Multi-proxy evidence for tectonic control on the expansion of C4 grasses in northwest Argentina

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Abstract
The timing of the rise of C4 grasses and the climatic conditions driving their expansion are widely debated, with recent studies suggesting that the expansion was more complex than previously thought. Proxy reconstructions from northwestern Argentina record multiple increases and decreases in C4 abundance throughout the late Miocene to early Pliocene, as well as variations in the timing of the spread of C4 grasses into the region. Here we present a multi-proxy paleovegetation reconstruction of the proportions of C3 and C4 vegetation using organic carbon and phytoliths preserved in paleosols at Entre Ríos in the Santa María Basin of Catamarca, Argentina between 6.2 and 3.3 Ma. Both \( \delta^{13} \)Corg and phytolith assemblages indicate a C3 dominated ecosystem with no evidence for substantial amounts of C4 vegetation from the late Miocene through mid-Pliocene, despite their rise to dominance elsewhere during this time. These data suggest that by 6.2 Ma the Santa María basin floor was at an elevation high enough to create locally cool conditions that allowed C3 vegetation to outcompete C4 grasses. Phytolith assemblages show that later uplift of the Sierra Calchaquies and Sierra Aconquija ranges through the Pliocene increased aridity and drove the expansion of C3 grasses at the expense of palms and other forest indicators. This multi-proxy paleovegetation reconstruction demonstrates that tectonics played an important role in controlling the late Miocene expansion C4 grasses by suppressing their spread into northwest Argentina.

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1. Introduction

The expansion of C4 grasses is one of the most dramatic ecosystem changes of the Cenozoic, but the primary driver of this expansion is widely debated. C4 grasses originated in the Oligocene (Edwards et al., 2010), and by the late Miocene–Pliocene had spread globally such that C4 grasses are now the dominant vegetation in many ecosystems (Cerling et al., 1997; Fox and Koch, 2003; Tipple and Pagani, 2007; Strömberg, 2011). This expansion was initially believed to be globally synchronous between 8 and 6 Ma, and was attributed to a long-term decline in atmospheric pCO2 (Cerling et al., 1997) or the cooling and drying of global climate (Pagani et al., 1999). Recent studies have found that the timing of the expansion was variable, and included regional step-wise increases in C4 abundance (Edwards et al., 2010; Fox et al., 2012).

Argentina has the highest prevalence of temperate grasslands in South America, however, paleovegetation reconstructions there show regional variability (MacFadden et al., 1996) as well as fluctuations in the local abundance of C4 vegetation throughout the late Miocene and early Pliocene (Kleinert and Strecker, 2001). The timing of the expansion of C4 grasses into northwest Argentina also varies depending on the type of proxy reconstruction, with the more sensitive tooth enamel proxy showing evidence for C4 grasses at Puerta de Corral Quemado (Fig. 1) by 7 Ma (Hynek et al., 2012), well before the expansion of C4 grasses at 3.5 Ma documented by pedogenic carbonates (Latorre et al., 1997). However, these vegetation reconstructions relied on methods that are sometimes subject to confounding factors inherent to many proxy records, and that may result in the misinterpretation of vegetation composition, such as post-burial diagenesis or low productivity ecosystem biasing for pedogenic carbonates (Sheldon and Tabor, 2009; Cotton et al., 2012) and dietary preference of an animal for mammal tooth enamel reconstructions (Koch, 1998). At the same time as the late Miocene expansion of C4 grasses, the central Andean ranges were also undergoing uplift, resulting in localized climate and environmental change (e.g. Strecker et al., 2007), further obscuring the driving force behind C4 expansion and the fluctuations in C4 abundance in the region. Therefore, the variable record of C4 vegetation in northwest Argentina could be caused by shifts...
in climate and environmental conditions, or could be an artifact of the misinterpretation of isotopic evidence from proxy based paleovegetation reconstructions, an idea that can be tested using alternative approaches.

To elucidate the C₄ vegetation history of northwestern Argentina, we present a multi-proxy approach to paleovegetation reconstruction for the late Miocene–Pliocene of the Santa María Basin, northwest Argentina, the same site as a portion of the pedogenic carbonate record of Kleinert and Strecker (2001). Here, we use both the carbon isotopic composition of organic material (δ¹³Corg), and phytoliths (plant silica bodies) preserved within paleosols to produce estimates of vegetation composition. The δ¹³Corg values of organic material or pedogenic carbonates preserved in paleosols can be used to reconstruct the relative abundance of C₃ and C₄ vegetation (Cerling and Quade, 1993) due to differences in the isotopic fractionation of carbon from atmospheric CO₂ of the different photosynthetic pathways (averaging −19.5% for C₃ and −5.5% for C₄; Koch, 1998). Though heavy burial may alter its isotopic composition (McCollom and Seewald, 2006), organic material preserved within the A-horizons of paleosols is not influenced by the same biases and isotopic resetting processes that may impact pedogenic carbonates (Koch, 1998; Cotton et al., 2012), and often can provide direct evidence of the isotopic composition of vegetation.

Phytoliths are silica bodies that are produced within the intercellular spaces of most vascular plants for structural support and also to deter herbivory (Piperno and Pearsall, 1998). Cell shape is variable among different vegetation types, and phytoliths that take the shape of these intercellular spaces have morphologies that are often taxonomically distinct (e.g., Strömberg, 2002). Specifically, the morphology of C₃ and C₄ grass cells differs due to photosynthetic differences and the evolution of Kranz Anatomy in C₄ photosynthesizers (Tipple and Pagani, 2007). These anatomical differences produce phytolith morphologies that are distinct enough to allow soil assemblages to be used to determine the relative proportion of C₃ to C₄ grasses in a given area (e.g., Strömberg, 2002, 2004). In addition to providing estimates of the amount of C₄ biomass, phytoliths can also be used to determine ecosystem changes such as transitions from woodland to open habitat (Strömberg, 2002), and can identify ecosystem heterogeneity and microhabitats (Miller et al., 2012) based on the morphological differences between woody and herbaceous phytoliths. Though production biases exist, with grasses producing more phytoliths than woody plants, Hyland et al. (2013) have recently determined correction factors to calibrate phytolith assemblages to percent vegetation cover. Together, the δ¹³Corg of preserved organic matter combined with phytolith data allow for a multi-proxy reconstruction of the C₄ paleovegetation history in the Santa María Basin.

2. Methods

Samples were collected in the community of Entre Ríos (26° 50′ 21.5″S, 66° 2′ 28.3″W, 2125 m a.s.l. at base of section), near the city of Santa María, Provincia de Catamarca, Argentina (Fig. 1). Samples come from paleosols within the Andaluquita Formation, which has been interpreted as a braided river and floodplain system (Bossi et al., 2001). Tops of paleosols were identified by the presence of burrows and rhizoliths, as well as by grain-size decreases from medium to fine sand towards the top of the paleosols. After surface material (at least 10 cm) was removed, fresh samples were collected from the tops of paleosol profiles for analysis of δ¹³Corg as well as phytolith assemblages. The tops of paleosol profiles were sampled because A horizons typically preserve the most phytoliths (Strömberg, 2002), and soil organic material may become isotopically enriched in ¹³C at depth in the soil due to processes of microbial decomposition that preferentially decay ¹²C (Wynn et al., 2005). Samples for organic carbon isotopic analysis were treated with methanol to remove modern organic material, then treated with multiple washes of a 7% HCl solution at 40°C to remove CaCO₃ until samples no longer effervesced. The samples were then rinsed with deionized water to remove excess acid, dried, homogenized, loaded into tin capsules for isotopic analysis, and analyzed in duplicate using a Costech elemental analyzer attached to a Finnigan Delta V + mass spectrometer at the University of Michigan. Calcareous rhizoliths from various depths in the paleosol profiles, as well as two pedogenic nodules collected from at least 30 cm below the paleosurface were analyzed for carbon and oxygen isotopic compositions (δ¹³Ccar, δ¹⁸Ocar) to compare to the δ¹³Corg and phytolith reconstructions. CaCO₃ was crushed and analyzed on a ThermoFinnigan MAT 253 isotope ratio mass
spectrometer attached to a KielIV autosampler at the University of Michigan. Carbon and oxygen isotopic ratios are reported in units of per mil (‰) relative to the international standard Vienna Pee Dee Belemnite (VPDB). The analytical uncertainty for the organic carbon measurements is \(<0.10\%_\text{oo}, <0.03\%_\text{oo}\) for inorganic carbon and \(<0.05\%_\text{oo}\) for oxygen isotopes.

Phytoliths were extracted from the A horizons of 20 paleosol profiles following the methods of Strömberg et al. (2007). Paleosol samples were crushed and treated with a 10% solution of HCl to remove CaCO₃, sieved and centrifuged to isolate the \(0–250\ \mu\text{m}\) size fraction, and organic material was removed using a Schulze’s solution of HNO₃ and KClO₃. Biogenic silica was then separated from clays, isolated through heavy liquid separation using zinc bromide, mounted on slides using Cargille Melmount 1.539, and then counted and photographed at 400–1000× magnification on a Leica petrographic microscope. Morphotypes were identified based on the reference collections of Strömberg (2002, 2004) and S.Y. Smith (e.g., Chen and Smith, 2013), and classified by vegetation type affinity where forest indicators (FI) were the sum of dicots, general forest indicators, conifers, non-grass woody plants, and Zingerberales, while grassland indicators (GI) were the sum of grass silica short cells (including pooid, general PACMAD, and other short cell groups). For the purposes of further ecosystem description and climatic interpretation, we have separated additional vegetation types such as palms (normally considered FI) and C₄ grasses (normally GI, including panicoid and chloridoid groups) into individual categories. The number of phytoliths of each vegetation type was converted to percentages relative to the total number of diagnostic phytoliths (>250 diagnostic bodies per sample) to create quantitative reconstructions of vegetation during the latest Miocene to early Pliocene. Counting error for quantitative reconstructions is generally \(<7.7\%\) (Strömberg, 2002), but is lower for broad-category C₃ and C₄ vegetation estimates (\(<15\%\); Hyland et al., 2013).

Two ash layers found near the bottom and top of the section were dated by \(^{40}\text{Ar}/^{39}\text{Ar}\) at the University of Michigan. Biotite grains (ranging in size from 1 to 5 mm) were hand-picked under a binocular microscope from ash samples, cleaned with deionized water to remove residual glass material, packaged in pure aluminum foil, and irradiated for 30 h in the medium flux location of the McMaster Nuclear Reactor at McMaster University in Hamilton, ON (see Supplementary material for method details).

3. Results

Our section at Entre Ríos was dated to 6.2–3.3 Ma based on the \(^{40}\text{Ar}/^{39}\text{Ar}\) ages. Eight ashes were identified, though only two were dated successfully due to contamination of older material from Paleozoic basement rocks (Marshall et al., 1979). A stratigraphic column including the location and a table containing a lithologic description of these ashes can be found in the Supplementary material (Supplemental Fig. 1, Table 1). The first ash, located 103 m above the bottom of the section, was dated to 5.72 ± 0.05 Ma. (Supplementary material, Fig. 2, Table 2). The second ash, located at the top of the section, was dated to 3.38 ± 0.53 Ma (Supplementary material, Fig. 3, Table 2). Specific ages for each paleosol were assigned by linear interpolation between known ages of volcanic ashes within the measured section. Due to issues with inherited argon prior to eruption in biotites in the central Andes, these ages are likely 100–200 ky older than true depositional age of the ash (Hora et al., 2010; Kay et al., 2011). However, these possible inaccuracies in the dating do not affect the major conclusions of this work. The new paleosol samples were compared to previously published isotopic data from pedogenic carbonates by correlating our sample ages to ages published alongside \(^{13}\text{C}_{\text{org}}\) of pedogenic calcium carbonate data by Kleinert and Strecke (2001).

The 628 m of studied section contain 29 Entisols. Paleosols were identified as Entisols based on the presence of rhizoliths and burrows, and the lack of any distinct horizonation or other pedogeographic features (Soil Survey Staff, 2010). The \(^{13}\text{C}_{\text{org}}\) of organic material preserved in the paleosols ranges from \(-27.5\) to \(-22.3\%_\text{oo}\), with a mean of \(-24.6 ± 1.4\%_\text{oo}\) (Supplementary material, Fig. 2B, Supplemental Data Table 3). Using the late Miocene atmospheric values (\(^{13}\text{C}_{\text{atm}}\) of \(-6.1\) to \(-6.5\%_\text{oo}\) (Passey et al., 2009), we can predict the average isotopic composition of a pure C₃ system for this time period to be \(-25.2\) to \(-25.6\%_\text{oo}\). Given that the isotopic composition of C₃ vegetation is highly variable due to factors like aridity and canopy cover (Tipple and Pagani, 2007; Diefendorf et al., 2010; Kohn, 2010), this predicted average isotopic composition can shift locally. From the \(^{13}\text{C}_{\text{org}}\) data published by Diefendorf et al. (2010), the average value for C₃ vegetation growing in the late Miocene in an arid to semi-arid environment (<1000 mm yr\(^{-1}\)) is \(-24.7\%_\text{oo}\). The average \(^{13}\text{C}_{\text{org}}\) value of \(-24.6\%_\text{oo}\) for the Entre Ríos section is therefore consistent with a C₃ dominated system in an arid to semi-arid environment (Diefendorf et al., 2010; Cotton et al., 2012).

Phytolith assemblages (Supplementary material, Fig. 2C, Supplemental Fig. 4) indicate that the Entre Ríos site was dominated by C₃ grasses (40–80% GI cover), with a varying proportion of forest-indicating morphologies (20–55% FI cover). Of the 20 paleosol phytolith assemblages examined, only 12 contained any C₄ morphotype phytoliths, and in each they comprised <2% of the total vegetation (Supplementary material, Supplemental Data Table 4). There is a trend of increasing abundance of grass morphotypes (C₃ and C₄ combined) throughout the section, where the average abundance of grass phytoliths is \(-50\%\) at 6.2 Ma and increases to \(-70\%\) around 4 Ma, demonstrating an expansion of grasses at this site from the late Miocene through early Pliocene, but one dominated by C₃ grasses rather than C₄ grasses. Substantial proportions (>5%) of phytoliths produced by palm trees were also found in six paleosol samples (between 5.8 and 4.7 Ma), implying a climate with a mean annual temperature greater than 10°C and a cold month mean temperature (CMMT) greater than 5°C (Sakai and Larcher, 1987).

The isotopic composition of pedogenic carbonates and calcareous rhizoliths ranges from \(-3.64\) to \(-8.14\%_\text{oo}\), and were similar to those of Kleinert and Strecke (2001, Fig. 2A). These carbonates were isotopically enriched by 3–4% compared to their expected range of \(-8\) to \(-12\%_\text{oo}\) if they had precipitated in isotopic equilibrium with CO₂ derived from the oxidation of soil organic matter (based on the \(^{13}\text{C}_{\text{org}}\) analyses, see Section 4.1).

4. Discussion

4.1. Comparison to pedogenic carbonate data

Our multi-proxy paleovegetation reconstruction based upon \(^{13}\text{C}_{\text{org}}\) and phytoliths indicate that Entre Ríos was dominated by C₃ vegetation from the latest Miocene to early Pliocene, in contrast to the \(^{13}\text{C}_{\text{cc}}\) results from this study and the work of Kleinert and Strecke (2001), which found multiple increases and decreases in C₄ abundance through the same time period. The \(^{13}\text{C}_{\text{cc}}\) of pedogenic carbonates reflects the isotopic composition of soil CO₂, which is composed of relatively isotopically depleted biologically derived respired CO₂ and isotopically enriched atmospheric CO₂ that diffuses into the soil (Ceuling, 1991). An enrichment in soil CO₂ of 4.4% occurs due to the faster diffusion of ¹³CO₂ out of the soil, and a temperature dependent fractionation during precipitation that enriches carbonates by approximately 10% more than soil CO₂ (Romanek et al., 1992). These fractionations lead to pedogenic carbonates that are typically isotopically enriched by 14–17‰ (defined as \(^{13}\text{C}_{\text{cc-atm}}\), where cc represents calcium carbonates.)
Fig. 2. Multi-proxy paleovegetation reconstruction from Entre Ríos. A: \(\delta^{13}C_{cc}\); red circles are from Kleinert and Strecker (2001) and black circles are from this study. B: \(\delta^{13}C_{org}\); error bars represent the range of observed isotopic values for multiple analyses. The gray area highlights the range of expected average \(\delta^{13}C_{org}\) values of pure C3 environments based on changes to \(\delta^{13}C_{atm}\) through the Miocene–Pliocene. The dotted line represents the average expected \(\delta^{13}C_{org}\) of C3 plants and the right edge of the gray shaded area is the maximum \(\delta^{13}C\) for a water stressed C3 plant (Passey et al., 2009). C: Phytolith paleovegetation reconstruction showing the abundances of C3 grasses, C4 grasses, forest indicators, and palm indicator morphologies.

carbonate and om represents organic matter) compared to the respired organic material from which most of the soil CO2 is generated (Cerling and Quade, 1993). Matching paleosol \(\delta^{13}C_{cc}\) and \(\delta^{13}C_{org}\) analyses at Entre Ríos have \(\Delta^{13}C_{cc-om}\) values ranging from 18.0 to 22.8‰. These high \(\Delta^{13}C_{cc-om}\) values are well outside the range observed in typical soils exhibiting isotopic equilibrium, which suggests that both materials cannot be recording the true isotopic composition of the aboveground vegetation. Low productivity ecosystems can produce soils with high \(\Delta^{13}C_{cc-om}\) values (Sheldon and Tabor, 2009; Cotton and Sheldon, 2012; Tabor et al., 2013). If the respired CO2 component of total soil CO2 is small, then the isotopic composition of atmospheric CO2 has a greater influence on the precipitating pedogenic carbonates. However, these soils would require concentrations of soil-respired CO2 an order of magnitude lower than are typically observed in grasslands to produce such high \(\Delta^{13}C_{cc-om}\) values (see Supplementary material for details on soil-respired CO2 calculations). It is unlikely that low productivity ecosystems alone contributed to these high \(\Delta^{13}C_{cc-om}\) values.

There are sample preparation and soil biogeochemical processes that could lead to misinterpretations of \(\delta^{13}C_{org}\) data. If soil carbonates were not entirely removed during sample preparation, this residual isotopically enriched carbonate would be combusted during analysis. This contamination of carbonate would increase the measured \(\delta^{13}C_{org}\) values of the preserved organic material and cause overestimation in the % C4 vegetation. However, it would make no difference for the phytolith microfossils, so the close match of those independent proxies makes incomplete carbonate removal unlikely. Additionally, there are no biogeochemical soil processes that act to preferentially remove \(^{13}C\) from soil organic material. Instead, the primary process that alters the \(\delta^{13}C_{org}\) of soil organic material is microbial decomposition, which enriches soil organic material in \(^{13}C\) compared to the overlying vegetation due to the preferential oxidation of \(^{12}C\) containing compounds (Wynn et al., 2005; Wynn, 2007) and can cause an overestimation in the % C4 vegetation rather than the underestimation of C4 grasses necessary for the pedogenic carbonates to accurately reflect paleovegetation. Because the two paleovegetation reconstruction methods are in strong agreement that the ecosystem was mainly C3 vegetation during the late Miocene through Pliocene, it is more likely that the pedogenic carbonates are not faithfully recording the isotopic composition of the vegetation than that the \(\delta^{13}C_{org}\) of preserved soil organic material is more isotopically depleted in \(^{13}C\) than the vegetation that had grown above it.

Pedogenic carbonates can overestimate the amount of C4 vegetation growing aboveground in many cases, such as in low productivity ecosystems as described previously (Sheldon and Tabor, 2009), or soils forming on a limestone parent (Hsieh and Yapp, 1999; Tabor et al., 2004), and may also be affected by dissolution and reprecipitation from groundwater or by diagenetic alteration (Sheldon and Tabor, 2009; Mintz et al., 2011; Cotton et al., 2012; Tabor et al., 2013). Kleinert and Strecker (2001) relied heavily...
on the use of calcareous rhizoliths to determine the isotopic composition of soil CO₂ at Entre Ríos. Rhizolith material is less likely to produce accurate reconstructions of past vegetation than the more typically used pedogenic carbonate nodules because rhizoliths are usually quite thin and friable (no more than several mm thick), and are susceptible to groundwater recrystallization and to isotopic resetting (Sheldon and Tabor, 2009). Rhizoliths are also generally located within the top 30 cm of a soil profile and precipitate from soil CO₂ that is isotopically enriched compared to soil CO₂ at depth (Cerling, 1984, 1991), which would lead to rhizoliths that are enriched in δ¹³C compared to preserved soil organic matter and carbonate precipitated lower in the soil profile. Nodular carbonates are usually found below 30 cm in a soil profile and are often larger, denser and finer grained, which preserves original micritic carbonate on the inside of the nodule, even if the outer layers have been recrystallized and isotopically reset (Sheldon and Tabor, 2009), though nodular size and texture alone do not guarantee samples free from isotopic resetting (Leier et al., 2009).

The rhizolith material from this study and Kleinert and Strecker (2001) is isotopically offset in both carbon and oxygen (Fig. 3) compared to the pedogenic carbonates published by Latorre et al. (1997) from nearby Puerta de Corral Quemado (PCQ, Fig. 1). Rhi- zolith material is isotopically more enriched in ¹³C by 2–3‰ compared to most of the nodular material from Latorre et al. (1997), except for the youngest carbonate nodules that indicate an increase in local C₄ vegetation at Puerta de Corral Quemado. The rhizolith material is also on average 2‰ more depleted in ¹⁸O than nodular samples. However, Fig. 3 shows that diagenetic carbonate from PCQ (Hynek et al., 2012) overlaps isotopically with both nodule and rhizolith carbonate from PCQ and Entre Ríos, and there is no clear distinction between primary and diagenetic carbonate. The oxygen isotopic depletion in the rhizoliths compared to the carbonate nodules as well as the comparison with diagenetic carbonate from PCQ suggests that the rhizoliths at Entre Ríos may have been isotopi- cally reset, and subsequent studies relying on that data should be reevaluated (see Section 4.3 for further discussion).

4.2. Comparison to Puerta de Corral Quemado

Isotopic analysis of pedogenic carbonates from nearby PCQ (Fig. 1, Latorre et al., 1997) also supports the conclusion that the area around Entre Ríos in northwest Argentina was dominated by C₃ vegetation, with carbonates showing little C₄ until ~3.5 Ma (Fig. 4). Hynek et al. (2012) used the isotopic composition of tooth enamel (δ¹³Cen) to reconstruct the diets of small rodents and ungulates through the Miocene/Pliocene boundary and found substantial contributions of C₄ vegetation (>20%) to the diets of the small rodents by 7 Ma, approximately 1 Ma before an increase in C₄ vegetation was observed in the ungulate diet (MacFadden et al., 1996). These data are notable because they demonstrate that C₄ vegetation must have been present in at least small quantities prior the rise in C₄ vegetation recorded by pedogenic carbonates at ~3.5 Ma (Fig. 4, Latorre et al., 1997). However, many of the rodent data indicate more C₄ vegetation than pedogenic carbonates at PCQ (Latorre et al., 1997) as well as the organic matter and phytoliths from Entre Ríos, clearly showing that rodents can enhance the C₄ signal by dietary preference, particularly during the time of tooth mineralization (Koch, 1998).

This dietary bias is a useful tool to reconstruct the early history of C₄ grass expansion into an area where a small percentage of C₄ grasses may go undetected in other isotopic proxies. Our isotopic and phytolith results are consistent with Hynek et al. (2012), and phytolith results confirm that there was indeed a small percentage of C₄ vegetation present in northwest Argentina by 6.2 Ma. However, due to these known dietary biases, the δ¹³Cen data cannot be used to reconstruct exact percentages of C₄ biomass in a particular ecosystem, and in this case phytoliths combined with the δ¹³Corg of preserved organic material provide a more accurate assessment of paleovegetation. Combining the phytolith and tooth enamel data also present an interesting result in that C₄ grasses were ecologically important by the late Miocene, even while only...
The lack of evidence for C₄ vegetation at Entre Ríos raises questions about why there was little C₄ vegetation present in northwestern Argentina during a time when C₄ grasses were expanding in many other places on Earth, including other sites in Argentina (e.g. MacFadden et al., 1996; Cerling et al., 1997; Fox and Koch, 2003). The modern abundance of C₄ grasses is related to the different mechanisms of C₃ versus C₄ photosynthesis. C₃ photosynthesis is the ancestral pathway that evolved over two billion years ago (Farquhar et al., 2011) and uses the enzyme RuBisCO to fix carbon. CO₂ passively diffuses into the cell through the stomata, making the pathway less efficient at lower concentrations of atmospheric CO₂. Moreover, RuBisCO reacts with both CO₂ and O₂, leading to the wasteful process of photorespiration. Under higher temperatures, RuBisCO has a greater affinity for O₂ and rates of photorespiration increase, reducing rates of photosynthesis. Thus, C₃ plants become less productive under higher temperatures. C₄ photosynthesis evolved more recently and uses other enzymes like PEP-carboxylase and coordinated anatomical changes to concentrate CO₂ around RuBisCO, increasing the efficiency of carbon fixation at low concentrations of atmospheric CO₂ and under high light and high temperature conditions as well as reducing photorespiration. C₄ plants consume energy in the process that concentrates CO₂ in the cell, and at low temperatures, the additional energy requirements of the C₄ pathway outweigh the impact of photorespiration on C₃ photosynthesis (Ehleringer, 1978; Ehleringer et al., 1997). Therefore, for a given CO₂ concentration, a theoretical temperature boundary exists below which C₃ photosynthesis is more energetically favorable and above which C₄ vegetation will out-compete C₃ vegetation.

Precipitation is also an important factor in the distribution of grasses, with C₄ plants outcompeting C₃ plants in areas dominated by warm season precipitation (Cerling and Quade, 1993; Paruelo and Lauenroth, 1996). Entre Ríos is located at the eastern Andean margin within the northern Sierras Pampeanas. To the east, the ~4000–5500 m high Sierra Calchaquies and Sierra Aconcagua constitute an important topographic barrier that separates the basin from the undeformed Andean foreland with elevations of <900 m (Fig. 1). To the west, the Santa María Valley is bounded by the ~4300 m high Sierra de Quilmes, which separates the valley from the Puna plateau (Fig. 1). The uplift of northern Sierra Pampeanas ranges effectively shields the Santa María Basin from significant amounts of eastwardly-derived precipitation, where Entre Ríos receives ~200 mm yr⁻¹ rainfall (Strecker et al., 1989). Around
hypothesis explained above, the point where C3 grasses begin to outcompete C4 grasses is a warm month mean temperature below 22 °C in areas receiving at least 25 mm precipitation in the warmest month (Collatz et al., 1998; Still et al., 2003) which in the modern central Andes occurs at ~1000 m (Cavagnaro, 1988; Cabido et al., 1997). Assuming a similar lapse rate to the modern, an elevation change from sea level to the modern elevation of 2125 m prior to our studied time period would cause a decrease in warm month mean temperature from approximately 30 to 13 °C (Cavagnaro, 1988; Cabido et al., 1997) and would have allowed C3 grasses to remain dominant while C4 grasses expanded in the low lands (MacFadden et al., 1996). This result suggests that tectonics modulated climate, and consequently the distribution of C4 grasses during the global expansion event. However, the lapse rate may have been lower in the late Miocene/Pliocene (Poulsen and Jeffery, 2011) due to a slightly warmer global climate (Pagani et al., 2010). In a warmer world with atmospheric CO2 concentrations similar to preindustrial values (Pagani et al., 1999; Cotton and Sheldon, 2012), one would expect to observe a similar C4 abundance–temperature relationship (Edwards et al., 2010). If the lapse rate were lower through the Miocene–Pliocene, we would expect to find C4 grasses at higher elevations. Given the lack of C4 vegetation through the section, it is likely that the Santa María basin was not only at near modern elevation by 6.2 Ma, but also that prior regional uplift formed a physical barrier to the expansion of C4 grasses in the Miocene.

The Santa María basin floor is thought to have been at a low elevation close to sea level at ~12 Ma due to the presence of shallow marine sediments (Bossi et al., 2001). The near modern elevation of the basin floor by 6.2 Ma at the start of our section at Entre Ríos suggests substantial regional uplift and basin fill at the southern Puna plateau margin through the late Miocene. This observation is in agreement with recent exhumation history models of the Sierra Aconquija range (Löbens et al., 2013) showing that exhumation began in the late Miocene by ~9 Ma. Additionally, studies from the southern rim of the Puna plateau at about 27°S, immediately north of the Flambilá Basin, suggesting a minimum paleorelief of ~1800 m between the present plateau border and that basin by late the Miocene (Carraza et al., 2006). Our multi-proxy paleovegetation reconstruction shows no changes in the percent of C4 grasses through the late Miocene–Pliocene. The lack of C4 grasses by 6 Ma requires a cool climate that at ~27°S and over a prolonged 3 Ma time period can only be found in a high elevation environment. This new data instead suggests instead that the Santa María Basin floor was already near modern elevations throughout the deposition of the Andalhuila formation and supports previous studies that indicate exhumation and basin fill between ~12 and 6 Ma.

The phytolith abundances from Entre Ríos also record an increasing amount of C3 grasses and decreasing forest vegetation and loss of palms through the section. Like pollen, certain types of plants produce more phytoliths than others. Hyland et al. (2013) show that grasses produce a much larger number of phytoliths than trees and shrubs. This production bias could cause an overestimation in the percentage of grasses that make up a particular ecosystem, and may lead to misidentifications of particular ecosystems. However, Hyland et al. (2013) find that the amount of production bias towards grasses is related to the soil order. For poorly developed soils such as Entisols, which is the dominant soil order at Entre Ríos, the bias is virtually non-existent and the percentage of forest indicator vs. grass indicator phytoliths in a paleosol assemblage is equal to the percent vegetation cover or percentage of biomass of a particular group of vegetation at a given site. We are confident that our identification of a C3 grassland and the trend of increasing percentages of C3 grasses through time at Entre Ríos is real and not an artifact of phytolith production biases. Phytoliths are an integrated local signal and incorporate ecosystem heterogeneity (Fredlund and Tieszen, 1994). Therefore, the increase of grasses from 50 to 70% represents a real change in the vegetation composition and a shift from a woodland to a wooded grassland instead of ecosystem heterogeneity (e.g. distance from a river channel; e.g., Miller et al., 2012). While the disappearance of palms could be interpreted as a decrease in CMMT, palm species also have large variations in precipitation and drought tolerance, and we cannot identify individual species using phytoliths. A decrease in palms can be explained by a decrease in temperature or an increase in aridity, while an increase in grasses is indicative of an increase in aridity, whether explicitly through decreases in precipitation or indirectly through fire regime (Edwards et al., 2010). Together, the overall decrease in forest indicators and increase in grasses suggests instead an increase in aridity, as grasses are more aridity/drought tolerant than most high-stature angiosperms. The increase in aridity necessary to drive this ecosystem change through the Pliocene suggests substantial uplift of the Sierra Calchaquies and Sierra Aconquija ranges flanking the Santa María basin, creating an orographic barrier to precipitation sourced from the east. These results are consistent with models for the uplift of the Sierras Pampeanas that describe thick-skinned deformation and segmentation into small, reverse fault-bounded basins between 6.5 Ma and the present (Strecker et al., 1989; Sobel and Strecke, 2003; Carraza et al., 2006; Löbens et al., 2013). Grassland and scrubland biomes occupy drier climatic conditions than forests, though fire regime also plays an important role in the distribution of grasses vs. trees (Bond et al., 2005). The expansion of grasses between 6.2 and 3.3 Ma suggests increased aridification of the local climate, and may also suggest an increase in fire frequency as well. The oxygen isotopic composition of both pedogenic carbonates and small mammal tooth enamel from PCQ become enriched in 18O by ~2% over the studied time period (Latorre et al., 1997; Hynek et al., 2012), which also indicates increased aridity in the region. Rech et al. (2010) and Bershaw et al. (2010) also observe an increase in aridity in nearby areas (the Atacama and Altiplano) through the late Miocene, attributed to the formation of rain shadows on the leeward side of the uplifted central Andes. This aridification and cooling as a result of uplift is likely the cause of the expansion of C3 grasses and the conversion from forest to grassland or scrubland in the Santa María Basin and surrounding uplands.

4.4. Comparison to modern ecosystem

We can also compare the vegetation of the late Miocene–Pliocene to modern vegetation to understand the evolution of ecosystems in the Andes through time. Powell et al. (2012) modeled the δ13Corg of soil organic matter for South America and estimate the modern δ13Corg at Entre Ríos to be ~−28.1‰, which is indicative of a pure C3 ecosystem. In order to compare this value directly to the average δ13Corg of the preserved soil organic material from Entre Ríos, we must correct for the change in the δ13C of atmospheric CO2 between the late Miocene (~−6.5‰; Passey et al., 2009) and today (~−8.3‰; Keeling et al., 2005). The average δ13Corg at Entre Ríos was ~24.6 ± 1.4‰, which under today's atmospheric conditions would be corrected to ~26.4 ± 1.4‰. Both the modeled value and the average δ13Corg from Entre Ríos are within error and indicate a pure C3 ecosystem.

While Powell et al. (2012) modeled value has not been validated by modern soil analyses from this site, modern elevation–species abundance relationships for grasses in Argentina would predict ~15% C4 species for sites near the elevation of Entre Ríos (Cabido et al., 1997; Cavagnaro, 1988). However, the percent species in a given area does not necessarily correlate to percent vegetation and thus, to the percent biomass contributed by C3 and
C₄ species to soil organic material. There could be many species that are present and rare, but which do not contribute substantially to vegetation cover. As a result, the modeled δ¹³C₉-org value of soil organic material (Powell et al., 2012) and the elevation−species abundance relationships are not necessarily inconsistent. Additionally, the modern species abundance studies were performed ~500 km south of Entre Ríos and are shown here mainly to demonstrate the approximate C₄ abundance−elevation relationship for the broader Andean region, because this relationship is not consistent globally. While these data are our best estimate for the regional abundance−elevation relationship, there could be error when applied to a different location such as Entre Ríos. The modern rodent tooth enamel from PCQ (Hynek et al., 2012) clearly indicates the presence of some C₄ grasses, so like the late Miocene–Pliocene, the true modern vegetation is most likely comprised of a small number of C₄ species that contribute a very small percentage of biomass to soil organic matter.

CAM plants are part of the modern ecosystem in the region surrounding Entre Ríos and it is possible that CAM plants were present in the late Miocene through Pliocene at Entre Ríos. However, it is not possible to reconstruct their abundances using isotopic or phytolith proxy based methods because biomass derived from CAM plants can have a carbon isotopic composition that spans the entire range of C₃ and C₄ photosynthesis (Koch, 1998) and CAM plants produce phytoliths made of calcium oxalate instead of opal produced by C₃ and C₄ plants, which rarely survive in the geologic record (Jones and Bryant, 1992). However, CAM plants are generally an insignificant proportion of grassland ecosystems (Fox et al., 2012), and are generally a small proportion of desert ecosystems (Murray and Wolf, 2013) so we would not expect them to contribute substantial proportions of biomass to the soils.

The phytolith paleovegetation reconstruction shows that by ~3.5 Ma, the area was roughly 70% C₃ grasses with 30% forest vegetation. However, some phytolith morphologies are produced by both trees and woody shrubs, which means that the 30% forest indicator morphologies could be derived largely from woody shrubs. Although there is no way to differentiate between forest and some shrub phytolith morphologies in order to determine the exact percent cover of shrubs and trees, the increased aridity observed at other nearby sites associated with Andean rain shadow development as well as the loss of palm phytoliths from Entre Ríos by the end of the section (Fig. 2) suggests that many of the forest indicator morphologies were likely produced by shrubs. The modern vegetation of Entre Ríos is mixed grassland and scrubland (USGS, 2012; Powell et al., 2012); therefore, phytoliths and isotopic evidence suggest that the modern ecosystem for the Santa María basin at the margin of the Puna Plateau was in place by 3.3 Ma.

5. Conclusions

A multi-proxy paleovegetation reconstruction using the δ¹³C₉-org of preserved organic material and phytolith assemblages in paleosols from Entre Ríos confirms the presence of C₄ grasses in northwest Argentina in the late Miocene–Pliocene. However, C₄ grasses in the region do not represent a substantial portion of the ecosystem during the global expansion event. This multi-proxy reconstruction is inconsistent with the conclusions of a previous paleovegetation reconstructions relying upon pedogenic carbonates and calcareous rhizoliths (Kleenert and Strecker, 2001) that showed that C₄ grasses constituted up to 50% of the ecosystem in the late Miocene through Pliocene. These isotopic data are likely biased toward overestimated C₄ proportions due to the influence of low productivity ecosystem and post-burial isotopic resetting. We conclude that because the distribution of C₄ grasses in Argentina is primarily temperature-driven, the fact that C₃ grasses were ecologically favored over C₄ grasses in Entre Ríos indicates that the Santa María basin on the margin of the Puna Plateau was at near-modern elevations by the late Miocene. A shift from woodland to wooded grassland is evidence of increased aridity through the Pliocene, caused by surface uplift of the Sierra Calchaquies and Sierra Aconcagua ranges flanking the basin consistent with the initiation of thick-skinned deformation of the Sierra Pampeanas at ~6 Ma. This multi-proxy paleovegetation reconstruction demonstrates significant tectonic control on the expansion of C₄ grasses during the late Miocene–Pliocene, leading to the development of modern Andean ecosystems.

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Appendix A. Supplementary material

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References


