically, Fe has a large and rather stable abundance in rocks and soil dust, and (iii) occasional anthropogenic contribution of Fe can be most likely ruled out before A.D. 1900 as it was not smelted in pre-Colonial and Colonial times in South America due to its relatively high melting point and the lack of an adequate metallurgical technology (20). As Fe and Al concentrations are very highly correlated ($r = 0.97$) and Efc of Al is constantly very close to 1, the choice of the major element taken as a crustal reference does not influence the results.

Five-year median concentrations, fluxes, and Efc values presented were calculated by computing the data comprised within the 5 y before the assigned date. For example, the median value linked to the year A.D. 1970 was computed by using the values between A.D. 1965.0 and A.D. 1969.9. However, between A.D. 1383 and A.D. 790 (or 123.11 and 128.49 m depth), there are several instances in which insufficient temporal resolution (i.e., less than one sample per year; Fig. S1) precluded the calculation of 5-y medians.

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