Appearance of an enigmatic Pb source in South America around 2000 BP: anthropogenic vs natural origin.

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Abstract

Neotropical wetlands in the paramo (a unique alpine-tundra ecosystem) region of South America have the potential to be natural archives for metal pollution by modern and past populations. An organic-rich sediment core from the El Triunfo mire, located in the paramo region, provides a record of natural and anthropogenic metal sources in the Northern Andes during the last four millennia. The Triunfo record is complex, as the mire is located in the Northern Volcanic Zone (NVZ) and receives direct input of volcanic material. Regardless of the volcanic input, calculated metal enrichment factors normalized to Sc show metal enrichment in the Northern Andes around 2000 years ago and again in recent industrial times. A number of samples show a shift to lower Pb isotope ratios indicating the appearance of a new, enigmatic Pb source around 2000 years ago. The topmost layer of the core shows the lowest Pb isotope ratios, reflecting input of modern anthropogenic Pb. In contrast to Pb, Nd isotopes do not show significant variations along the entire core, indicating mostly volcanic material input to the mire. The decoupling between Nd and Pb isotopes indicates that the enigmatic Pb source must be anthropogenic in origin.

Based on the dominant atmospheric currents in the region, the El Triunfo mire can receive input from long-distance and local sources. Dispersion simulations validate the possibility of pollutant particle transport from Europe to the northern hemisphere Neotropics. As the first metal enrichment coincides with the Roman Empire times, the El Triunfo Pb isotopes are compared to contemporary peat records from Europe. All records show similar decrease in the Pb isotope ratios due to anthropogenic Pb input. Small Pb isotope differences between a record from Spain and El Triunfo indicate that the enigmatic Pb that appeared around 2000 years ago in the mire is unlikely to have originated from long-distance Roman Empire pollution.

Instead, a group of deposits, namely San Lucas, San Martin de Loba, and El Bagre, located in north-central Colombia, show low Pb isotope ratios that can potentially explain the observed Pb signal in the El Triunfo sediments. The deposits are located up wind, along the predominant atmospheric currents in the region. Therefore, it is plausible that mining activities in the area of San-Lucas, San-Martin, and/or El Bagre released Pb in the atmosphere that was transported and deposited in the El Triunfo mire. These deposits are not associated with the known regions of influence of any of the early pre-Hispanic cultures in Colombia and there is no evidence for mining in this region around 2000 years ago. However, given that all other possibilities are unlikely, the appearance of lower Pb isotope ratios in the mire suggests the onset of mining in the region at least 400 years earlier than the available archaeological evidence at present. The El Triunfo mire record can be used as indirect evidence for significant metal exploitation by early pre-Hispanic cultures in the northern Andes as early as 2000 years ago.

Introduction

Over the past few millennia human activities have increasingly disrupted the natural geochemical cycles of a number of metals (e.g., Nriagu, 1996). Modern and historical mining and smelting of sulfide ores release trace metals such as Cu, Zn, Pb, and other metals with similar geochemical behavior, in the near-surface environment. Natural archives such as peat deposits, lake sediments, and ice cores can provide a historical record of metal pollution by modern and past populations. Far-reaching anthropogenic Pb pollution during the 20^{th} century was first documented in ice cores in Greenland (Murozomi et al., 1969). Subsequently, historical and modern Pb and other metals pollution was confirmed at sites across the world through analysis of multiple natural archives, including ice cores (Hong et al. 1994; Uglietti et al. 2015; Eicheler et al. 2017), lake sediments (Brannvall et al. 2001; Renberg et al. 2001, Cooke et al. 2009; Escobar et al. 2013), peat deposits (Shotyk et al. 1996; Kylander et al. 2005; Kamenov et al. 2009; Martinez-Cortizas et al. 2013; Vleeschouwer et al. 2014), river sediments (Lima et al. 2005), coastal marsh deposits (Leblanc et al. 2000; Alfonso et al. 2001; Kemp et al. 2012), and corals (Shen and Boyle, 1987). Regions in Europe (Bränvall et al. 2001; Renberg et al. 2001) and North America (Kamenov et al. 2009; Kemp et al. 2012) have been so well studied that the historical Pb pollution in sediments can be used as a geochronological tool.

Early South American inhabitants developed metallurgical techniques centuries prior to the arrival of Europeans in the "New World" (e.g., Macfarlane and Lechtman, 2014). The earliest direct evidence for Cu smelting in South America comes from Peruvian archaeological artefacts dated to around 1000 BC (Lechtman, 1979). The atmospheric Cu pollution from these early smelting activities is detectable in ice-core records from the Illimani glacier in Bolivia (Eicheler et al. 2017). Additional evidence for anthropogenic metal contamination in South

America comes from several lake sediment sequences (Cooke et al. 2007, 2008, 2009), two tropical ice-core studies (Uglietti et al. 2015, Eicheler et al. 2017), and a peat record from Tierra del Fuego (Vleeschouwer et al. 2014). The ice core record indicates only Cu extraction from around 1000 BC to around 0 AD, with the first significant Pb pollution due to silver metallurgy detectable around 500 AD (Eicheler et al. 2017). This is in agreement with the lake records from Peru and Bolivia, which also indicate the first significant anthropogenic Pb pollution in South America occured around 500 AD (Cook et al., 2008). However, metal abundances in a peat record from Tierra del Fuego indicate that the anthropogenic metal extraction may have begun much earlier, around 2000 BC in South America (Vleeschouwer et al. 2014).

The northern Andes host a unique alpine-tundra ecosystem called paramo. These high-elevation paramo ecosystems are located mainly in the northwestern corner of South America (Colombia, Ecuador, Peru, and Venezuela) and also in Central America (Costa Rica). These paramo ecosystems are high biodiversity regions that serve as fresh water sources for millions of people (Giraldo-Giraldo et al. 2017). Recently cores from paramo wetlands have been explored as archives for environmental and climate change through pollen and testate amoebae studies (Giraldo-Giraldo et al. 2017; Liu et al. 2019). The paramo peatlands can also serve as important archives for recent and past environmental metal pollution. However, as many paramo ecosystems are located in regions of active volcanoes, they receive significant volcanic input, which complicates the metal record. Regardless, it may be possible to unravel a Neotropical metal record through time from a paramo wetland core, if the volcanic input can be separated from the non-volcanic atmospheric input. In this work we investigate the history of metal deposition, including Pb, in northern South America over the past 4,000 years using a ^{14}C-dated mire core from the central Colombian Andean Cordillera paramo ecosystem. The comprehensive record of metal abundances and Pb and Nd isotopes in this Neotropical wetland deposit provides a chronological record of natural vs anthropogenic controls on the metal deposition in the region.

Methods

The El Triunfo mire is part of the Northern Andean paramo ecoregion and is located in the Central Colombian Andean Cordillera at 3600 m asl (4.98°N, 75.33°W), around 10 kilometers north of the active Nevado del Ruiz volcano (Fig. 1a,b). The mire lies in a depression created by late Quaternary glacial activity (Herd, 1982, also see Giraldo-Giraldo et al. 2017 for photograph of the area). The bedrock geology of the area is dominated by Neogene andesites, pyroclastics, and glacial volcanic deposits (Fig. 1b). The mire is surrounded by hills composed of Neogene andesites (Herd, 1982; Thouret et al. 1995). At present only one surface outcrop of the local andesite bedrock is accessible in the mire's drainage basin. The Triunfo andesite sample analyzed in this work was collected from this outcrop. The mire is fed hydrologically by direct precipitation and runoff that drains through the volcanic deposits. The drainage basin is characterized by paramo vegetation above 3800 m asl and by Andean forest below 3800 m asl.

A sediment core (TRIU 1) was collected from the El Triunfo mire in 2012 using a stainless-steel Russian-style corer (Giraldo-Giraldo et al. 2017). The extracted core was described in the field, wrapped in plastic film and packed in PVC pipes. The core was stored at 4°C at the Universidad de Caldas. A clean slicing and sub-sampling procedure using stainless steel tools was applied to ensure minimal metal contamination and disturbance. The core is composed of peat, organic-rich sediments, and volcanic ash, sometimes showing shallow (few cm to 10 cm) bioturbation by plant roots and inter-bedded with lapilli (Cardona and Monroy, 2015; Giraldo-Giraldo et al. 2017). Seven volcanic ash layers, composed of ash and lapilli, were identified in the core (Giraldo-Giraldo et al. 2017). The lapilli analyzed in this work were picked with clean Teflon-coated tweezers from five volcanic ash layers in the interval between 270 cm and 135 cm depth. Radiocarbon dates were run on bulk samples from 11 depths throughout the sediment core. The age model was built using Bacon Software (Blaauw and Christen, 2011).

Twenty-five samples from the sediment core, lapilli from five ash layers, and one andesite rock sample were selected for trace element and isotope analyses. All reagents used for sample preparation were Optima-grade and sample preparation was performed in a Class 1000 Clean Lab equipped with Class 10 laminar flow hoods, at the Department of Geological Sciences, University of Florida, following methods described in Kamenov et al. (2009). About 1 g of sediment was weighed in acid-cleaned ceramic crucibles and ashed at 550 °C for 5 hours to determine organic matter content by weight loss on ignition (LOI, Table 1). No loss of elements of interest occurred during ashing, as all elements reported in this work have boiling points higher than 550 °C. Remaining mineral ash was transferred to acid-cleaned Teflon vials and digested with HF and HNO_3. Trace element analyses were performed on an Element2 HR-ICP-MS in medium resolution with Re and Rh used as internal standards, following the procedure described in Kamenov et al. (2009). We measured elemental concentrations in the HF–HNO_3-digested mineral material that remained after ashing. Using the LOI (organic matter) values, we calculated element concentrations in the bulk sediments on a dry weight basis. Error values on reported concentrations are better than ±5% for all elements except heavy rare earth elements (HREE), which show errors better than ±10%.

The remaining sample solution, after trace element analyses, was evaporated to dryness to prepare for Pb and Nd separation. The dry residue was dissolved in 1N HBr and loaded on columns packed with Dowex 1X-8 resin to separate Pb for isotope analysis. The sample was washed 3x with 1 ml of 1N HBr and the Pb fraction was collected in 1 ml of 3N HNO_3. The 1N

HBr wash was collected for subsequent Nd separation, as Nd is not adsorbed on the Dowex resin. Nd was further purified for isotope analysis following standard chromatographic methods. Pb and Nd isotopes were determined on a ‘‘Nu Plasma” MC-ICP-MS, following methods described in Kamenov et al. (2009). The reported Nd isotopic compositions are relative to JNdi-1 $^{143}Nd/^{144}Nd$ = 0.512115 (±0.000017, 2σ), or ε_{Nd} = -10.2 (±0.3, 2σ). Pb isotopic compositions were also determined on the MC-ICP-MS, with Tl normalization. The Pb isotope data for NBS 981 (n=3) analyzed together with the samples are as follows: $^{206}Pb/^{204}Pb$ = 16.935 (±0.0020, 2σ), $^{207}Pb/^{204}Pb$ = 15.487 (±0.0025, 2σ), $^{208}Pb/^{204}Pb$ = 36.688 (±0.0064, 2σ). These values are within error of the long-term NBS 981 (n>100) for the UF lab: $^{206}Pb/^{204}Pb$ = 16.937 (±0.004, 2σ), $^{207}Pb/^{204}Pb$ = 15.490 (±0.004, 2σ), $^{208}Pb/^{204}Pb$ = 36.695 (±0.009, 2σ).

Results

The eleven radiocarbon dates on bulk sediment are in stratigraphic order with no age reversals (Table 1, Fig. 2). The entire sediment record has an average sedimentation rate around 0.166 cm/yr (Giraldo-Giraldo et al. 2017). Nine of the eleven samples yielded dates younger than 2,000 yr BP (Table 1, Fig 2). Trace element data for the analyzed sediment, lapilli, and local andesite samples are presented in the supplementary on-line material (SOM). Loss on ignition (LOI), corresponding to the organic matter content in the sediments, ranged from 4.5% to 92% (Table 2). This is a consequence of differential inputs of volcanic ash over time from volcanic activity in the Northern Andean Volcanic (NVZ) zone. The El Triunfo mire is located in a region of several active volcanoes (Northern Group Volcanoes) known to have erupted multiple times over the last several thousand years (e.g., Laeger et al. 2013). In particular, the active Nevado del Ruiz volcano is only around 10 kilometers to the south of the mire (Fig. 1b). Another active volcano, Nevado Santa Isabel is located around 20 kilometers SSW of the mire (Giraldo-Giraldo et al. 2017).

In order to account for variable presence of volcanic ash in the mire sediments the metal concentrations are normalized to Sc. Sc is often used for normalization as it is a conservative element and has no significant anthropogenic source (e.g., Krachler et al. 2003; Kamenov et al. 2009). Enrichment Factors (EF) for each element are calculated by dividing the normalized element concentration (element/Sc) by the corresponding background concentration of the element, i.e. the ratio of the element concentration to Sc concentration in the pre-anthropogenic background. The pre-anthropogenic background values are based on the average values for each element in the three deepest measured samples in the core. Therefore, the calculated EFs (Fig.3 and SOM) represent enrichment relative to the concentrations in the three deepest, presumably pre-anthropogenic intervals in the core. EFs vs age plots for all elements analyzed in this work are available in the SOM. Figure 3 shows the EF changes through time for several elements including As, Cu, Cd, Sb, Zn, Tl, Ni, and Pb. EFs for As, Cu, Cd and Ni, show first increase around 2500 years ago, whereas EFs for Zn, Sb, Tl, and Pb show first increase around 2000 years ago (Fig. 3). All of the elements plotted on Figure 3 show most significant EFs increase in the top part of the core. The rest of the elements analyzed in this work either follow the EF trends observed in Figure 3 (e.g., V, Cr, Co, Sr) or exhibit overall random EFs with depth (e.g., Li, Ga, Rb, Zr, Nb, Cs, REE, Hf, Ta). Ba and Sn show clear enrichment at the top of the core (SOM).

Pb and Nd isotope data for the analyzed sediment samples are presented in Table 2. Pb and Nd isotopic values for the local andesite sample and lapilli from five depth intervals are presented in Table 3. Nd isotopes in the lapilli and andesite samples show relatively small range from +1.9 to +4.5 for ε_{Nd} (Table 3). Similarly, Nd isotopes in the sediments show relatively small ε_{Nd} variations, between +1.5 and +3.5, throughout the sediment column (Fig. 4). Overall, the observed ε_{Nd} values in the sediments are similar to the lapilli, but slightly lower than the local andesite sample (Tables 2 and 3 and Fig. 4). Pb isotopes in the sediment samples show overall lower values than those of the local andesite and lapilli (Tables 2 and 3, Fig. 4). However, in contrast to ε_{Nd}, the sediment Pb isotopes show a relatively wider range of values, with lowest Pb isotopic values measured in the topmost layer of the core (Fig. 4, Table 2).

Discussion

Natural vs anthropogenic metal contributions to the peat

The metals analyzed in this work can be divided into two major groups according to their EF trends with depth (age) in the mire core. Metals not typically associated with sulfide ore mining and smelting, such as Li, Rb, Y, Zr, Nb, and REE, do not show particular EF trends with age (SOM). These metals were not mined by humans in historical times and should reflect the natural (including volcanic ash, local runoff, and long distance atmospheric dust) input to the mire. In contrast, metals that tend to occur in sulfide ores that were mined by humans in the archaeological past, tend to show first increase in their EFs around 2500-2000 years ago, followed by significantly elevated EFs near the top of the core (Fig. 3). The top part of the core clearly displays enrichments in metals that are widely used in the modern economy, such as Pb, V, Ni, Cu, Zn (Fig. 3 and SOM). Such metal enrichments are commonly observed in peat archives providing metal pollution records from the onset of the Industrial Revolution to modern times in Europe (Krachler et al. 2003) and North America (Kamenov et al. 2009). Therefore, the enrichment in the above metals in El Triunfo was most likely the result of modern regional and global anthropogenic activities. It is interesting to note that Sr and Ba also show highly elevated EFs in the top part of the core (SOM), which can potentially be attributed to modern construction activities. For example, major changes in Sr isotopes observed in the top section in a peat core from Florida were the result of modern construction activities and limestone quarrying in the state (Kamenov et al. 2009). Furthermore, the El Triunfo core shows two spikes of elevated EFs for Sr around 2000 and 1500 years ago (SOM). These spikes could be an indication of changes in the natural dust source during these times, or alternatively they could be a result of regional or intercontinental construction activities during the archaeological past.

In contrast to the top part of the core, the first increase in EFs around 2500-2000 years ago (Fig. 3) cannot be directly attributed to anthropogenic activities only on the basis of the observed EFs. The observed EFs are overall minor and could be simply a result of variations in the natural input to the mire. For example, Shotyk et al. (2002) observed elevated EFs (relative to average continental crust abundances) for Zn, Sb, Cu, and As, in ancient, pre-anthropogenic peat layers. The enrichment in these ancient peats was attributed to natural enrichment of these elements in fine fractions of soils during rock weathering (Shotyk et al. 2002). In the case of El Triunfo, Pb and Nd isotopes can provide further constraints if the early minor EFs increase is due to changes in the natural or anthropogenic input of metals to the sediments. The earlier episode of EFs increase is also accompanied with a shift in Pb isotopes towards lower values (Figs. 3 and 4), indicating the appearance of a new source of Pb to the mire, and, by analogy, other metals with similar geochemical behavior.

Volcanoes in the NVZ, where El Triunfo is located, are characterized by elevated Pb isotopic ratios (e.g., $^{206}Pb/^{204}Pb$>18.6, Chiaradia and Fontbote, 2002). This is clearly the case for the local El Triunfo andesite, which has a $^{206}Pb/^{204}Pb$ value of 18.947 (Fig. 4) and the lapilli ($^{206}Pb/^{204}Pb$ from 18.925 to 18.942, Table 3). Similarly, ore deposits in the NVZ (e.g., Ecuador and Colombia) reflect the isotopic compositions of the local volcanic rocks and are characterized by $^{206}Pb/^{204}Pb$ ratios higher than 18.6 (Chiaradia and Fontbote, 2002). Therefore, NVZ input, either from direct volcanic ash deposition or anthropogenic, via ancient smelting of ores associated with NVZ volcano-magmatic systems, would be either close or higher than 18.6. Furthermore, as can be seen on Figure 2b, the local bedrock is composed of Paleocene granitoids, Neogene andesites, and younger volcanic products. Therefore, any local terrigenous input (e.g., via direct runoff from the surrounding area) will carry the NVZ Pb isotopic signature. In addition, even ground water input to the mire would be expected to carry NVZ "volcanic" Pb isotopic signature as the bedrock around and under the mire is entirely composed of volcanic rocks (Fig. 1b).

In contrast, the Central Volcanic Zone (CVZ) in the Central Andes, located to the south of NVZ, is characterized by $^{206}Pb/^{204}Pb$ values less than 18.5 (Mamani et al, 2008). Lavas in the Transition Zone (TZ) between the NVZ and CVZ are characterized by intermediate Pb isotopic compositions (Fig. 4) but with $^{206}Pb/^{204}Pb$ higher than 18.5 (Mamani et al, 2008). A number of El Triunfo sediment samples deposited after 2000 BP display $^{206}Pb/^{204}Pb$ less than 18.5, which is characteristic of the CVZ lavas (Fig. 4). Therefore, natural inputs from CVZ volcanoes can potentially explain the observed shift to lower Pb isotope ratios in the El Triunfo core. However, although the Pb isotopes are within the range of the CVZ, the corresponding Nd isotopes in the sediments do not support input from CVZ source. The CVZ lavas are characterized with much lower Nd isotopes compared to the El Triunfo core (Fig. 4). CVZ lavas are characterized with ε_{Nd} below -4, majority in the range of -6 to -10, and as low as -12, a result of incorporation of Precambrian basement component in their magma source (Mamani et al. 2008). Therefore, volcanic ash from CVZ cannot explain the shift towards lower Pb isotopes as there is no corresponding significant shift in the ε_{Nd} values (Fig. 4). Instead, the El Triunfo Nd isotopes are overall consistent with local NVZ input. Although the single local andesite sample analyzed in this work shows ε_{Nd}=4.5 (Fig. 4), the nearby active volcanoes Santa Isabel and Cerro Machin show a range in ε_{Nd} from 0.2 to 3.9 (Errazuriz-Henao, 2017). Furthermore, the analyzed lapilli samples from the core are also within the above range and overall very similar to the sediments (Table 3). Therefore, all of the sediment samples plot within the $^{\varepsilon}$Nd range expected for the active volcanoes in the NVZ (Fig. 4). The decoupling between Pb and Nd isotopes indicates Pb contribution from a source enriched in ore metals, but with very low REE content. This is consistent with metal input due to mining and smelting of sulfide ores, possibly indicative of anthropogenic influence on the El Triunfo metal record.

Atmospheric transport of particulates in the region

The pollen record from El Triunfo mire shows no evidence for major human activity in the drainage basin during the last 4000 years (Giraldo-Giraldo et al. 2017). Deforestation in the area started about 100 years ago and potato agriculture and dairy cattle ranching are the primary human activities in the watershed today (Giraldo-Giraldo et al. 2017). Therefore, any pre-20th century metal enrichment in the mire relative to the natural volcanic input must be a result of atmospheric deposition. As discussed above, in order to explain the changes in the Pb isotopes we must consider contribution from a non-local source that is not part of the NVZ. The dominant atmospheric circulation in the region flows from east to west (Fig. 5) and particulates from Europe and Africa can reach South America carried by the trade winds (Gangoiti et al. 2006). Therefore, in addition to local inputs from South America, El Triunfo mire can potentially receive dust input from Europe and/or Africa (Fig. 5). Saharan dust, however, displays fairly radiogenic Pb isotopes with $^{206}Pb/^{204}Pb>18.7$ (e.g., Kylander et al. 2005) and therefore cannot explain the appearance of the low-radiogenic Pb in the peat record. However, 20th century anthropogenic European Pb shows lower Pb isotopes, a fact used by Hamelin et al. (1989) to identify European Pb in dust samples collected on Barbados from 1969 to 1987. This work showed that anthropogenic pollution from Europe could be transported across the Atlantic Ocean. Further evidence of European anthropogenic pollution was identified in nitrate and non-sea-salt sulfate concentrations of aerosol samples from Barbados (Savoie et al. 1992 and Savoie et al. 2002). Gangoiti et al. (2006) showed that European particles are more efficiently transported from June to September. This is because daytime convergence of the coupled sea-breeze and upslope flows at the southern coast of the Mediterranean into the Atlas Mountains, and the arid landmass of North Africa, lifts the European pollution upward from over the Mediterranean Sea into the Saharan Air Layer. This layer forms over the main landmass in North Africa, where both the European pollutants and emissions from the Mediterranean coastal region of North Africa mix with desert dust. Inter-continental transport efficiency, from cities in southern Iberia into the Caribbean, ranges between 65% and 78% during the warm season (Gangoiti et al., 2006). Boy and Wilcke (2008) documented African dust deposition in the tropical Andean montane rainforest of Ecuador (1900-2200 m asl). The African dust plume can cross the Amazon Basin from east to west, where high rates of wet deposition are expected, before being washed out and accumulated in the rainforest of Ecuador. The Amazon Basin is an important sink for Saharan dust, but it is possible that significant amounts of dust carrying European pollution to reach the central Colombian Andean Cordillera from the Caribbean Sea via a NE to SW trajectory (Fig. 5).

Recent metal increase and possibility for Pb downcore contamination or diffusion

A number of metals that can be attributed to anthropogenic activities, such as Pb, V, Cr, Co, Ni, Cu, Zn, As, Sr, Cd, Sn, Sb, Ba, Tl, Bi and U show EF increases in the top sediment layers of the El Triunfo mire (Fig. 3 and SOM). As mentioned above, such increase in anthropogenic metals is commonly observed in recent environmental records (e.g., peat, sediment, and ice cores) and is attributed to human economic activities. At present, more than 80% of Colombia's ~48 million people live in medium- and large-size cities in the three Andean Cordilleras. Manizales, a city of about 400,000 inhabitants, is the urban area closest to (~15 km NW) the study site. Manizales was founded in 1848 and had an economy based on agriculture, cattle and trade, with only limited industry until the 1920s. After the 1920s, an influx of revenue from high international coffee prices helped create industries for textile production, cocoa processing, coffee mills, newspaper publishing, the state-owned liquor company and others (Rodríguez, 1993). Nevertheless, by the 1940s, manufacturing was still in early development stages. The number of manufacturing companies, however, increased to 86 by 1973 (Rodríguez 1993), and to 808 in 2015 (regional business census). Major sectors included food, textiles, publishing, wood processing, metal products, machinery and leather processing. Gasoline-based transportation at the regional and national levels became dominant during the 1960s. Until the beginning of the 20th century, products and people in the area moved on foot or by horse. Expansion of the coffee business stimulated more efficient means of transport by the 1920s, such as cable cars and railroads. Roads, however, were used mostly for regional transportation until the 1940s. During the 1960s, however, railroad lines were abandoned and roads became the dominant means of transportation at the regional and national level (Rodríguez, 1993). The two largest cities in Colombia, Bogota (~9 million inhabitants) and Medellin (~3.5 million inhabitants), are also relatively close, within 165 km of the study site. Therefore, urban development and industrial activities in Colombia, leaded gasoline usage, and mining and ore processing, most likely contributed to the observed metal enrichments in the top layers of the El Triunfo core.

As the highest EFs for anthropogenic metals are observed at the top part of the core, then downcore diffusion of Pb may be responsible for the observed Pb concentrations and isotopic changes. The lowest Pb isotopes are observed in the topmost layer (Table 2). Therefore, Pb contamination downcore from this topmost material, either via diffusion or bioturbation or even unintentional contamination during core collection, could be the reason for the observed isotopic record. However, the observed EFs do not show gradual downcore change as would be expected for diffusion (Fig. 3). In addition, it is important to note that the top most layer has the lowest Pb content, only 0.2 ppm, compared to the whole El Triunfo sediment column (SOM). The low Pb content is due to "dilution" by the high organic matter content (high LOI, Table 2). The analyzed top four layers of the core are peat (LOI from 83.2% to 91.7%) and overall show much lower Pb concentrations due to organic matter dilution compared to the lower sections (SOM). Therefore, downcore diffusion or contamination from the top peat layers of the core is not a plausible scenario. Furthermore, numerous studies have demonstrated that Pb is immobile in sediments with high-organic content such as peat (e.g., Shotyk et al. 1996; MacKenzie et al. 1997; Weiss et al. 1999; Kylander et al. 2005), which also will prevent Pb downcore migration from the top peat layers.

The topmost peat layer of El Triunfo core shows the lowest Pb isotopes and if this Pb migrated downcore we would expect to see gradual Pb isotopic change. However, as can be seen on Figure 4, the Pb isotopic changes downcore are not consistent with diffusion. The top-most Pb is followed by three samples showing gradual increase towards the natural Pb, then the fifth sample shows again low Pb isotopes indicating anthropogenic input. Downcore after the fifth sample two more samples plot in the natural Pb background region, then the following sample shows low Pb isotopes indicating again anthropogenic input (Fig. 4). Some samples that were deposited in historical times but show elevated Pb isotopes are a result of high volcanic ash input and resultant low organic matter (e.g., samples at depths 126 cm and 192 cm with low LOI, Table 2).

Compared in Pb isotope space, the El Triunfo Pb isotopes show very similar behavior to the European Pb data (Fig. 6). The Pb isotopes extend from the natural Pb end-member with highest isotope ratios to the modern anthropogenic Pb with lowest Pb isotopes in the modern top layers (Fig. 6). The observed trends in Europe and El Triunfo (Fig. 6) are a result of input of anthropogenic Pb, which since archaeological times has been less radiogenic than the natural Pb in the regions plotted on Figure 6. This is a result of differences in time-integrated U-Th-Pb systematics of the bedrock and ore mineralogy, which typically results in less-radiogenic anthropogenic Pb released during mining (e.g., Kamenov and Gulson, 2014).

The least radiogenic Pb is always recorded in the most recent (top) layers in European peat cores and this is mostly a result of leaded gasoline usage during the 20th century in Europe (e.g., Shotyk et al. 1998; Kylander at al. 2005). The El Triunfo core also shows the least radiogenic Pb isotopes in the top layer, which can be either a result of modern intercontinental Pb input from Europe or usage of Pb gasoline additives in Colombia that were imported from Europe. The Colombian state petroleum company (Ecopetrol) holds the rights to import and refine gasoline in the country. In the early 1980s, Ecopetrol reduced the lead content in gasoline from 0.84 g/liter to 0.04 g/liter, and Pb was eliminated in January 1991 (Onursal and Gautam, 1997). No information is readily available to trace the origin of Pb used in the Colombian gasoline before the complete ban in 1991. Modern human teeth from Chile and Uruguay show low Pb isotopes, similar to modern European teeth, indicating that European Pb additives were likely used extensively in the South American leaded gasoline (Kamenov and Gulson, 2014). Furthermore, aerosols collected over South America in 1994-1999 showed relatively low Pb isotopes, also likely due to usage of alkyllead from a common supplier (Böllhofer and Rosman, 2000). However, it is not clear if European Pb additives were used in Colombian gasoline. Aerosol sample from Colombia (Bogota) collected in October 1997 showed $^{206}Pb/^{204}Pb=18.5$ (Böllhofer and Rosman, 2000), but this is after the leaded gasoline ban in the country. Therefore, at this point we cannot conclude if the Pb isotopic signature in the top-most layer was due to local usage of Pb additives imported from Europe, or was a result of long-distance transport of anthropogenic Pb from Europe.

Intercontinental origin of the metal enrichment

From the available environmental archives for South America only the Pb record from the Tierra del Fuego peat core shows a conspicuous change towards lower Pb isotope ratios around 2000 years ago, indicating Pb incorporation from an unknown source (Vleeschouwer et al. 2014). The Pb isotopic shift around 2000 years ago at Tierra del Fuego could be due to long-distance transport of Pb and other anthropogenic metals from Europe or it could be a result of a discrete period of anthropogenic Pb extraction in South America. Although both El Triunfo and Tierra del Fuego core records show shift to lower Pb isotope values around 2000 years ago, it is somewhat unlikely that the two cores recorded a South American event, given the predominant atmospheric currents in the region (Fig. 5). Based on the above discussion of atmospheric input, it is possible that the observed changes in EFs and Pb isotopes around 2000 years ago in both cores were due to historical anthropogenic activities in Europe. This early period of increases in EFs in the El Triunfo mire (Fig. 3) is overall synchronous with the Roman Empire period in

Europe. Pb pollution from the Roman Empire has been identified in lake sediments and peat records across Europe (e.g., Shotyk et al. 1996; Shotyk et al. 1998; Kylander et al. 2005; Martinez-Cortizas et al. 2002; Martinez-Cortizas et al. 2013) and as far away as Greenland (Hong et al., 1994) and the Canadian Arctic (Zheng et al. 2007). Roman Pb pollution has not yet been reported in the northern Neotropics, despite the potential for long-range transport of dust by atmospheric currents to the Northern Hemisphere Neotropics (Gangoiti et al. 2006). Large quantities of Pb were delivered to the atmosphere as a by-product of early silver smelting by the Greeks and Romans. About 80,000–100,000 tons of Pb were produced annually during the peak of the Roman Empire, about 2000 years ago (Settle and Patterson, 1980; Nriagu, 1983, 1996). Mining occurred primarily in Spain, and to a lesser extent, in other parts of Europe (e.g., Kylander et al. 2005). In Figure 6, the El Triunfo Pb isotope data are compared to Spanish ore deposits and peat records from Spain (Kylander et al. 2005) and Switzerland (Shotyk et al. 2002). The linear trends in the Spanish and Swiss records are due to mixing between the regional natural Pb end-member and variable contributions from modern and ancient anthropogenic Pb. Note that the Tierra del Fuego peat record did not include ^{204}Pb measurements and therefore, it cannot be compared to the high-precision Pb isotope data plotted on Figure 6. Although all three Pb isotope records show similar trends in Pb isotope space, El Triunfo Pb data plot at relatively lower ^{207}Pb/^{204}Pb for given ^{206}Pb/^{204}Pb compared to Spanish peat and Spanish ore deposits that were mined in the past (Fig. 6). Furthermore, in ^{208}Pb/^{204}Pb space the Spanish ore data plot at overall higher values for given ^{206}Pb/^{204}Pb when compared to the peat samples (Fig. 6). Unfortunately, this can in part be the result of analytical artifacts during the Pb isotope analyses as the Spanish ore data were obtained by TIMS, vs MC-ICP-MS data for the El Triunfo sediments. TIMS Pb isotope data can be fractionated in the instrument source (filament) and this analytical artifact results in steep trends, similar to the Spanish ore data plotted on Figure 6. However, the Spanish peat record of Kylander et al (2005) is Pb isotopes measured by MC-ICP-MS and so is directly comparable to the El Triunfo Pb data. Both records plotted on Figure 6 are normalized to the same values of NBS 981. Notably, Kylander et al. (2005) data also plot at lower $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ for given $^{206}Pb/^{204}Pb$ compared to the Spain ore deposits, confirming the analytical issues arising from comparing TIMS and high-precision Pb isotopes measured by MC-ICP-MS. Regardless, the El Triunfo Pb data plot at even lower $^{207}Pb/^{204}Pb$ when compared to the Spanish peat record (Fig. 6). The Spanish peat location is close to the Spanish ore deposits mined during the Roman Empire times. Therefore, the fact that the El Triunfo Pb trend is distinct from the Spanish peat and also plots at even lower $^{207}Pb/^{204}Pb$ compared to the Spain ores (Fig. 6), indicates that the appearance of less radiogenic Pb around 2000 years ago in the mire (Fig. 4) is not very likely to be a result of long-distance pollution related to Roman Empire anthropogenic activities.

South American origin of the metal enrichment

A number of ore deposits in the Central Andes, which are characterized with relatively low Pb isotope ratios, are grouped in the so called "Ore Pb isotope Province IV" (Kamenov et al. 2002; Macfarlane and Lechman, 2014). Ore Province IV extends from southern Peru (around 15˚S) to southern Bolivia (around 22˚S) and several deposits in Bolivia are characterized with low enough $^{206}Pb/^{204}Pb$ that they could potentially serve as the low-radiogenic Pb end-member required to explain the El Triunfo core record (Fig. 7). However, as discussed above, the predominant atmospheric transport in the region of the El Triunfo mire is from E to W or NE to SW (Fig. 5). Therefore, metal pollution transport from ancient metal-extraction activities in the Central Andes (present-day Bolivia) is not in agreement with the atmospheric circulation in the region. Furthermore, the ice core record from Illimani glacier in Bolivia indicates only Cu extraction from around 3000 years to around 2000 years ago, with first significant Pb pollution detectable around 1500 years ago (500 AD) (Eicheler et al. 2017). El Triunfo record shows elevated Cu EF around 2500 years ago (Fig. 3). Although unclear what is the Cu source for this elevated EF, it is within the period of significant Cu exploitation in the Andes (Eicheler et al. 2017). However, it is highly unlikely that the El Triunfo core will record Pb pollution originating from Bolivia, which was not simultaneously recorded in the Illimani glacier ice core. Therefore, the El Triunfo Pb isotopic change predates the first known Pb pollution from the Central Andes by 500 years.

If intercontinental and Central Andean (southern hemisphere) Pb sources are not plausible Pb contributors, then the only remaining possibility is local Pb input. The earliest evidence for large-scale pre-Columbian metallurgy in Colombia is dated to around AD 400 (Plazas and Falchetti, 1978). Furthermore, silver-rich galena deposits are rare in Colombia. Most of the silver is found in native gold/electrum deposits. Although all pre-Columbian cultures in Colombia worked and traded gold, the available archaeological evidence to date suggests that large-scale mining activities were concentrated in only a few areas. Deposits of vein gold in Buritica (Department of Antioquia) and Marmato (Department of Caldas), were heavily exploited (Scott, 2012) (Fig. 1). At present Buritica is still one of the largest and most productive gold mining regions in Colombia (Scott, 2012). Available Pb isotope data for Buritica and Marmato mining districts (Fig. 1) show $^{206}Pb/^{204}Pb>18.9$ (Tassinari et al., 2008; Leal-Mejia, 2011) and therefore they cannot be the source of the low-radiogenic Pb end-member in Triunfo.

There are several large gold deposits (San Lucas, San Martin de Loba, and El Bagre) in the Central Andean Cordillera associated with Segovia and San Martin-Norosi batholiths (Fig.

1a). The Quimbaya cultural region extends over present-day Buritica, but the deposits in the Segovia and San Martin-Norosi batholiths are not associated with the area of influence of any known pre-Hispanic cultures (Fig. 1a). Furthermore, there is no archaeological evidence to support pre-Columbian exploitation of these ores. According to Leal-Mejia (2011), the earliest reports for exploitation of these ores is dated to 18^{th} century. However, the ore deposits in San Lucas, San Martin de Loba, and El Bagre contain galena and show low-radiogenic Pb isotopes (Fig. 7). Furthermore, the deposits are located N-NE of the El Triunfo mire (Fig. 1). Based on the predominant atmospheric currents in the region (Fig. 5), we would expect to see influence on the El Triunfo metal record if these deposits were mined in the past. The Pb isotope data for the deposits show relatively large scatter and steep trend ($^{207}Pb/^{204}Pb$ for San Lucas-San Martin ores), which is likely due to TIMS analytical artifacts. The top-most peat sample plots outside San-Lucas-San Martin ore fields (Fig. 7), but this is 20^{th} century anthropogenic Pb, as discussed above. In addition, the 2^{nd} lowest Pb isotope sample (depth 103 cm) also plots outside the ore fields in $^{208}Pb/^{204}Pb$ (Fig. 7). This sample was deposited during Colonial Times and can potentially be affected by Pb imports, or the offset can be due to TIMS analytical artefacts.

Regardless that the data were obtained by TIMS (Leal-Mejia, 2011), the overall position of the ores in Pb isotope space can potentially explain the core record in El Triunfo mire (Fig. 7). There are a couple of possible scenarios to explain the mire record with Pb contribution from the San Lucas, San Martin de Loba, and El Bagre ores. It is possible that Pb from El Bagre ores contributed extensively to the record as one of the peat samples (depth 399 cm, Table 2) overlaps with the least radiogenic El Bagre ore Pb (Fig. 7). Alternatively, as San Lucas-San Martin Pb is less-radiogenic, the peat record could be explained by mixing of Pb from these deposits with the natural Pb from the NVZ. Either scenario would indicate exploitation of the deposits around

2000 years ago, although no archeological evidence exist yet for such activities. Overall, given the proximity of San Lucas, San Martin, and El Bagre to El Triunfo, the ores low Pb isotopes, and their up wind location from the mire, it is possible that early anthropogenic pollution from exploitation of gold, silver and sulfide ores from these regions created the enigmatic Pb isotopic shift in the core record.

Conclusions

Elemental and Pb-Nd isotope analyses of a ^{14}C-dated organic-rich sediment core from the paramo region of Colombia provides a record of the metal deposition during the last 4000 years in northern South America. The El Triunfo mire deposit receives direct volcanic ash input due to its location in the volcanically active Northern Andean Volcanic Zone. Regardless of the complexity of the record due to presence of volcanic ash, the normalized to Sc trace element profiles show two significant intervals of metal enrichment. The metal enrichment intervals are also accompanied with pronounced shift in Pb isotopes to less radiogenic values. At the same time, no significant change is observed in the Nd isotope ratios throughout the core. The decoupling of Nd and Pb isotopes is indicative of introduction of anthropogenic Pb, and other metals sharing similar geochemical behavior, to the mire as a result of mining of sulfide ores. The predominant atmospheric currents in the region are from east to west and northeast to southwest, providing pathways for long-range, intercontinental metal input from Europe and/or Africa to South America. The earliest distinct shift to lower Pb isotopic ratios, around 2000 years ago, is overall similar to several peat records from Europe and potentially can be explained with Roman Empire Pb pollution. Detailed analysis of the El Triunfo high-precision Pb isotope data show small but significant differences when compared to contemporary peat records from

Europe. This indicates that the anthropogenic Pb in El Triunfo is not exactly the same as the anthropogenic Pb associated with the Roman Empire.

A number of ore deposits with low-radiogenic Pb in Bolivia (Central Andes) can potentially explain the observed anthropogenic Pb in El Triunfo, but no archaeological or environmental archive evidence exists for exploitation of these Pb ores around 2000 years ago. Furthermore, the predominant atmospheric currents are not favorable for atmospheric particle transport from Central to Northern Andes. Ore deposits in the Northern Andean Volcanic Zone are overall characterized with elevated Pb isotopes and also cannot explain the appearance of the low radiogenic Pb in the peat record around 2000 years ago. In addition, the earliest evidence for large-scale pre-Columbian metallurgy in Colombia is dated to 400 AD (Plazas and Falchetti, 1978). A group of known ore deposits (San Lucas, San Martin, and El Bagre) in north-central Colombia, associated with Segovia and San Martin and Norosi batholiths, contain galena with Pb isotopic signatures that can potentially explain the El Triunfo record. The region is located between the areas of influence of Tairona, Zenu, and Quimbaya pre-Hispanic societies in Colombia, and the earliest evidence for mining in the area is dated to 18th century (Leal-Mejia, 2011). Although no archaeological evidence exists yet for the exploitation of these ores, the El Triunfo record provides indirect evidence for significant metal exploitation around 2000 years ago in northern South America.

The metal enrichment and Pb isotopic changes in the top part of the core are a result of modern economic activities in the region. The increase in metal EFs in the top of the core for some elements commonly used in modern economies is as much as 15 times higher than the enrichment observed around 2000 years ago. The ecological effects of this modern metal pollution on the highly vulnerable paramo ecosystems are still unknown.

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Figure Captions

Figure 1. (A) Map showing the location of the study site El Triunfo (star) located in the Central Colombian Andean Cordillera, mining sites discussed in this work, and areas of influence of Pre-Hispanic societies. (B) Geological map of the El Triunfo area, modified after Mosquera et al. (1998).

Figure 2. Age model for the El Triunfo core.

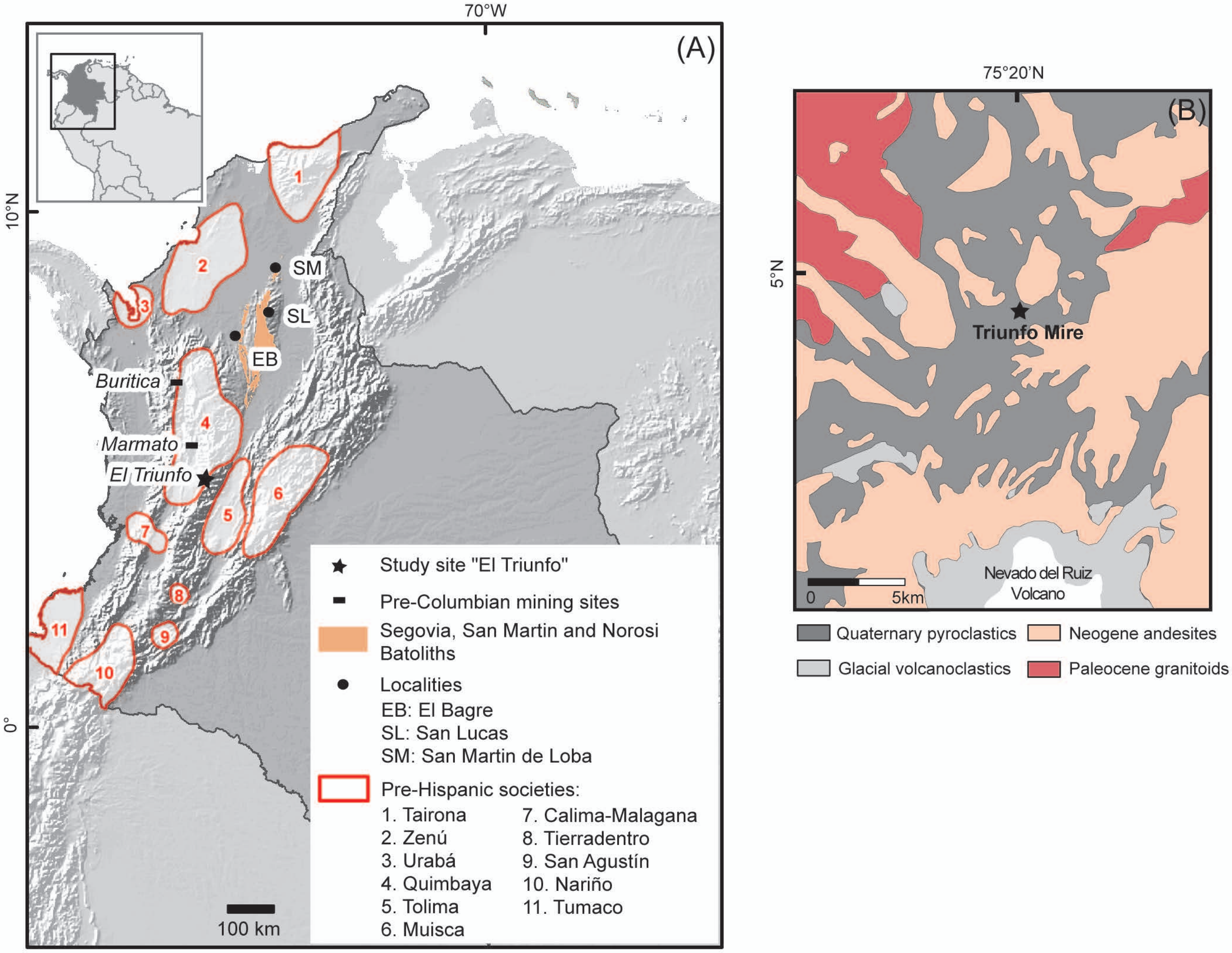
Figure 3. Enrichment factors (EF) variations through time in El Triunfo core for (A) Arsenic, (B) Copper, (C) Cadmium, (D) Antimony, (E) Zinc, (F) Thallium, (G) Nickel, and (H) Lead. Data and EF calculations available in the supplementary on-line material (SOM).

Figure 4. (A) Variations through time in $^{206}Pb/^{204}Pb$ in El Triunfo core compared to ranges in $^{206}Pb/^{204}Pb$ for the Northern Volcanic Zone (NVZ), Transition Zone (TZ), and Central Volcanic Zone (CVZ) lavas. Data for NVZ, CVZ, TZ from Chiaradia and Fontbonte (2002), and Mamani et al. (2008). The red line represents the local Triunfo andesite $^{206}Pb/^{204}Pb$ value. (B) Variations through time in Epsilon Nd values in El Triunfo core. Data for NVZ, CVZ, TZ from Mamani et al. (2008) and Errazuriz-Henao, (2017). Note that there are no significant changes in the Nd isotopes throughout the core and all data are within the expected natural range for the NVZ. In contrast, a number of samples between 2000 BP and present day show Pb isotopes significantly lower than the NVZ Pb isotope values, suggesting anthropogenic Pb addition.

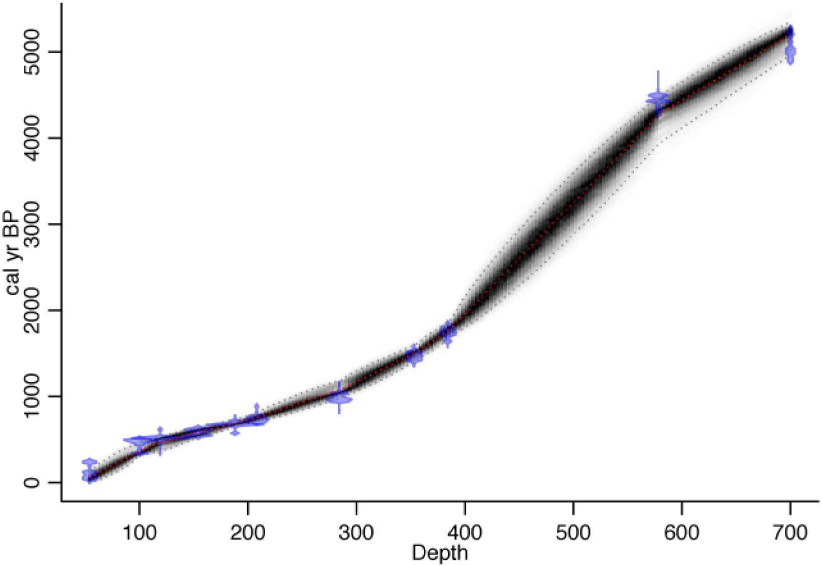
Figure 5. Particle burden of the tracer released from a selection of European cities (Gangoiti et al. 2006), 32 days after the initial release. (A) Total atmospheric column. (B) Vertical cross section, centered at constant latitude 5°N (4-6N). Particle cloud, inside the circle, corresponds to the arrival of the vertical to the site (Gangoiti et al. 2006).

Figure 6. Pb isotope data from El Triunfo core compared to peat records from Europe and Spain ore deposits. Data for Spain peat from Kylander et al. (2005), Switzerland peat from Shotyk et al. (2002), and Spain ore deposits from Santos Zalduegui et al. (2004). All three records show similar trends, indicating variable mixing between the natural end-member for the given region and anthropogenic Pb with lower Pb isotopes. Note El Triunfo data plot at lower $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ for given $^{206}Pb/^{204}Pb$ compared to Spain ore deposits, for more discussion see the text.

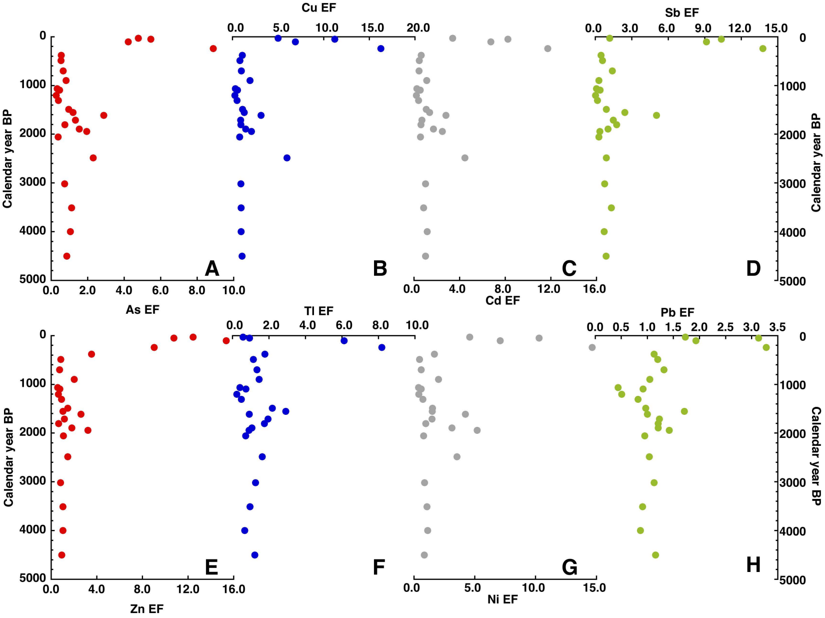
Figure 7. Pb isotope data from El Triunfo core compared to possible sources in South America. Data for Santa Isabel lava from Errazuriz-Henao, (2017), Bolivian ores from Macfrarlane and Lechtman (2014) and Kamenov et al. (2002), and San Lucas, San Martin, and El Bagre ores from Leal-Mejia (2011). Mix Col Ores shows approximately where the mixture of Pb from the two ore areas will plot. Note that the mix can be anywhere in between the two ore regions, depending on the relative contribution from each deposit, for more discussion see the text.



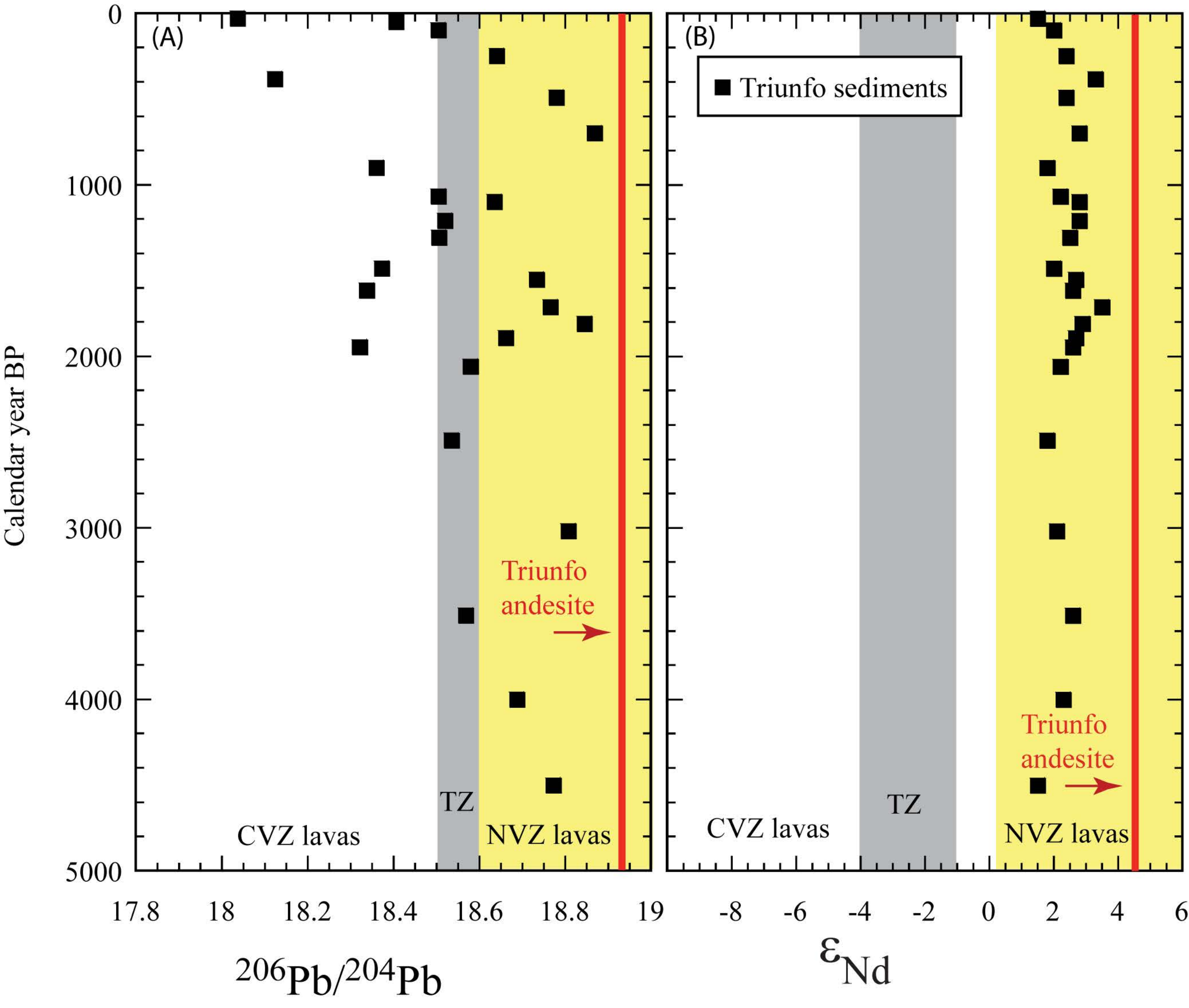
70°W
(A)
10°N
0°
1
2
3
4
5
6
7
8
9
10
11
SM
SL
EB
Buritica
Marmato
El Triunfo
Study site "El Triunfo"
Pre-Columbian mining sites
Segovia, San Martin and Norosi Batoliths
Localities
EB: El Bagre
SL: San Lucas
SM: San Martin de Loba
Pre-Hispanic societies:
1. Tairona
2. Zenú
3. Urabá
4. Quimbaya
5. Tolima
6. Muisca
7. Calima-Malagana
8. Tierradentro
9. San Agustín
10. Nariño
11. Tumaco
100 km
75°20'N
(B)
5°N
Triunfo Mire
Nevado del Ruiz
Volcano
0
5km
Quaternary pyroclastics
Neogene andesites
Glacial volcanoclastics
Paleocene granitoids



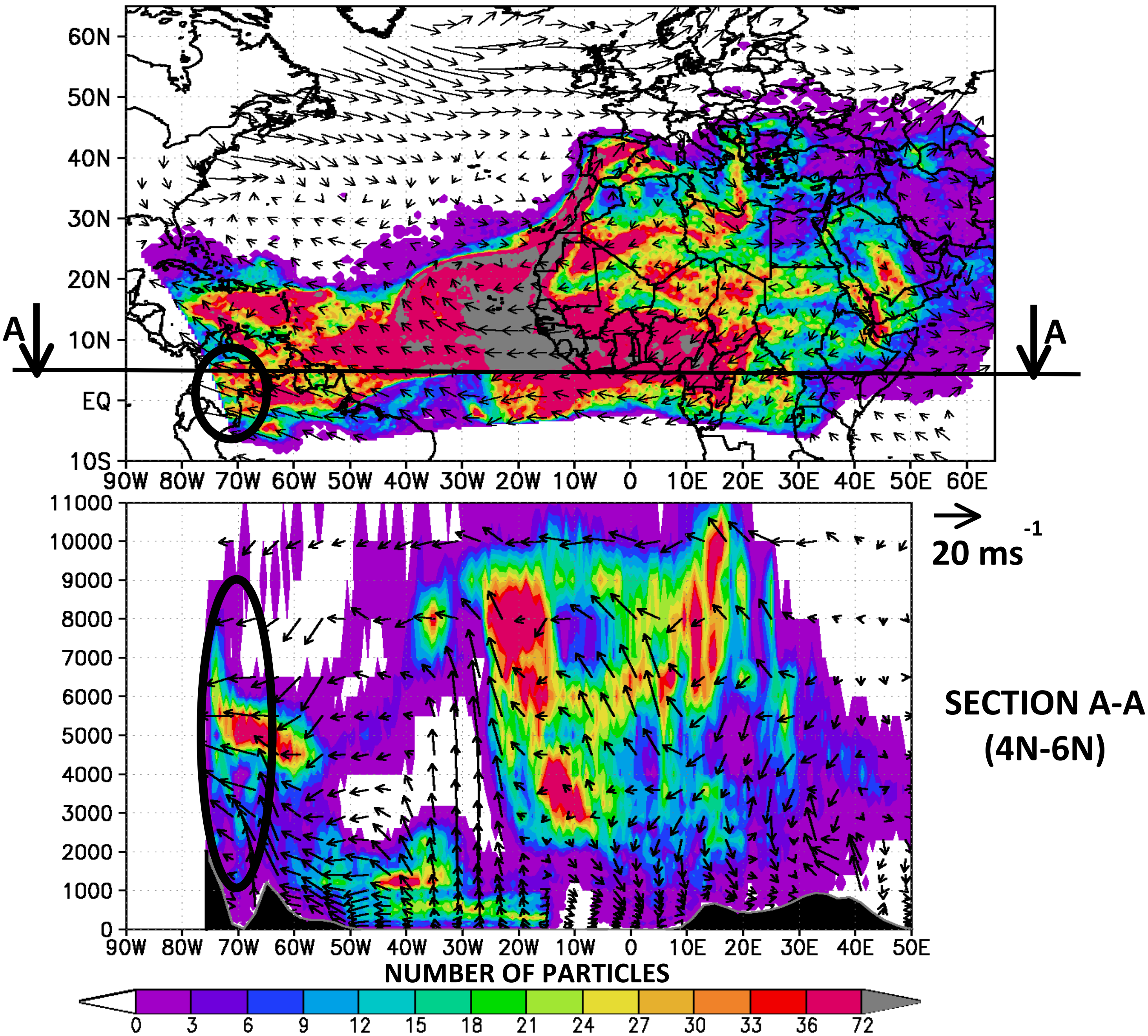
cal yr BP
0
1000
2000
3000
4000
5000
100
200
300
400
500
600
700
Depth



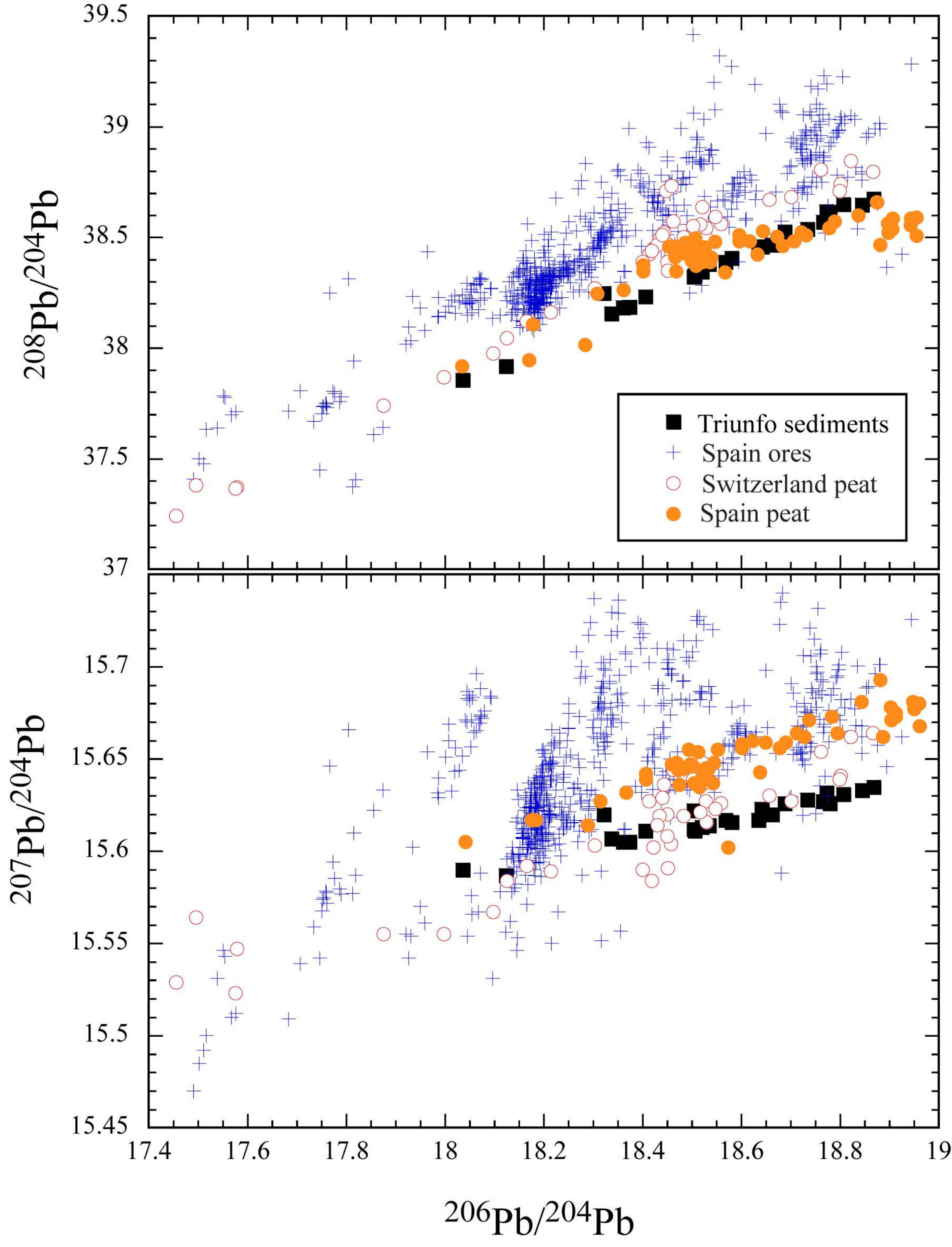
Cu EF
Sb EF
Calendar year BP
As EF
Cd EF
A
B
C
D
Tl EF
Pb EF
Zn EF
Ni EF
E
F
G
H

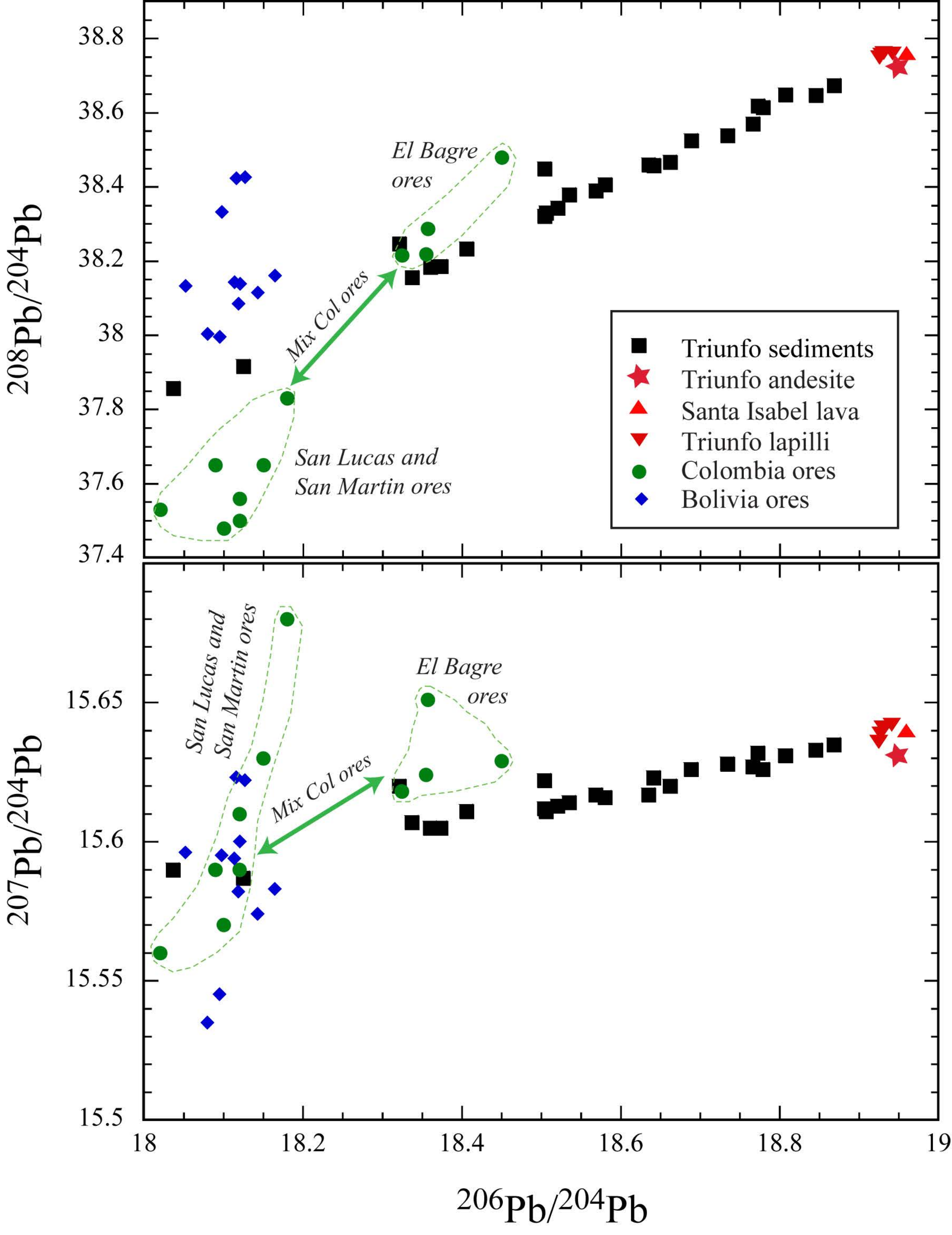


(A)
(B)
Triunfo sediments
Calendar year BP
0
1000
2000
3000
4000
5000
17.8
18
18.2
18.4
18.6
18.8
19
-8
-6
-4
-2
0
2
4
6
Triunfo andesite
TZ
CVZ lavas
NVZ lavas
$^{206}Pb/^{204}Pb$
ε_{Nd}



60N
50N
40N
30N
20N
10N
EQ
10S
90W 80W 70W 60W 50W 40W 30W 20W 10W 0 10E 20E 30E 40E 50E 60E
A
A
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
90W 80W 70W 60W 50W 40W 30W 20W 10W 0 10E 20E 30E 40E 50E
20 ms-1
SECTION A-A
(4N-6N)
NUMBER OF PARTICLES
0 3 6 9 12 15 18 21 24 27 30 33 36 72


39.5
39
38.5
38
37.5
37
$^{208}Pb/^{204}Pb$
Triunfo sediments
Spain ores
Switzerland peat
Spain peat
15.7
15.65
15.6
15.55
15.5
15.45
$^{207}Pb/^{204}Pb$
17.4
17.6
17.8
18
18.2
18.4
18.6
18.8
19
$^{206}Pb/^{204}Pb$



$^{208}Pb/^{204}Pb$
38.8
38.6
38.4
38.2
38
37.8
37.6
37.4
El Bagre ores
Mix Col ores
San Lucas and San Martin ores
Triunfo sediments
Triunfo andesite
Santa Isabel lava
Triunfo lapilli
Colombia ores
Bolivia ores
$^{207}Pb/^{204}Pb$
15.65
15.6
15.55
15.5
San Lucas and San Martin ores
El Bagre ores
Mix Col ores
18
18.2
18.4
18.6
18.8
19
$^{206}Pb/^{204}Pb$

Table 1. Chronology of El Triunfo core.

Lab code	Sample	Depth	Radiocarbon Age	(+/-)	interpolated cal years BP			
					min	max	median	wt mean
368996	TRIU53-55	54	90	30	-4.6	137.4	52.2	59.7
330145	TRIU-100	100	410	30	307.5	472.6	348.6	364.7
368997	TRIU118-120	119	480	30	365.6	532.4	468.3	465.6
368998	TRIU153-155	154	570	30	527.0	636.4	588.1	582.8
369001	TRIU188-189	188	730	30	654.6	732.7	682.2	686.9
368999	TRIU208-209	208	830	30	707.7	810.8	753.3	754.7
369000	TRIU283-285	284	1070	30	974.1	1184.3	1054.7	1076.3
369002	TRIU353-354	353	1580	30	1411.0	1594.9	1499.8	1498.6
369003	TRIU384-385	384	1810	30	1661.3	1862.8	1763.7	1763.3
369004	TRIU578-579	578	3970	30	3922.3	4466.5	4279.0	4260.5
330146	TRIU-700	700	4430	40	4965.9	5354.1	5216.6	5200.4

Table 2. Depth (cm) vs weighted mean ^{14}C calibrated age, Loss on Ignition (LOI, %), Pb and Nd isotopes for analyzed samples from the El Triunfo core. Trace element data for each sample available in the on-line supplement.

Depth	Age BP	LOI	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{143}Nd/^{144}Nd$	Eps Nd
20	30 (?)	83.2	18.036	15.590	37.857	0.512716	1.5
40	50 (?)	92.0	18.406	15.611	38.233	0.511962	-
60.0	99	90.6	18.504	15.622	38.449	0.512741	2.0
82.0	245	91.7	18.641	15.623	38.458	0.51276	2.4
103.0	382	43.8	18.124	15.587	37.917	0.512806	3.3
126.0	489	4.5	18.779	15.626	38.614	0.512763	2.4
192.0	701	7.2	18.868	15.635	38.674	0.512782	2.8
242.0	898	70.0	18.360	15.605	38.184	0.512728	1.8
282.0	1068	27.6	18.504	15.612	38.322	0.512752	2.2
288.0	1098	16.3	18.635	15.617	38.460	0.512779	2.8
306.0	1207	6.4	18.520	15.613	38.344	0.512784	2.8
322.0	1307	12.0	18.506	15.611	38.331	0.512767	2.5
351.0	1486	72.4	18.373	15.605	38.186	0.512743	2.0
360.0	1554	62.7	18.734	15.628	38.538	0.512776	2.7
367.0	1615	90.4	18.337	15.607	38.156	0.512769	2.6
378.0	1711	54.1	18.766	15.627	38.570	0.512815	3.5
388.0	1808	14.0	18.845	15.633	38.647	0.512788	2.9
395.0	1894	80.6	18.662	15.620	38.467	0.512776	2.7
399.0	1946	88.1	18.321	15.620	38.247	0.512772	2.6
408.0	2059	14.0	18.580	15.616	38.407	0.512753	2.2
441.0	2489	80.5	18.535	15.614	38.379	0.512729	1.8
482.0	3020	54.6	18.807	15.631	38.649	0.512745	2.1
520.0	3511	66.5	18.568	15.617	38.389	0.512772	2.6
558.0	4001	76.6	18.688	15.626	38.525	0.512755	2.3
608.0	4502	64.8	18.772	15.632	38.618	0.512713	1.5

Table 3. Pb and Nd isotopes for El Triunfo andesite and lapilli. Trace element data available in the on-line supplement. Lapilli were selected from ash layers, sample names represent core depth (cm).

sample	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{143}Nd/^{144}Nd$	Eps Nd
Lapilli 135cm	18.926	15.636	38.749	0.512756	2.3
Lapilli 180cm	18.928	15.639	38.755	0.512741	2.0
Lapilli 200cm	18.942	15.642	38.759	0.512778	2.7
Lapilli 235cm	18.925	15.636	38.749	0.512738	1.9
Lapilli 270cm	18.931	15.641	38.760	0.512762	2.4
Andesite (outcrop)	18.947	15.631	38.732	0.51287	4.5