A geochemical study of lacustrine sediments: towards palaeo-climatic reconstructions of high Andean biomes in Colombia
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CHAPTER 3

CO$_2$- and temperature-controlled altitudinal shifts of C$_4$- and C$_3$-dominated grasslands allow reconstruction of palaeoatmospheric $p$CO$_2$

During the Pleistocene the vegetation changes in the high Colombian Andes included changes from C$_3$ to C$_4$ plants. This is inferred from $\delta^{13}$C values of the C$_{31}$ n-alkane from the Funza-2 sedimentary record taken from the high plain of Bogotá at 2550 m elevation. The environmental factors thought to be responsible for these changes were investigated using a single point simulation of the BIOME3 vegetation model, including changes in precipitation, temperature and atmospheric CO$_2$ concentrations. The model shows that changes are for a major part caused by these latter two factors. The isotopic signature of the n-alkanes of several extant C$_3$ and C$_4$ grasses from the area were determined to calibrate the interpretation of the isotopic record. From the geochemical record, we estimated the altitudinal distribution of C$_3$ and C$_4$ plants, using present grass distribution patterns based on floristic data as a template. This information, in combination with palaeotemperature estimates, enabled the reconstruction of atmospheric CO$_2$ concentrations. The reconstructed CO$_2$ concentrations follow the trends of the Vostok Antarctic ice core through three glacial and two interglacial stages. The lowest calculated CO$_2$ concentration is ca. 210 ppmV for the glacial maxima and within the range of lowest values from Vostok, our highest value (310 ppmV) is for interglacial MIS 7. This represents a new method to reconstruct palaeoatmospheric $p$CO$_2$. It is less accurate than measurements from ice cores, but has potential to be used for sediments that are much older than the ice cores.
3.1. Introduction

3.1.1. Photosynthetic pathways and environmental conditions

Throughout the plant kingdom two major photosynthetic pathways predominate. The largest group of plants use the C<sub>3</sub> pathway, these include most trees and shrubs and many other plants. The other pathway of CO<sub>2</sub> fixation is the Hatch Slack or C<sub>4</sub> dicarboxylic acid pathway (Hatch and Slack 1966), which is particularly common among tropical grass species. C<sub>3</sub> photosynthesis evolved around the Rubisco CO<sub>2</sub> fixing enzyme. In the Earth’s history Rubisco appeared around 3 billion years ago (Hayes 1994), when CO<sub>2</sub> concentrations were much higher and O<sub>2</sub> concentrations much lower than today (Kasting 1987; Berner and Canfield 1989). Under present-day atmospheric CO<sub>2</sub> and O<sub>2</sub> concentrations, the carboxylation of the Rubisco enzyme suffers from competition with oxygenase, especially at high temperatures. This is called photorespiration and significantly limits the photosynthesis of C<sub>3</sub> plants. The C<sub>4</sub> photosynthetic pathway evolved to cope with this problem; it is much more effective in CO<sub>2</sub> uptake than the C<sub>3</sub> pathway, due to a CO<sub>2</sub> concentrating mechanism. In C<sub>4</sub> plants the CO<sub>2</sub> is actively concentrated around Rubisco, preventing photorespiration. This allows C<sub>4</sub> plants to assimilate CO<sub>2</sub> with less water consumption, giving it higher water use efficiency (WUE) (Downes 1969). However, the CO<sub>2</sub> concentrating mechanism requires additional energy to operate. Thus, in general, C<sub>4</sub> plants grow under warmer conditions than C<sub>3</sub> plants and in areas where they can out-compete C<sub>3</sub> plants because of their higher WUE.

Three sub-groups of the C<sub>4</sub> pathway are known, those that use the nicotinamide adenine dinucleotide phosphate malate dehydrogenase enzyme (NADP-me) to form malate, those that use nicotinamide adenine dinucleotide phosphate malate dehydrogenase enzyme (NAD-me) and those using phosphoenolpyruvate carboxykinase enzyme (PCK) to release CO<sub>2</sub> from their internally stored carbon pools (Hatch et al. 1975). All three groups have a different leaf morphology and physiology and grow under slightly different environmental conditions, but have in common that they are mostly found in tropical regions. Patterns of water availability have been found to explain the distribution of the three C<sub>4</sub> sub-groups (Hattersley 1982). Those using NADP-me tend to favour more mesic and non-saline habitats, while those with NAD-me tend to favour more arid and saline environments, but the reasons for this are unclear (Hattersley 1982). However, the distribution of plants with the C<sub>4</sub> photosynthetic pathway as a whole seems to be largely determined by temperature (Sage et al. 1999).

3.1.2. The potential effect of CO<sub>2</sub> on vegetation

Vegetation models, such as BIOME3 (Prentice et al. 1992; Haxeltine and Prentice 1996), show that under lower partial atmospheric pressures of CO<sub>2</sub> (pCO<sub>2</sub>) global vegetation patterns change (Haxeltine and Prentice 1996; Doherty et al. 2000).
BIOME3 also predicts that montane vegetation belts are sensitive to changes in $p\text{CO}_2$ (Jolly and Haxeltine 1997). In their single point simulation of BIOME3 they showed that in tropical Africa, at high elevation, ericaceous scrub vegetation replaces montane forest when $p\text{CO}_2$ is reduced. $C_4$ grassland was also simulated, when both $p\text{CO}_2$ and precipitation were reduced.

A model describing the cross-over for $C_3$ versus $C_4$ plants was reported by Ehleringer et al. (1997) and Cerling et al. (1997) and is based upon formulas from (Farquhar and von Caemmerer 1982) and constants reported by Jordan and Ogren (1984). The model predicts that those plants that obtain the highest quantum yield from photosynthesis will dominate over the others. The point where their quantum yield is equal is defined as the ‘cross-over temperature’ ($T_{50\%}$). All temperatures above $T_{50\%}$ would favour $C_4$ plants, and all values below $T_{50\%}$ favour $C_3$ plants. For this paper we define that $T_{50\%}$ is equivalent to a vegetation coverage of 50% $C_3$ plants and 50% $C_4$ plants. $T_{50\%}$ is a function of $p\text{CO}_2$ (Collatz et al. 1998) and is expressed by Equation 3.1 and shown in Figure 2.1:

$$T_{50\%} = \frac{10}{\ln Q_{10}} \ln \left( \frac{1 + 0.5 \frac{\alpha C_3}{\alpha C_4}}{0.8 \cdot p\text{CO}_2 \cdot s_{25}} \right) + 25^\circ \text{C}$$

where $s_{25}$ is the specificity of the Rubisco enzyme for $\text{CO}_2$ relative to $\text{O}_2$ at 25°C, $Q_{10}$ is the relative change in $s$ due to a 10°C temperature change, $p\text{O}_2$ the partial pressure of $\text{O}_2$ in the atmosphere (21 kPa), $p\text{CO}_2$ the partial pressure of $\text{CO}_2$ in the atmosphere, $\alpha C_3$ is the intrinsic quantum efficiency of $C_3$ photosynthesis and $\alpha C_4$ is the intrinsic quantum efficiency of $C_4$ photosynthesis (Collatz et al. 1998).

Ehleringer et al. (1997) demonstrated that at the present-day $p\text{CO}_2$ of 36 Pa $T_{50\%}$ is around 17°C and that both latitudinal and altitudinal gradients of $C_3$ and $C_4$ grasses seem to have a cross-over point close to 17°C, just as the model would predict. Collatz et al. (Collatz et al. 1998) used the same model to show, and explain, changes in the $C_3$ and $C_4$ grassland composition since the industrial revolution. They compared this with historical data and showed that grassland composition had changed dramatically since the industrial revolution, the onset of the anthropogenic rise in atmospheric $\text{CO}_2$ concentrations.

During the glaciations of the last 400 ka of the Pleistocene, significant changes in atmospheric $\text{CO}_2$ have occurred. The Antarctic ice core record of Vostok shows that global $\text{CO}_2$ concentrations dropped at least 100 ppmV during glaciations (Petit et al. 1999). Vegetation models predict that this must have had a considerable impact on terrestrial vegetation (Cowling and Sykes 2000). Also the distribution of the $C_3$ and $C_4$ grasses must have changed in favour of $C_4$ grasses as Equation 3.1 implies.
3.1.3. Proxies for the presence of C₄ grass in palaeo-environments

Several proxies have been used to infer past changes in the contribution of C₃ versus C₄ plants to the vegetation. Fossil pollen assemblages are not suited to determine these contributions among grasses (Poaceae), since their pollen grains are virtually identical (Moore et al. 1991). Phytoliths and stable isotopes are the most widely accepted proxies. Phytoliths are biogenic opaline silica bodies present in plant cells. For some plant taxa they can be highly diagnostic and can be used in a similar way as fossil pollen assemblages. Although phytoliths from C₃ and C₄ plants do not differ fundamentally, assemblages from particularly highly diagnostic grass phytoliths allow the identification of grasses to sub-family level and in this way the diversity of ancient grasslands can be investigated (Fredlund and Tieszen 1997; Alexandre et al. 1997; Barboni et al. 1999).

The stable carbon isotopic composition of plant biomass is a tool that allows identification of C₃ or C₄ pathways, but does not allow classification of grasses to tribe level or division into sub-groups. As a result of their different metabolic pathways, C₃ and C₄ plants have distinct carbon isotopic signatures. Organic material produced by C₃ plants has characteristic δ¹³C values around -27‰ (O'Leary 1981), whereas that of C₄ plants is much more enriched in δ¹³C and shows characteristic values of around -12‰ (Bender 1971). Hattersley (1982) showed that there is a small but significant difference in δ¹³C of the total organic matter (TOC) between the three C₄ sub-types. C₃ plants along altitudinal gradients show decreased fractionation with increasing elevation, giving rise to an enrichment of 2‰ for C₃ plants at 4000 m, due to changing p/pₐ ratios (Bird et al. 1994; Körner et al. 1988).

For the palaeorecord TOC of soils can be analysed for its stable carbon isotopic ratios. The presence of C₄ plant material would manifest itself in elevated δ¹³C values (e.g. Schwartz et al. 1986; Guillet et al. 1988). In very ancient soils organic material can be completely oxidised, in this case soil carbonates can be analysed which may have retained the isotopic ratios of the organic matter (Cerling et al. 1997). However, often the TOC of sediments represents a very complex mixture of diverse sources and it is impossible to accurately assess C₄ plant contributions from the δ¹³C of TOC. Therefore, it is better to look at a plant-specific proxy instead. Terrestrial plants produce leaf waxes. In the constituents of leaf waxes the isotopic signatures of the photosynthetic pathways are retained. Plant wax n-alkanes are biosynthesised with characteristic odd-over-even-carbon number predominances of the long-chain (C₂₇-C₃₅) components. These distributions make these n-alkanes a good proxy for terrestrial plants (Eglinton and Hamilton 1967). The n-alkanes are also highly resistant against biochemical degradation and survive diagenesis in the sedimentary record (Cranwell 1981). They can be easily dispersed by wind, can be associated with plant detritus or be adhered to dust particles and can thus end up in lake sediments. Leaf lipids are much more depleted in ¹³C than the total biomass as a result of different metabolic pathways. Leaf wax n-alkanes have δ¹³C values about 8‰ more depleted than the biomass: for C₃ plants -35‰ and for C₄ plants -19‰ (Rieley et al. 1991; Rieley et al.
However, the isotopic compositions of $C_4$ plant $n$-alkanes have not been thoroughly studied yet, since only a few $C_4$ plants have been analysed.

### 3.1.4. Palaeo-evidence for increasing contributions of $C_4$ plants at times of low atmospheric $CO_2$ concentrations

Several studies have been reported of which many focus on the last 20 million years. Quade et al. (1995) and Quade and Cerling (1995) reported a 20-Myr-old pedogenic carbonate isotope record from Asia, revealing a shift from $C_3$- to $C_4$-derived biomass between 8 and 6 Ma. Cerling et al. (1997) show that this shift is global and is reflected not only in soil carbonates but also in fossil tooth enamel from grass grazing herbivores (MacFadden et al. 1996) and terrestrial organic carbon preserved in marine sediments. They proposed that this phenomenon was the result of declining $CO_2$ levels during the Neogene.

Several stable carbon isotopic records of the Quaternary period have been reported to show changes in $C_3$ versus $C_4$ plant vegetation contributions. These are mainly from the tropical regions. In Africa several records of $\delta^{13}C_{\text{TOM}}$ in lake sediments and in bogs have been reported. The Kashiru peat bog record from Burundi (the same location of the BIOME3 simulation by Jolly and Haxeltine 1997) indicates a shift from $C_3$ to $C_4$ biomass between 15000 and 10000 yr BP (Aucour et al. 1994). Lake Barombi Mbo in West Cameroon (Giresse et al. 1994) and Lake Bosumtwi in Ghana (Talbot and Johannessen 1992) show similar trends in their sedimentary $\delta^{13}C_{\text{TOM}}$ records. In these studies, the pollen assemblages indicated that the most likely source for the $C_4$ plant isotopic signal were grasses and sedges (Cyperaceae).

Street-Perrott et al. (1997) show that high altitude lake sediments from Mount Kenya have recorded the presence of $C_4$ grasses during the last glacial maximum (LGM), using stable carbon isotopes of organic matter and individual molecules. The occurrence of $\delta^{13}C$-enriched *Botryococcus* algal remains (Huang et al. 1999) led the authors to also investigate the $\delta^{13}C$ composition of leaf wax $n$-alkanes. The records from Sacred Lake (Street-Perrott et al. 1997) and Lake Nkunga (Ficken et al. 1998) both show $\text{TOM}$ and $n$-alkanes with enriched $\delta^{13}C$ values at roughly similar intervals. The authors thoroughly investigated the sedimentary record with $\delta^{13}C$ of molecular markers for aquatic vegetation and algae but also with pollen and diatom records. The expansion of $C_4$ grasses during the early glacial toward the LGM was attributed to a combination of lowered atmospheric $pCO_2$ and a reduced rainfall.

The $\delta^{13}C_{\text{TOM}}$ record of Funza-2 on the high plain of Bogotá shows enrichments that may be explained by a significant expansion of $C_4$ grasses at glacial times (Boom et al. 2001). At high altitudes in the Colombian Andes (3000 m or more) some exceptional patches of $C_4$ grasslands presently occur. Boom et al. (2001) proposed that these patches of high altitude $C_4$ grassland are relict vegetation patches from the last glacial climate. During glacial periods $C_4$ grasses may have flourished in places where today exclusively $C_3$ grasslands appear, as has been reported for Mt Kenya (Street-Perrott et al. 1997; Ficken et al. 1998). Marchant et al. (2002) shows that there are significant
changes in the high altitude grassland biomes during glacial-interglacial intervals. However, a $C_4$ grassland biome could not be identified yet using pollen-derived data sets.

Here we report the $\delta^{13}C$ record of leaf wax $n$-alkanes of tropical high altitude lake sediments from the Colombian Andes to reveal shifts in $C_3$ versus $C_4$ plant vegetation. We investigate the behaviour of the $C_4$ grass biome under varying precipitation, temperature and $CO_2$ conditions using the independent BIOME3 vegetation model. Finally, we attempt to reconstruct atmospheric $CO_2$ concentrations, based upon the principles of the model by Ehleringer et al. (1997). The reconstructed $CO_2$ concentrations are compared with results obtained directly from air bubbles within the Vostok ice core (Petit et al. 1999).

3.2. Area descriptions, methods and materials studied

3.2.1. The area

The study area is the high plain of Bogotá, the floor of an old sedimentary basin, located at 2550 m elevation in the Colombian Eastern Cordillera (Figure 3.1). A large shallow lake existed here from 3.2 Ma until the basin drained around 28 kyr BP. The Colombian capital, Bogotá, is now located on the high plain.

On the surrounding slopes of the Andes, from low to high elevation, several characteristic vegetation zones can be distinguished: subandean forest, which presently ranges from 1000 to 2300 m of elevation, Andean forest (2300-3200 m), subparamo (3200-3500 m) and grass paramo (3500-4200 m) (Figure 3.2A). The transition from Andean forest to subparamo, i.e. the upper forest line, presently lies at 3200 m, corresponding to the annual 9.5°C isotherm (van der Hammen and González 1960; Hooghiemstra 1984; Mommersteeg 1998). The grass biomes of today are the paramos. These cool/temperate tropical alpine grasslands are dominated by the $C_3$ grass *Calamagrostis effusa*. The present-day cross-over point between $C_4$ and $C_3$ grass species based upon floristic data lies at 1900 m (Boom et al. 2001: Figure 3.2C).

3.2.2. Samples

The Funza-2 core (4°50’N, 74°12’W) was drilled in 1988 with Longyear drilling equipment of the Colombian Geological Survey (Ingeominas) in the sedimentary basin of Bogotá. The core was sampled within 3 weeks after collection; the core is stored under cool conditions (approximately 10-15°C) in Bogotá whereas the sub-samples were stored in a cold room (4°C) in Amsterdam. Along the core interval of 20-60 m, samples were collected at approximately 1-m intervals for pollen and $\delta^{13}C$ analysis.

Time control of Funza-2 sediments is based on absolute dating (Andriessen et al. 1993) of Funza-2 and Funza-1 core sediments, inter-core correlation of Funza-2 and Funza-1 based on visual match, and visual match correlation between $\delta^{18}O$ record ODP 677 (Shackleton et al. 1990) and both Funza cores (Van’t Veer and Hooghiemstra
Figure 3.1. Map showing the location of the study area in the Eastern Cordillera of Colombia. The location of site Funza-2 on the high plain of Bogotá is indicated. The inset shows a climate diagram representative for the study area (climate data from: Kuhry 1988).
2000; unpublished data). The sites of Funza-2 and Funza-1 lie ca. 1 km apart in the centre of the basin. The pollen diagrams show down core changing contributions of pollen originating from the four main vegetation belts of these tropical mountains. The Funza-2 core interval of 0.55 m represents the period of approximately 300.28 kyr BP.

Six characteristic and abundant grass species (Poaceae) of the study area were collected in the field for chemical analysis. Andropogon leucostachyus, which is C\textsubscript{4} of the NADP-me sub-type, Melinis minutiflora, of the PCK type, and Sporobolus sp., either the C\textsubscript{4} NAD-me sub-type or the PCK type (depending on the species), were sampled between 2000 and 2500 m of elevation. Calamagrostris effusa, Chusquea scandens (a bamboo) and Cortaderia sp., all of the C\textsubscript{3} type, were collected around 3000 m.

3.2.3. Analytical methods

Sediment samples were freeze-dried and subsequently ultrasonically extracted with methanol, methanol:dichloromethane (1:1) and dichloromethane. From the combined fractions the solvents were removed \textit{in vacuo} and the apolar and polar components were separated from the residues using aluminium oxide column chromatography and hexane:dichloromethane (9:1) and ethyl acetate as eluent, respectively.

The apolar components were analysed using gas chromatography, identified using gas chromatography-mass spectrometry (GC/MS) and the $\delta^{13}$C values of individual compounds were established using isotope ratio monitoring gas chromatography-mass spectrometry (irm-GC/MS). By definition, the stable carbon isotopic composition of a sample is given by: $\delta^{13}$C ($\%$ > $= 1000[(R_{\text{sample}} / R_{\text{PDB}}) - 1]$, where $R$ = $^{13}$C/$^{12}$C and PDB is the Pee Dee Belemnite marine carbonate standard.

GC/MS was performed using a Hewlett Packard 5890 Series II gas chromatograph coupled to a VG Autospec Ultima mass spectrometer operated at 70 eV with a mass range $m/z$ of 800.50 and a cycle time of 1.6 s. The GC was equipped with a fused silica capillary column (25 m $\times$ 0.32 mm) coated with CP-Sil 5 (film thickness 0.12 mm). The carrier gas was helium and on-column injection was applied.

irm-GC/MS has been used to measure the $\delta^{13}$C values of the individual compounds and was described by Hayes et al. (1990). The Hewlett Packard 5890 Series II GC was equipped with a fused silica capillary column (25 m $\times$ 0.32 mm) coated with CP-Sil 5 (film thickness 0.12 mm). The carrier gas was helium and on-column injection was applied. The isotopic compositions were calculated by integration of the masses 44, 45 and 46 ion currents (Merrit et al. 1994).

3.2.4. Model operation

An established vegetation model (BIOME3) was used to investigate the effect of the climatic variables temperature, precipitation and atmospheric CO$_2$ concentration
upon local vegetation (Haxeltine and Prentice 1996). This model is able to simulate potential vegetation biomes using climate and soil data as input. The original BIOME3 program was unchanged. We adjusted the driver software (a routine that handles the input and output of data of the model) in such a way that it will vary two climatic variables for a single location. When the model is executed and fed with the appropriate climatic and soil data it is able to reproduce the results reported by Jolly and Haxeltine (1997).

The model was fed with input that consisted of average monthly climate data obtained from a climate station at Funza, representative of local climate (Kuhry 1988). Mean monthly precipitation for January until December, reaching a total of 780 mm/yr, and temperatures are shown in the climate diagram (Figure 3.1). All other variables including soil parameters were taken from the grid cell containing our study site of the Leemans and Cramer (1991) data base. Atmospheric $CO_2$ concentration at high elevation is similar to that at sea level. However, the $pCO_2$ will decline at higher elevations as a result of the altitudinal decline of atmospheric pressure. Atmospheric pressure at 2550 m was calculated to be 740 mbar using the hydrostatic pressure formula (McIlveen 1992).

3.3. Results and discussion

3.3.1. $\delta^{13}C$ of n-alkanes from extant grasses

To test the $\delta^{13}C$ composition of leaf wax n-alkanes as proxies for terrestrial vegetation, the isotopic values for leaf lipids of several plants were determined in the study area. The distribution and corresponding $\delta^{13}C$ values of the n-alkanes from six of the most characteristic grasses were analysed. The distribution of the n-alkanes is quite variable among the analysed grass species (Figure 3.3). Different specimens of the same species sometimes also show variable distributions (unpublished results). The isotopic ratios of the leaf wax n-alkanes are in agreement with the findings of Rieley et al. (1993) and Collister et al. (1994). The $\delta^{13}C$ values of the n-alkanes of the C\textsubscript{4} grasses are around -20\% and those of the C\textsubscript{3} grasses are around -35\%. Isotopic enrichment of the n-alkanes due to the altitude effect (Bird et al. 1994; Körner et al. 1988) is not noticeable in these grass specimens. Traditionally the C\textsubscript{29} and C\textsubscript{31} n-alkanes are both considered biomarkers for higher plants (Tissot and Welte 1984). However, in the three most abundant analysed C\textsubscript{4} grasses the n-C\textsubscript{31} is much more dominant. Therefore, we selected the n-C\textsubscript{31} alkane as the marker to show changes in vegetation through analysis of leaf wax lipids.

3.3.2. $\delta^{13}C$ values of fossil n-alkanes from Funza-2 core sediments

The fossil n-alkanes found in the sedimentary record are derived from a wide variety of plants. But there might be other sources of n-alkanes in a lacustrine environment. Cultures of the A-race of the freshwater alga *Botryococcus braunii* are
Figure 3.2.  Altitudinal vegetation distribution (observed and tentative) in the study area.  (A) Present-day vegetation belts. The basin lies in the Andean forest belt and the upper forest line is at 3200 m; only the most elevated areas (>3200 m) around the high plain are covered by treeless paramo vegetation.  (B) Reconstructed vegetation setting during the LGM (approximately 18 kyr BP) based on many (>30) pollen records from locations between 2000 and 3800 m elevation. Presence of the palaeo-lake is shown (in fact the lake drained between 30 and 25 kyr BP). The upper forest line lies at approximately 1900 m and the basin is surrounded by grass paramo vegetation (adapted after: van der Hammen 1974).  (C) Present-day altitudinal distribution of plants with a $C_3$ and $C_4$ photosynthetic metabolism, based on data from the literature and own observations (Boom et al. 2001), and unpublished data.  (D) Tentative reconstruction for 18 kyr BP of maximum possible extent of $C_4$ grass distribution based on Ehleringer's model, when CO$_2$ is reduced to 180 ppmV and temperature is today's value $T_{30\%}$ is predicted at 10°C. Most of the paramo might be dominated by $C_4$ plants; only the most elevated (and coldest) areas might have been covered by $C_3$ plants. This setting of parameters illustrates that changes in atmospheric $p$CO$_2$ may only partly explain migrations of vegetation belts.  (note: the original figure was published in colour).
known to produce \( n-C_{25} \) and \( n-C_{27} \) alkadienes (Metzger et al. 1986) which may upon diagenesis be transformed into \( C_{25} \) and \( C_{27} \) \( n \)-alkanes, seriously interfering with the higher plant \( n \)-alkane record. It is also known that \( B. braunii \) lipids can be enriched in \(^{13}\)C (see chapter 4) which could be confused with a possible \( C_4 \) higher plant origin. Indeed, highly enriched \(^{13}\)C values (up to -10\%\(^o\)) were noted for \( n-C_{25} \), (-12\%\(^o\) for \( n-C_{27} \) and -18\%\(^o\) for \( n-C_{29} \)). Therefore, the \( n-C_{11} \) alkane was selected to investigate the changes in \( C_3 \) and \( C_4 \) plant contribution. The \(^{13}\)C values of the \( n-C_{11} \) alkanes in sediments of the Funza-2 core vary between -32\%\(^o\) and -26\%\(^o\)(Figure 3.5) and represent an average
composition of the leaf waxes of the surrounding vegetation of the palaeo-lake. Assuming an end-member linear mixing model in terms of $\delta^{13}$C for C$_3$ and C$_4$ photosynthesis it is possible to estimate the proportion of C$_4$ versus C$_3$ vegetation (e.g. Huang et al. 2000)). We define the coverage of C$_3$ plants, the vegetation index, VI, as follows:

$$VI = \left( \delta^{13}C_{C4, end-member} - \delta^{13}C_{C3, end-member} \right) / \left( \delta^{13}C_{C4, end-member} - \delta^{13}C_{C3, end-member} \right)$$

VI will have a value between 0 meaning 100% C$_4$ domination and 1 meaning 100% C$_3$ domination. On the basis of the analysed grass species, the end-members for the present study are -20%o for C$_4$ and -35%o for C$_3$ leaf wax n-alkanes. Throughout the Quaternary the isotopic composition of atmospheric CO$_2$ has not varied more than 1%o (Smith et al. 1999). This small variation should have had only a minor effect on the end-member method. The most depleted n-C$_{31}$, with $\delta^{13}$C values of around -32‰, can thus be related to an almost pure C$_3$ source. This occurs in the core interval that corresponds to the interglacial of marine isotope stage (MIS) 7, around 48 m core depth and around 31 m in MIS 5. In both intervals the contribution of the Andean forest belt is high, and the contribution of C$_4$ plants is likely to be very limited. The most enriched n-C$_{31}$ is in the second half of MIS 7 going into glacial MIS 6, and again in MIS 4. The most enriched value of -26‰ at 35 m would imply a C$_4$ coverage of as much as 60%. A 100% C$_4$-dominated vegetation type cannot be expected, since there are always plants associated with these vegetation types that are of the C$_3$ type. The high altitude C$_4$ Sporobolus lasiophyllus grassland observed today probably comes closest to the glacial vegetation type containing 60% C$_4$ plants. This modern vegetation type has a high coverage of C$_3$ plant taxa such as Arctophyllum and Espeletiopsis, while the coverage of the C$_4$ grass Sporobolus is only 35% (Boon et al. 2001; Cleef 1981). The interpretation of the end-member mixing model in terms of surrounding vegetation is a simplification, since high elevation C$_3$ plant detritus can be transported down slope and dilute the C$_4$ signal.

3.3.3. Palaeotemperature reconstruction

The pollen diagram of Funza-2 is summarised in Figure 3.4. Four distinct vegetation zones are recognised: the subandean forest, the Andean forest with Quercus and Alnus, the subparamo and the grass paramo. The taxa included in the pollen sum have been described by Hooghiemstra (Hooghiemstra 1984). During the Pleistocene, the upper forest line migrated along the slopes from maximally 3400 m (warmest interglacial climate) to minimally 1800 m (coldest glacial climate) (Figure 3.2A,B). Palaeotemperatures at 2550 m have been inferred from the estimations of the altitudinal position of the upper forest line using a lapse rate of 0.6°C for each 100 m of forest line displacement (for procedures see: van der Hammen and González 1960; Hooghiemstra 1984), indicating a temperature change from +1.2°C to -7.8°C compared with today (Van’t Veer and Hooghiemstra 2000). The vegetation history and floral evolution of this area are known
Figure 3.4. Downcore changes in the upper part of core Funza-2 showing the pollen record, $\delta^{13}$C n-alkane record, the palaeotemperature estimates, the reconstructed CO$_2$ values, and Vostok ice core CO$_2$ concentrations after Petit et al. (1999).
in detail based on many pollen records from the basins of Bogotá and Fúquene. Our vegetation-based temperature record should be reliable and temperature estimates in most of the record have an estimated error of ±0.5°C. The possible effect of changes in CO₂ on the tree line estimation remains to be further investigated. Farrera et al. (1999) evaluated the temperature records of the tropics and acknowledged the effect of changing CO₂ upon tree line-derived records but do not give a conclusive answer to the problem. Street-Perrott et al. (1997) suggested that temperature records needed to be adjusted, but they only investigated changes from C₄ to C₃ vegetation, which do not provide an answer to what the actual effect of changes in pCO₂ is upon a forest shrub ecotone. The only evidence of a CO₂ effect upon a forest shrub ecotone so far comes from modelling (Jolly and Haxeltine 1997; Cowling and Sykes 1999). We assume that the possible effect of CO₂ upon the tree line is included in the error estimate and for lack of better temperature proxies, we accept the pollen-derived temperature record from Funza.

The Funza-2 pollen record shows at the base of glacial MIS 8 the presence of grass-rich paramo vegetation at 2550 m altitude, indicative of glacial cold conditions (Figure 3.5). The temperature estimate for this section is c. 6°C, the coldest of the entire section. A similar, though less extreme, dominance of grass pollen is observed for MIS 6 and 4, also glacials with cold phases. The ⁸¹⁸O record of n-C₃₁ (Figure 3.4) shows that the MIS 8, 6 and 4 are also characterised by an increased amount of C₄ vegetation, likely to result from C₄ grasses. However, it is also known that glacials MIS 8, 6 and 4 are characterised by significantly reduced pCO₂ levels (Petit et al. 1999). At first sight it seems contradictory that the C₄ plant contribution to the vegetation cover increases during colder glacials, since C₄ plants are favoured at higher temperatures. However, a lower pCO₂ will allow C₄ plants to compete with C₃ plants at lower temperatures than today (Figure 2.1). Thus, the change in C₃ versus C₄ plant abundance through time is an interplay of two variables, temperature and CO₂, as defined by T₅₀% in Equation 3.1.

3.3.4. BIOME3 simulations

To find out what kind of climatic factors potentially trigger the changes from a C₄ grassland to a C₃-dominated biome at the location of the high plain of Bogotá, the BIOME3 vegetation model (Haxeltine and Prentice 1996) was used. The model was fed with climate data from a weather station near the village of Funza on the high plain of Bogotá (see climate diagram in Figure 3.2; Kuhry 1988).
Figure 3.5. Single point simulations of the BIOME3 model for Funza. (A) BIOME3 simulation for the locality of Funza, with a constant, present-day precipitation regime of 760 mm/yr. The graph shows the results of simulated biomes when temperature gets colder and/or when CO$_2$ gets lower than today. (B) BIOME3 simulation for Funza with constant LGM CO$_2$ of 200 ppmV. This graph shows what is simulated for the Funza location under glacial atmospheric CO$_2$ and decreasing temperature and precipitation regime.
Three climatic variables were investigated: precipitation, temperature and atmospheric CO$_2$ concentration. The model is then executed and produces a series of biomes, which have been plotted into a two-dimensional grid, with the climatic variables. Figure 3.5 shows two plots showing some of the output of this modelling exercise. Figure 3.5A shows the outcome when precipitation is kept constant, and in Figure 3.6B the CO$_2$ concentration is kept constant at the glacial value of 200 ppmV.

The model simulates a forest-type biome for the high plain of Bogotá at present conditions (this biome is located in the top right of the plot in Figure 3.5A). Since the original classification scheme of BIOME3 is a global set of biomes, it does not include categories more specific to our study area, the tropical Andes. Since we have no additional data how to distinguish between the various types of forest biomes in our area, we assigned all woody plant functional types (PFTs) with a net primary production (NPP) of more than 600 g C/m$^2$ yr to an ‘Andean forest’ biome. The result is equivalent to the experiments of (Jolly and Haxeltine 1997), except that they used an NPP of 300 g C/m$^2$ yr for the distinction of ‘Afro-montane’ forest and ericaceous scrub vegetation. The value of 600 g C/m$^2$ yr calibrates the model with the present-day forest line at 9.5°C. All woody PFTs with an NPP lower than 600 g C/m$^2$ yr are classified as subparamo biomes (still containing a large amount of small trees and woody shrub vegetation). The biomes resulting from the model can probably be separated into a multitude of sub-biomes, but in this paper, we focus only on the C$_4$ plant-containing biomes. Thus, we make no further distinction among the forest and paramo biomes. All simulated non-woody PFT-containing biomes are left as they originally are implemented in the classification scheme of the model.

When the temperature is lowered from 13.4°C to 8.4°C at a pre-industrial CO$_2$ concentration of 290 ppmV, the Andean forest biome is replaced by the subparamo biome. This is roughly consistent with field observations of the present-day upper forest line, which is located at the 9.5°C year isotherm (van der Hammen and González 1960). When the CO$_2$ concentration is reduced, the Andean forest is replaced by subparamo if the temperature is >8°C. At the lowest CO$_2$ concentrations, a C$_4$ non-woody PFT is simulated at present-day temperatures and is classified as a moist savanna biome. This biome shows up when atmospheric CO$_2$ concentrations are <210 ppmV, and when the temperature is >12°C, this moist C$_4$ savanna is no longer predicted (Figure 3.5A).

A simulation using a fixed atmospheric CO$_2$ concentration of 360 ppmV and varying temperature and precipitation only simulates Andean forest and subparamo biomes (not shown). Running the model with an atmospheric CO$_2$ concentration of 200 ppmV, representing the lowest glacial values, and varying temperature and precipitation, moist C$_4$ savanna biome is simulated again at a temperature of >12°C as previously predicted in Figure 3.5A. When under these conditions the precipitation regime is reduced to 50% of the present-day values, moist savanna will change into a C$_4$ dry savanna (Figure 3.5B). Temperatures <12°C at 200 ppmV CO$_2$ atmospheric concentration give a subparamo biome type, regardless of precipitation.
The most important outcome from these model exercises is that the non-woody PFT-containing biomes are actually \( C_4 \) grass biomes. This supports our interpretation of the isotopic record of Funza-2, indicating that \( C_4 \) plants can be an important component of the vegetation on the high plain of Bogotá under certain climatic conditions (e.g., glacial conditions). The model shows that \( CO_2 \) plays a key role in the appearance of the \( C_4 \) biome on the high plain of Bogotá. The model output also hints as to why there is not a continuous presence of \( C_4 \) grasses in the study area during glacials, even when \( pCO_2 \) is significantly low. The \( C_4 \) biomes are very sensitive to temperature and cannot exist when temperatures are \(<2^\circ C\). We can question whether the model is accurate enough to rely on these numbers, but it is additional evidence that temperature plays an important role in the altitudinal distribution of \( C_4 \) dominated vegetation. We interpret the simulated biome zones not as having sharp boundaries, but as gradually grading into one another.

The \( C_4 \) grass expansion as seen in the \( \delta^{13}C \) of the \( n-C_{29} \) alkane record does not reach a single maximum during the coldest phase of a glacial although atmospheric \( CO_2 \) may be low enough. The BIOME3 simulation shows that this can be explained by glacial temperatures that drop below the threshold at which the \( C_4 \) biome cannot compete with the \( C_3 \) subparamo biome.

### 3.3.5. Atmospheric \( pCO_2 \) reconstructions for the past

The isotopic record of \( n \)-alkanes from Funza showed that the contribution of \( C_3 \) plants and \( C_4 \) grass to the vegetation surrounding the lake has changed through time. The contribution of \( C_3 \) versus \( C_4 \) plants can be estimated using an end-member mixing model. The BIOME3 vegetation model has shown that temperature and atmospheric \( CO_2 \) concentrations are the key variables needed to explain the shifts from \( C_3 \) to \( C_4 \) vegetation types. Equation 3.1 gives \( T_{50\%} \) as a function of temperature and \( pCO_2 \). When an estimation of the elevation of \( T_{50\%} \) can be made, \( pCO_2 \) can be calculated, because temperature is known from the independent pollen-based reconstructions. The \( \delta^{13}C \) values of leaf waxes give us an estimation of the percentage of \( C_3 \) (or \( C_4 \) plant cover (Rieley et al. 1993; Collister et al. 1994; Huang et al. 2000). Naturally, this is a simplification of reality, since due to the topography of the catchment area, plant detritus waxes come not only from the local area but also, to some extent, from other elevations. From pollen and floristic data we know that the \( C_4 \) plants in this region must be mainly grasses. \( C_4 \) grass abundance declines with increasing altitude (Livingstone and Clayton 1980; Sage et al. 1999; Rundel 1980). Boom et al. (2001) showed that the distribution in Colombia and Ecuador follows very similar patterns. Present-day grass distribution data indicate how this altitudinal gradient is defined. We use a third-order polynomial trend function, \( f_{(C_{4\%})} \) (Figure 3.6) to describe the altitudinal grass distribution as reported by Boom et al. (2001) in terms of the VI (Equation 3.2).

\[
 f_{(VI)} = 2850 \cdot VI^2 - 4949 \cdot VI + 5497 \cdot VI + 94 \]

3.3
The function \( f_{(vi)} \) describes the composition of \( C_3 \) plants within the total vegetation as opposed to \( C_4 \) plants. In Figure 3.7 this curve is shown, on the \( y \)-axis the elevations have been translated into modern-day temperatures. 2550 m elevation corresponds to 13.4°C. With a lapse rate of 0.6°C/100 m, equivalent to the rate used for the tree line-derived temperature estimates (Hooghiemstra 1984), we translated elevation into temperature. \( T_{vi} \) is the present-day temperature that corresponds to the estimated composition of \( C_3 \) vegetation on the distribution curve.

\[
T_{vi} = \{[2550 \text{ m} - f_{(vi)}] 0.6°C/100 \text{ m}\} + 13.4°C
\]  

\( T_{50\%} \) is \( T_{vi} \) at which 50% \( C_3 \) and 50% \( C_4 \) grasses occur. \( T_{50\%} \) will not be constant in time, because \( T_{50\%} \) is a function of \( C_0 \) (Equation 3.1). To reconstruct \( T_{50\%} \) through time, we define \( T_{50\%,\text{palaeo}} \). Each analysed sample from the Funza has its palaeo-temperature estimate, and will plot a point on Figure 3.6, which is offset from the modern-day distribution line with \( \Delta T_{vi} \). The palaeo-distribution line belonging to the analysed point has an offset \( \Delta T_{50\%} \), which follows from Equation 3.1. If we assume that the general trend in the distribution of \( C_3 \) versus \( C_4 \) grasses remains unchanged, the offset of any point on the distribution line is equal to \( \Delta T_{50\%} \). Hence, any point on the palaeo-distribution line is offset by \( \Delta T_{50\%} \). Thus \( \Delta T_{vi} = \Delta T_{50\%} \) and \( T_{50\%,\text{palaeo}} \) can then be calculated throughout the palaeorecord, simply by:

\[
T_{50\%,\text{palaeo}} = T_{50\%,\text{modern}} + \Delta T_{vi}
\]  

\( \Delta T_{vi} \) is estimated from the palaeo-temperature estimate of the high plain of Bogotá, and \( T_{vi} \) is deduced from the modern-day distribution curve. Hence \( \Delta T_{50\%} \) is defined as the palaeotemperature subtracted by a temperature.

\[
\Delta T_{vi} = T_{\text{palaeo at 2550 m}} - T_{vi}
\]  

Now \( T_{50\%,\text{palaeo}} \) can be substituted into Equation 3.1 and \( pCO_2 \) can be calculated. The values for all the constants of Equation 3.1 were taken from Collatz et al. (1998). Instead of using a high elevation corrected value for atmospheric \( pO_2 \), we used a modern-day sea level value of 21 kPa; this causes our calculated \( pCO_2 \) to correspond to sea level too. For convenience we converted \( pCO_2 \) into concentrations and the results are plotted in Figure 3.5. The errors of our reconstruction were calculated using a maximum and minimum for \( T_{\text{palaeo at 2550 m}} \) (+0.5°C) and \( \delta^{13}C \) of the \( n-C_3 \), (+0.6‰); obviously this does not include possible errors introduced with one of the assumption we made. The \( CO_2 \) concentrations measured in the ice core of Vostok, Antarctica (Petit et al. 1999) are plotted for comparison in Figure 3.4.
The reconstructed palaeo-atmospheric CO$_2$ concentrations seem to fit reasonably well with the ice core data. Our approach to reconstruct palaeo-CO$_2$ ignores the influence of rainfall on the distribution of C$_4$ and C$_3$ plants. Sage et al. (1999) mention that aridity can modify temperature-driven altitudinal trends. A systematic error due to the humidity is probably relatively small because our results (both BIOME3 and CO$_2$ reconstruction) show that CO$_2$ and temperature are the main driving forces behind the C$_3$-C$_4$ vegetation changes in the Funza catchment area and environmental setting.

In the reconstruction there is a systematic slight over-estimation of $p$CO$_2$ for interglacials. This is attributed to the fact that the vegetation dynamics are over-simplified and only changes in grass vegetation are considered. When the isotopic record indicates the presence of C$_4$ plants, grasses are indeed the most likely components. In glacial periods when the isotopic signal indicates a larger C$_3$ plant contribution, a significant proportion can indeed be attributed to cool-temperate C$_3$.

![Figure 3.6. Altitudinal grass distribution function. The distribution of present-day C$_3$ grasses versus C$_4$ grasses is plotted along a temperature and altitude gradient. Three known points are shown: $T_{v1}$, $T_{v2}$, and $T_{v1,\text{paleo}}$. From this $\Delta T_{50\%}$ can be inferred and the palaeo-cross-over point can be calculated, allowing a palaeo-$p$CO$_2$ reconstruction.](image)

The reconstructed palaeo-atmospheric CO$_2$ concentrations seem to fit reasonably well with the ice core data. Our approach to reconstruct palaeo-CO$_2$ ignores the influence of rainfall on the distribution of C$_4$ and C$_3$ plants. Sage et al. (1999) mention that aridity can modify temperature-driven altitudinal trends. A systematic error due to the humidity is probably relatively small because our results (both BIOME3 and CO$_2$ reconstruction) show that CO$_2$ and temperature are the main driving forces behind the C$_3$-C$_4$ vegetation changes in the Funza catchment area and environmental setting.

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grasses. But during the warmer interglacials, much grass vegetation is replaced by C\textsubscript{3} forest, as the pollen diagram indicates. In these situations the distribution curve based upon grasses (Figure 3.6) is no longer valid and this likely causes the calculation to produce an over-estimation of \( pCO_2 \).

### 3.4. Conclusions

Using stable carbon isotopes of fossil leaf waxes we have shown that there were significant changes in C\textsubscript{3} versus C\textsubscript{4} vegetation on the high plain of Bogotá during the last 400 ka. Using the vegetation model BIOME3 it was shown that under low glacial atmospheric CO\textsubscript{2} concentrations, C\textsubscript{4} grass biomes dominate the high plain. The C\textsubscript{4} biome is sensitive to both CO\textsubscript{2} concentration and temperature; when glacial temperatures get too cold a C\textsubscript{3} biome is favoured. The modelled cross-over point, \( T_{50\%} \), makes it possible to reconstruct atmospheric CO\textsubscript{2} concentrations. The results match fairly well with those of the Antarctic ice core, Vostok (Petit et al. 1999). The method certainly needs more exploration; more relevant parameters (such as the incorporation of a forest model, instead of a plain grass model), which are presently missing but might be included to increase the accuracy and realism of the method. Although this method could never replace first-order proxy records from ice cores, it does provide a challenging way to reconstruct very long lacustrine sedimentary records of changing atmospheric \( pCO_2 \) at any desired resolution until the beginning of the Quaternary.

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### 3.6. References


Aucour A-M, Hillaire-Marcel C, Bonnefille R (1994) Late Quaternary biomass changes from \( ^{13}C \) measurements in a highland peatbog from equatorial Africa (Burundi). Quaternary Research 41:225-233

Bender MM (1971) Variations on the $^{13}$C ratios of plants in relation to the pathway of photosynthetic carbon dioxide fixation. Phytochemistry 10:1244


66


Kasting JF (1987) Theoretical constraints of oxygen and dioxide concentrations in the precambrian atmosphere. Precambrian Research 205-299


Mommersteeg H (1998) Vegetation development and cyclic and abrupt climatic change during the Late Quaternary, Ph.D. Thesis, University of Amsterdam


