



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



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ARTICLE INFO

Article history:

Received 10 March 2013

Received in revised form 5 March 2014

Accepted 9 March 2014

Available online xxxx

Editor: G. Henderson

Keywords:

C₄ grasses
stable isotopes
phytoliths
Andes

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 $\delta^{13}\text{C}_{\text{org}}$ 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; Tipler 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

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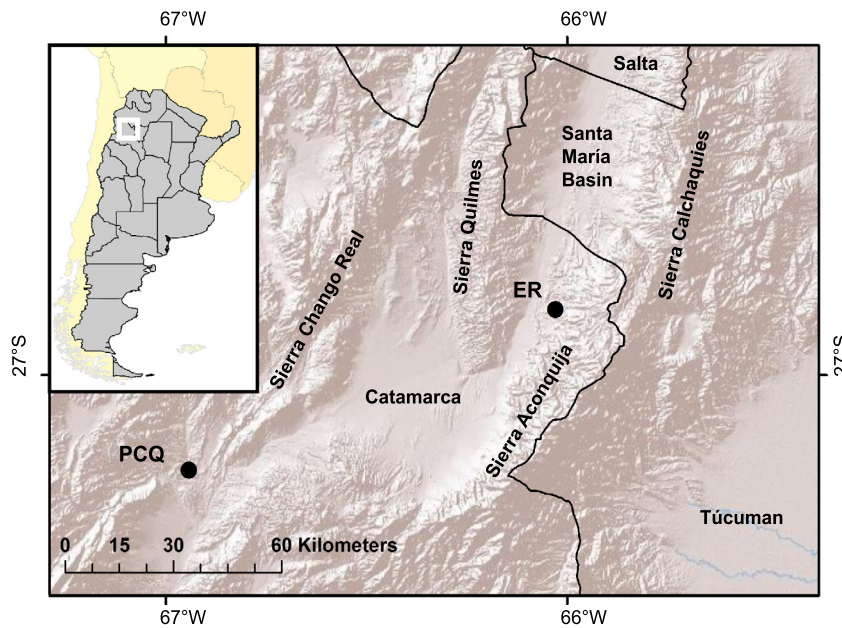


Fig. 1. Location map of sample sites in northwest Argentina. Entre Ríos (ER) is the focus of this study and of Kleinert and Strecker (2001), and results are compared to previous studies at Puerta de Corral Quemado (PCQ, Latorre et al., 1997; Hynek et al., 2012).

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 C_4 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 ($\delta^{13}C_{org}$), and phytoliths (plant silica bodies) preserved within paleosols to produce estimates of vegetation composition. The $\delta^{13}C_{org}$ values of organic material or pedogenic carbonates preserved in paleosols can be used to reconstruct the relative abundance of C_3 and C_4 vegetation (Cerling and Quade, 1993) due to differences in the isotopic fractionation of carbon from atmospheric CO_2 of the different photosynthetic pathways (averaging -19.5% for C_3 and -5.5% for C_4 ; Koch, 1998). Though heating from very deep 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 C_3 and C_4 grass cells differs due to photosynthetic differences and the evolution of Kranz Anatomy in C_4 photosynthesizers (Tippie 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 C_3 to C_4 grasses in a given area (e.g., Strömberg, 2002, 2004). In addition to providing estimates of the amount of C_4 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 $\delta^{13}C_{org}$ of preserved organic matter combined with phytolith data allow for a multi-proxy reconstruction of the C_4 paleovegetation history in the Santa María Basin.

2. Methods

Samples were collected in the community of Entre Ríos ($26^{\circ}50'21.5''S$, $66^{\circ}2'28.3''W$, 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 Andalhuala 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 $\delta^{13}C_{org}$ 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 ^{13}C at depth in the soil due to processes of microbial decomposition that preferentially decay ^{12}C (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 $40^{\circ}C$ to remove $CaCO_3$ 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 ($\delta^{13}C_{cc}$, $\delta^{18}O_{cc}$) to compare to the $\delta^{13}C_{org}$ and phytolith reconstructions. $CaCO_3$ was crushed and analyzed on a ThermoFinnigan MAT 253 isotope ratio mass

spectrometer attached to a Kiel IV 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‰, <0.03‰ for inorganic carbon and <0.05‰ 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 μm 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 Meltmount 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 *Zingiberales*, 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 (~1.5%; Hyland et al., 2013).

Two ash layers found near the bottom and top of the section were dated by ⁴⁰Ar/³⁹Ar 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 ⁴⁰Ar/³⁹Ar 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 δ¹³C_{cc} of pedogenic calcium carbonate data by Kleinert and Strecker (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 pedogenic features (Soil Survey Staff, 2010). The δ¹³C_{org} of organic material preserved in the paleosols ranges from −27.5 to −22.3‰, with a mean of −24.6 ± 1.4‰ (Supplementary material, Fig. 2B, Supplemental Data Table 3). Using the late Miocene atmospheric values (δ¹³C_{atm}) of −6.1 to −6.5‰ (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‰. Given that the isotopic composition of C₃ vegetation is highly variable due to factors like aridity and canopy cover (Tippie and Pagani, 2007; Diefendorf et al., 2010; Kohn, 2010), this predicted average isotopic composition can shift locally. From the δ¹³C_{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‰. The average δ¹³C_{org} value of −24.6‰ 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‰, and were similar to those of Kleinert and Strecker (2001, Fig. 2A). These carbonates were isotopically enriched by 3–4‰ compared to their expected range of −8 to −12‰ if they had precipitated in isotopic equilibrium with CO₂ derived from the oxidation of soil organic matter (based on the δ¹³C_{org} analyses, see Section 4.1).

4. Discussion

4.1. Comparison to pedogenic carbonate data

Our multi-proxy paleovegetation reconstruction based upon δ¹³C_{org} and phytoliths indicate that Entre Ríos was dominated by C₃ vegetation from the latest Miocene to early Pliocene, in contrast to the δ¹³C_{cc} results from this study and the work of Kleinert and Strecker (2001), which found multiple increases and decreases in C₄ abundance through the same time period. The δ¹³C_{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 (Cerling, 1991). An enrichment in soil CO₂ of 4.4‰ occurs due to the faster diffusion of ¹²CO₂ 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 Δ¹³C_{cc-om}, where cc represents calcium

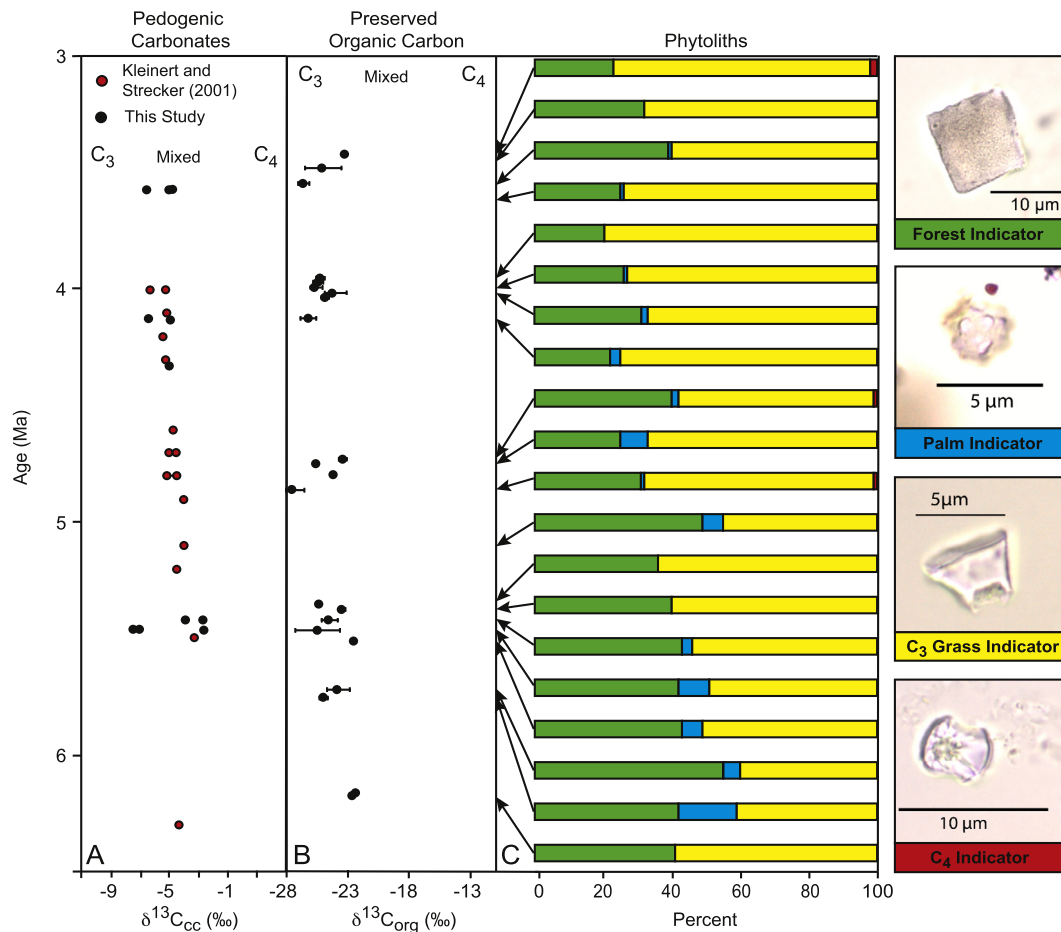


Fig. 2. Multi-proxy paleovegetation reconstruction from Entre Ríos. A: $\delta^{13}\text{C}_{\text{Cc}}$; red circles are from Kleinert and Strecker (2001) and black circles are from this study. B: $\delta^{13}\text{C}_{\text{Org}}$; error bars represent the range of observed isotopic values for multiple analyses. The gray area highlights the range of expected average $\delta^{13}\text{C}_{\text{Org}}$ values of pure C_3 environments based on changes to $\delta^{13}\text{C}_{\text{atm}}$ through the Miocene–Pliocene. The dotted line represents the average expected $\delta^{13}\text{C}_{\text{Org}}$ of C_3 plants and the right edge of the gray shaded area is the maximum $\delta^{13}\text{C}$ for a water stressed C_3 plant (Passey et al., 2009). C: Phytolith paleovegetation reconstruction showing the abundances of C_3 grasses, C_4 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 CO_2 is generated (Cerling and Quade, 1993). Matching paleosol $\delta^{13}\text{C}_{\text{Cc}}$ and $\delta^{13}\text{C}_{\text{Org}}$ analyses at Entre Ríos have $\Delta^{13}\text{C}_{\text{Cc-om}}$ values ranging from 18.0 to 22.8‰. These high $\Delta^{13}\text{C}_{\text{Cc-om}}$ 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 $\Delta^{13}\text{C}_{\text{Cc-om}}$ values (Sheldon and Tabor, 2009; Cotton and Sheldon, 2012; Tabor et al., 2013). If the respired CO_2 component of total soil CO_2 is small, then the isotopic composition of atmospheric CO_2 has a greater influence on the precipitating pedogenic carbonates. However, these soils would require concentrations of soil-respired CO_2 an order of magnitude lower than are typically observed in grasslands to produce such high $\Delta^{13}\text{C}_{\text{Cc-om}}$ values (see Supplementary material for details on soil-respired CO_2 calculations). It is unlikely that low productivity ecosystems alone contributed to these high $\Delta^{13}\text{C}_{\text{Cc-om}}$ values.

There are sample preparation and soil biogeochemical processes that could lead to misinterpretations of $\delta^{13}\text{C}_{\text{Org}}$ 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 $\delta^{13}\text{C}_{\text{Org}}$ values of the preserved organic material and cause overestimation in the % C_4 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 $\delta^{13}\text{C}_{\text{Org}}$ 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 % C_4 vegetation rather than the underestimation of C_4 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 C_3 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 $\delta^{13}\text{C}_{\text{Org}}$ 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 C_4 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

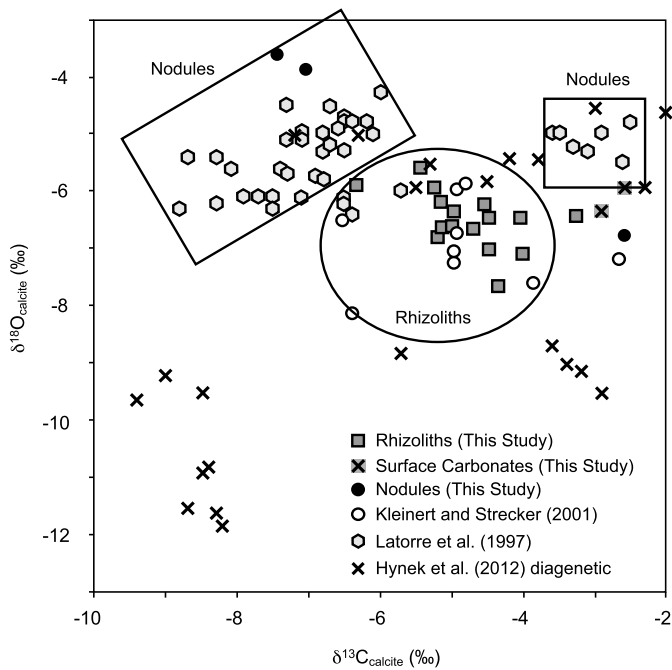


Fig. 3. $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ for carbonates from this study, Kleinert and Strecker (2001) and Latorre et al. (1997), as well as diagenetic carbonate from Hynek et al. (2012). Rhizoliths and surface carbonates are isotopically enriched in both carbon and oxygen compared to nodular carbonate, but the diagenetic carbon overlaps with both the nodule and rhizolith carbonate.

on the use of calcareous rhizoliths to determine the isotopic composition of soil CO_2 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 CO_2 that is isotopically enriched compared to soil CO_2 at depth (Cerling, 1984, 1991), which would lead to rhizoliths that are enriched in $\delta^{13}\text{C}$ 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). Rhizolith material is isotopically more enriched in ^{13}C 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 C_4 vegetation at Puerta de Corral Quemado. The rhizolith material is also on average 2‰ more depleted in ^{18}O 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 isotopically reset, and subsequent studies relying on that data should be reevaluated (see Section 4.3 for further discussion).

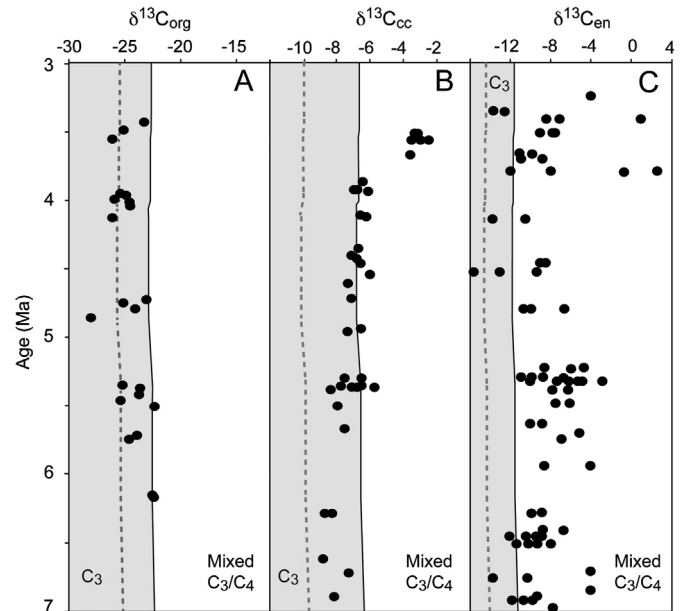


Fig. 4. $\delta^{13}\text{C}_{\text{org}}$ from Entre Ríos (this study), (A) compared to the $\delta^{13}\text{C}_{\text{cc}}$ from Latorre et al. (1997); (B), and the $\delta^{13}\text{C}_{\text{en}}$ from Hynek et al. (2012); (C) The gray regions represent pure C_3 ecosystems and the white represents a mixed C_3/C_4 ecosystem or diet. The gray dotted line represent the average $\delta^{13}\text{C}$ value for soil organic material and pedogenic carbonates forming in a pure C_3 ecosystem (A and B) and a rodent consuming only C_3 vegetation (C) and the right edge of the gray shaded area represents the maximum $\delta^{13}\text{C}$ that may be found in a water stressed area. These lines shift slightly due to the changing $\delta^{13}\text{C}$ of atmospheric CO_2 and are based on the model by Passey et al. (2009). The right side of each panel is the maximum isotopic composition possible in a pure C_4 system.

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 C_3 vegetation, with carbonates showing little C_4 until ~ 3.5 Ma (Fig. 4). Hynek et al. (2012) used the isotopic composition of tooth enamel ($\delta^{13}\text{C}_{\text{en}}$) to reconstruct the diets of small rodents and ungulates through the Miocene/Pliocene boundary and found substantial contributions of C_4 vegetation (>20%) to the diets of the small rodents by 7 Ma, approximately 1 Ma before an increase in C_4 vegetation was observed in the ungulate diet (MacFadden et al., 1996). These data are notable because they demonstrate that C_4 vegetation must have been present in at least small quantities prior the rise in C_4 vegetation recorded by 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 C_4 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 C_4 grass expansion into an area where a small percentage of C_4 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 C_4 vegetation present in northwest Argentina by 6.2 Ma. However, due to these known dietary biases, the $\delta^{13}\text{C}_{\text{en}}$ data cannot be used to reconstruct exact percentages of C_4 biomass in a particular ecosystem, and in this case phytoliths combined with the $\delta^{13}\text{C}_{\text{org}}$ 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 C_4 grasses were ecologically important by the late Miocene, even while only

being present in very small (<5%) abundances. This data suggests that C_4 grasses may have also become important in many regions long before other proxies record their presence, and that phytoliths provide a technique for resolving low abundances of ecologically important vegetation types.

It is possible that the differences between the vegetation at Entre Ríos and PCQ are caused by ecosystem heterogeneity and that each paleovegetation reconstruction is representing a different habitat with a distinct vegetation composition. The section at Entre Ríos is comprised of Entisols, or poorly developed early succession soils forming on a parent material of medium grain size sand. The paleosols at PCQ are finer grained and contain distinct Bk horizons (Latorre et al., 1997), indicating that those soils were better developed than the Entisols found at Entre Ríos. The differences in vegetation reconstructions at these two sites could be caused by differing depositional environments or climatic regimes, such as timing of precipitation, which would contribute to spatial ecosystem gradients.

4.3. C_4 grasses and the rise of the Sierras Pampeanas

The lack of evidence for C_4 vegetation at Entre Ríos raises questions about why there was little C_4 vegetation present in northwestern Argentina during a time when C_4 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 C_4 grasses is related to the different mechanisms of C_3 versus C_4 photosynthesis. C_3 photosynthesis is the ancestral pathway that evolved over two billion years ago (Farquhar et al., 2011) and uses the enzyme RuBisCO to fix carbon. CO_2 passively diffuses into the cell through the stomata, making the pathway less efficient at lower concentrations of atmospheric CO_2 . Moreover, RuBisCO reacts with both CO_2 and O_2 , leading to the wasteful process of photorespiration. Under higher temperatures, RuBisCO has a greater affinity for O_2 and rates of photorespiration increase, reducing rates of photosynthesis. Thus, C_3 plants become less productive under higher temperatures. C_4 photosynthesis evolved more recently and uses other enzymes like PEP-carboxylase and coordinated anatomical changes to concentrate CO_2 around RuBisCO, increasing the efficiency of carbon fixation at low concentrations of atmospheric CO_2 and under high light and high temperature conditions as well as reducing photorespiration. C_4 plants consume energy in the process that concentrates CO_2 in the cell, and at low temperatures, the additional energy requirements of the C_4 pathway outweigh the impact of photorespiration on C_3 photosynthesis (Ehleringer, 1978; Ehleringer et al., 1997). Therefore, for a given CO_2 concentration, a theoretical temperature boundary exists below which C_3 photosynthesis is more energetically favorable and above which C_4 vegetation will out-compete C_3 vegetation.

Precipitation is also an important factor in the distribution of grasses, with C_4 plants outcompeting C_3 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 Aconquija 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

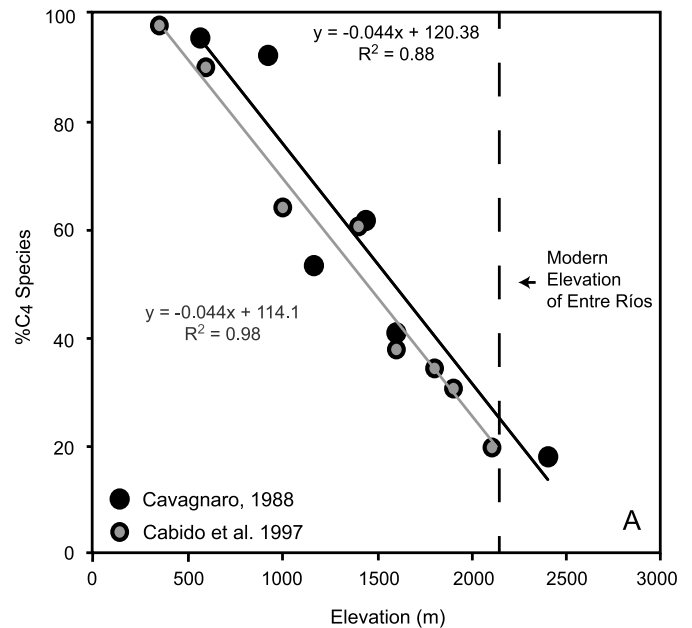


Fig. 5. The elevational dependence of the abundance of C_4 vegetation in central Argentina, reproduced from Cabido et al. (1997) and Cavagnaro (1988). The dashed line represents the modern elevation at Entre Ríos. Based on this relationship and the multi-proxy vegetation reconstruction from Entre Ríos, we would expect near modern elevations for the Andes by the late Miocene to Pliocene.

70% of the precipitation falls during austral summer (Mosier et al., 2013; Hijmans et al., 2005), a precipitation regime favorable to C_4 plants.

In northwestern Argentina, temperature is the primary control on the modern distribution of C_3 and C_4 vegetation, as shown in Fig. 5 (Teeri and Stowe, 1976; Cavagnaro, 1988; Cabido et al., 1997; Ehleringer et al., 1997). As elevation is the main control on temperature in the Andes, the abundance of C_4 grasses decreases with increasing elevation (Cavagnaro, 1988; Cabido et al., 1997; Bremond et al., 2012). C_3 grasses were dominant at Entre Ríos during the late Miocene through mid-Pliocene (Fig. 2), which suggests that either 1) Santa María valley was already at a high enough elevation to cause a locally cool climate, or 2) that precipitation fell mainly during the cool months, enabling C_3 grasses to outcompete C_4 grasses (Paruelo and Lauenroth, 1996; Paruelo et al., 1998). Ehlers and Poulsen (2009) show that as the Altiplano and Puna plateau reach 50–75% of their modern elevation (widely believed to have occurred by the late Miocene, regardless of plateau uplift mechanism, e.g. Barnes and Ehlers, 2009; Garzzone et al., 2008; Strecker et al., 2007), summer precipitation over the eastern Andes increases substantially due to a change in the moisture source from the south Pacific to the equatorial Atlantic, indicating the onset of the South American monsoon. Increased sedimentation rates observed during the late Miocene (Uba et al., 2007) also provide evidence for the onset of the South American monsoon prior to the deposition of the Andalhuala formation at Entre Ríos. Summer dominated precipitation patterns in the area should have favored C_4 over C_3 grasses. The lack of C_4 vegetation in an area with a favorable precipitation regime indicates that like modern Andean ecosystems, temperature was the primary control on vegetation composition at Entre Ríos.

The Pliocene was a period of global warmth while the concentration of atmospheric CO_2 was roughly equivalent to preindustrial values (Pagani et al., 1999, 2010; Seki et al., 2010). These high temperatures and low CO_2 concentrations conditions should have favored C_4 photosynthesis (Ehleringer, 1978; Ehleringer et al., 1997), making the low abundances of C_4 grasses at Entre Ríos particularly anomalous. Based on the crossover temperature

hypothesis explained above, the point where C₃ grasses begin to outcompete C₄ grasses is a warm month mean temperatures 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 Fiambalá Basin, suggesting a minimum paleorelief of ~1800 m between the present plateau border and that basin by late the Miocene (Carrapa 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 Andalhuala 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 Strecker, 2003; Carrapa 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‰ though 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 $\delta^{13}\text{C}_{\text{org}}$ of soil organic matter for South America and estimate the modern $\delta^{13}\text{C}_{\text{org}}$ 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 $\delta^{13}\text{C}_{\text{org}}$ of the preserved soil organic material from Entre Ríos, we must correct for the change in the $\delta^{13}\text{C}$ of atmospheric CO₂ between the late Miocene (~ -6.5‰ ; Passey et al., 2009) and today (-8.3‰ ; Keeling et al., 2005). The average $\delta^{13}\text{C}_{\text{org}}$ at Entre Ríos was $-24.6 \pm 1.4\text{‰}$, which under today's atmospheric conditions would be corrected to $-26.4 \pm 1.4\text{‰}$. Both the modeled value and the average $\delta^{13}\text{C}_{\text{org}}$ 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 $\delta^{13}\text{C}_{\text{org}}$ 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 $\delta^{13}\text{C}_{\text{org}}$ 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 (Kleinert 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 Aconquija 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.

Acknowledgements

The authors would like to thank Jorge Guillou and SEGEMAR in Salta (Argentina), Tess Nugent and Lora Wingate for sample preparation and analysis, Selena Smith and Nadja Insel for helpful discussions, Chris Hall for radioisotopic dating, several anonymous reviewers as well as David Fox for comments on an earlier version of the manuscript. Funding was provided by ExxonMobil Research and Engineering Company (J.M.C.), the Geological Society of America (J.M.C., E.G.H.), and the University of Michigan Rackham Graduate School (J.M.C., E.G.H.).

Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2014.03.014>.

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