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Distichia peat — A new stable isotope paleoclimate proxy for the Andes

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ABSTRACT

Global climate variability is a well-documented fact; however, the human contribution to climate change is now being vigorously debated. Therefore, a better understanding of past natural climate variability may help to establish the actual anthropogenic contribution to the observed climatic trend. A variety of high-resolution proxies now exist for documenting climate variability that has occurred in the northern hemisphere over the last 10 ka. In contrast, high-resolution paleoclimate records are more limited for regions such as high altitudes in the Andes/South America. However, many regions of the Andes contain a rich, but as yet overlooked, paleoclimate archive in the form of thick peat deposited *in situ* by the *Distichia* plant. In our study, based on altitudinal transect from the Peruvian Andes, we found a statistically significant and strong relationship between the stable carbon isotope composition of *Distichia* and air temperature ($R = 0.92$ $p < 0.01$). We also confirmed good preservation of relative differences in the original stable carbon isotope composition in peat derived from this plant. Our calibration showed that a decrease of ~0.97 ± 0.23‰ in the stable carbon isotope composition of *Distichia* peat reflects a 1 °C increase in mean air temperature of the growing seasons. This relationship can be used as a new high-resolution proxy for reconstruction of paleotemperature variations over the past several thousand years in the Andes Mountains based on *Distichia* peat cores.

1. Introduction

The cycling of elements between plant material and the soil is much slower in cold climates than in tropical climates, due to reduced rates of plant primary production and slower rates of decomposition of plant material. In addition, if conditions are also wet, plant material undergoes very limited organic decay, so that the litter frequently forms significant amounts of peat. Consequently, elements bound within plant organic matter accumulated under cold, wet conditions can be preserved *in situ* for several millennia, making this material a potentially significant geochemical archive of past climates changes (*e.g.*, Daley et al., 2010; Jones et al., 2010; Tillman et al., 2010a,b). In this respect, peat from bogs and fens in Europe and North America has been extensively studied for over 100 years (Sernander, 1908), but primarily in terms of the degree of decomposition, the C:N ratio, as well as pollen and macrofossil analyses (*e.g.*, Barber, 1982; Johnson and Damman, 1993; Kuhry and Vitt, 1996; van Geel, 1978). The results of these studies have been used to investigate past climate changes, essentially providing a general assessment of wet–dry and warm–cold conditions (*e.g.*, Aaby, 1976; Blackford and Chambers, 1993).

Peat is formed by fossilized organic matter that originates from different plant species, depending on habitat and reflecting geographic location, ecological conditions, and environmental influences. The subject of the present study, *Distichia* peat, has not been invoked previously as a paleoclimate proxy; consequently, no results of stable isotope analyses are currently available in literature. However, *Sphagnum* peat, the most widespread peat in the northern hemisphere, has been the subject of several stable isotope studies, and can be used here as the closest analogy to *Distichia* peat. Nevertheless, key morphological and physiological differences distinguish *Sphagnum* (*Bryophyta* — a non-vascular plant) and *Distichia* (*Juncaceae* — a vascular plant), and accordingly, the stable isotope fractionation would be expected to differ between these two unrelated genera.

Sphagnum peat and *Sphagnum* mosses became the subject of stable isotope paleoclimate studies about 30 years ago (*e.g.*, Brenninkmeijer et al., 1982). However, the majority of publications appeared in the 90s (*e.g.*, Aucour et al., 1994, 1996; Figge and White, 1995; Jędrysek et al., 1995; Macko et al., 1991; Price et al., 1997; Proctor et al., 1992; White et al., 1994). Most of the recent studies have confirmed the value of *Sphagnum* peat as a useful archive of paleoenvironmental and paleoclimate conditions; however, its range of applications with respect to different stable isotope proxies varies as have advances in calibration (*e.g.*, $\delta^{13}C$ — Daley et al., 2010; Loader et al., 2007; $\delta^{18}O$ — Tillman et al., 2010a,b; Zanazzi and Mora, 2005; $\delta^{34}S$ — Bottrell and Coulson, 2003; Novák et al., 2005; $\delta^{15}N$ — Asada et al., 2005; Engel et al., 2010). Stable carbon and oxygen isotope compositions are now

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recognized as the most promising as paleoclimate proxies (*e.g.*, Aucour et al., 1996; Skrzypek et al., 2007a; Zanazzi and Mora, 2005); therefore, our present study has focused on these two elements.

The δ^{13}C value is most commonly studied in bulk organic matter (*e.g.*, Brader et al., 2010; Loader et al., 2007; Ménot-Combes et al., 2004) or in extracted cellulose (*e.g.*, Moschen et al., 2009; Tillman et al., 2010a,b), but other specific compounds have also been tested as proxies (Akagi et al., 2004; Brader et al., 2010; McClymont et al., 2010; Pancost et al., 2000). A few studies reported an offset between the δ^{13}C of cellulose and that of the bulk organic matter in mosses (*e.g.*, Ménot-Combes et al., 2004; Skrzypek et al., 2007b), but this offset seems to be quite constant in *Sphagnum* peat (*e.g.*, Tillman et al., 2010a,b). What this suggests is that the relative variation in both cellulose and bulk organic matter is a valid reflection of the variation in environmental parameters. In early experiments (*e.g.*, Brenninkmeijer et al., 1982), organic peat matter was analyzed in bulk, with no separation. However, differences between peat-forming plants, as well as between the stems and leaves of *Sphagnum*, have been reported recently (*e.g.*, Loader et al., 2007; Moschen et al., 2009). Nevertheless, several recent studies have successfully utilized bulk, unseparated organic matter from *Sphagnum*-dominated peat (*e.g.*, Andersson and Schoning, 2010; Jones et al., 2010; Skrzypek and Jędrysek, 2005) and still obtained good correlation with other proxies.

The appropriate interpretation of relative differences in δ^{13}C and δ^{18}O in peat cores requires the calibration of δ-values against environmental parameters, such as air temperature (T_{air}), precipitation, relative humidity (RH) or atmospheric carbon dioxide concentration (pCO$_2$). However, only a few studies have attempted to quantify the observed stable isotope variations (*e.g.*, as ‰ per °C). In general, three different types of calibrations could be distinguished, each with its own benefits and challenges. The most commonly used has been indirect calibration of the stable isotope variation in peat cores against other more established proxies from the same region, which are believed to reflect the same environmental/climate changes (*e.g.*, Daley et al., 2010; Skrzypek and Jędrysek, 2005; Tillman et al., 2010a,b), or against multiproxies from the same core (*e.g.*, pollen or amoebal species; Andersson and Schoning, 2010; Jones et al., 2010; Lamentowicz et al., 2008; Loisel et al., 2010; Pendall et al., 2001; Skrzypek et al., 2009). The major challenge of this method is proving sufficiently that the compared proxies truly reflect a change of the same environmental or climatic parameters, and that they are not propagations of other extraneous relationships. The second approach is to calculate changes in δ^{13}C or δ^{18}O in a dated core against historical climate records (*e.g.*, Tillman et al., 2010b). This type of calibration can be challenging due to requirements for very high precision in dating a collected material and ensuring that all plant fragments used for stable isotope analyses represent the same time span. A third, simpler approach could be utilization of short peat cores and mosses collected from close proximity, but from very different altitudes, and therefore reflecting different clime conditions (e.g., Ménot and Burns, 2001, Skrzypek et al., 2007a). This type of calibration along altitudinal transects requires selection of very similar sampling places (to exclude other local parameters that could potentially influence stable isotope compositions) and continuous monitoring of local parameters, *e.g.*, RH, T_{air}, or pCO$_2$.

Relatively few studies have been conducted on *Sphagnum* mosses along attitudinal transects (*e.g.*, Ménot and Burns, 2001; Ménot-Combes et al., 2002; Skrzypek et al., 2007a,b; Skrzypek et al., 2010a). Although several other studies have traced the δ^{13}C and δ^{18}O changes along altitudinal transects for various plants, these studies were rarely based on direct measurement at the place of sampling and seldom used data from neighborhood weather stations. In addition, measurements were frequently based on groups of plants, not on a particular species (*e.g.*, Hietz et al., 1999; Körner et al., 1988, 1991). Separation of plant species now appears to be critical in order to obtained robust regressions (Wang et al., 2010), so that the most effective experiment would likely be a set of laboratory experiments in chambers with controlled atmosphere, pCO$_2$, T_{air} and RH; however, this type of study has not yet been conducted for stable isotope composition of peat mosses.

Two major factors are believed to influence the stable carbon isotope composition (δ^{13}C) of peat-forming mosses: T_{air} and wetness (*e.g.*, Jones et al., 2010; Lamentowicz et al., 2008; Loader et al., 2007; Skrzypek et al., 2007a). Other environmental factors, including concentration of CO$_2$, seem to have relatively minor influences on moss δ^{13}C (<0.1‰/100 m, Ménot and Burns, 2001). However, the first initial studies by White et al. (1994) and Figge and White (1995), linked atmospheric pCO$_2$ based on δ^{13}C of peat, and ice-core data, while, a possible influence of T_{air} was also noted. Following the approach adopted by McCarroll and Loader (2004), the δ^{13}C of peat can be corrected for the variation of pCO$_2$ in the atmosphere, based on other proxies (Tillman et al., 2010a,b).

Ménot and Burns (2001) and Skrzypek et al. (2007a, 2010a) made the first quantitative experimental assessment of the direct relationship between δ^{13}C of peat-forming plants and the mean T_{air} of the growing season, measured directly in the field at the plant growth site. Other studies also confirmed good preservation of the original stable carbon isotope composition of mosses in peat (Engel et al., 2010; Skrzypek et al., 2010a) and a similar range of relative variation was observed in extracted cellulose and in total organic matter from mosses (Skrzypek et al., 2007b). Under certain conditions, the primary stable carbon isotope composition was well preserved in the *Sphagnum* peat that forms in nutrient-poor and acidic environments with limited oxygen availability. Changes in this composition also primarily reflected the changes in T_{air} during the growing season (Skrzypek et al., 2007a, 2010a). Therefore, the δ^{13}C value of peat appears to have potential for inferring paleoclimate conditions. All of these previous studies on *Sphagnum* peat provide valuable guidance for assessment of potential new proxies, such as *Distichia* peat for the Andes region of South America.

Distichia muscoides, a native species of the Andes wetland ecosystems (Fig. 1), plays a similar ecological role to that played by *Sphagnum* mosses in European or North American bogs. It is the dominant species (nearly 100% of freshwater wetland biomass) in bogs at elevations between 3500 and 5100 m above sea level (ASL). However, while *D. muscoides* is a widespread vascular plant in the Andes and forms very thick *in situ* peat deposits (>10 m), very little is known about its physiological limits, its growth, or its peat accumulation rates. Although *Distichia* peat represents a potential paleoclimate proxy for large regions of the Andes, it has not yet been studied in a paleoclimate context using stable isotope analyses. This potential new proxy could be suitable for unraveling the Holocene

Fig. 1. *Distichia* peatland near the sampling point no. CC–6 at ~4849 m ASL in the Cordillera Chila/southern Peruvian Andes. Inset: a closer view of *Distichia muscoides*. (photo Z. Engel).

paleotemperature variation in the Andes Mountains over the recent several thousands of years, with a resolution higher than 50 years (*e.g.*, Graf, 1999; Janský et al., 2011). New terrestrial proxies are especially needed for high-mountain environments in the region of the South American Andes where other high-resolution proxies, such as ice cores or tree rings, are very rare for climatic and ecological reasons (*e.g.*, Ekdahl et al., 2008; Hoffmann et al., 2003).

Mountain environments are dominated by denudation, which lowers the earth surface and removes sediments from the landscape. Therefore, detailed sedimentary and landform records are very rare phenomena for high mountain regions. In contrast, very well preserved sedimentary records, rich in paleoecological evidence, are available from high-elevation plateaus or foothill areas. In Southern Peru, the Altiplano region (about 150 km from study area) represents a unique area rich in sedimentary archives. Information gained from lake-level data, lacustrine deposits, pollen records, diatom and ostracod assemblages from large lakes, including Titicaca, has been used for reconstructions of paleoenvironmental conditions since the Last Glacial period (*e.g.*, Argollo and Mourguiart, 2000; Fritz et al., 2010; Gosling et al., 2008; Placzek et al., 2006; Rowe et al., 2003; Tapia et al., 2003; Wirrmann and Mourguiart, 1995). Paleotemperature and precipitation conditions have been inferred from sediment cores and calcite using stable isotopes analyses (*e.g.*, Cross et al., 2000, 2001; Fritz et al., 2006; Seltzer et al., 2000). Paleoclimatic conditions have also been inferred from fluvial systems and archeological sites (*e.g.*, Binford et al., 1997; Farabaugh and Rigsby, 2005; Grosjean et al., 2007). However, none of the sedimentary archives from the Altiplano provide evidence for local paleoclimatic conditions in the semi-arid Western Cordillera.

Paleoclimate proxies in the Western Cordillera are quite limited. In contrast to mountain regions in Eurasia and North America, the Andean environment lacks sufficient high-resolution paleotemperature records, since tree-ring chronologies are not available for sites at high elevations, due to climate as well as to intense human cutting and grazing (tree line at 3900 m ASL; Ellenberg, 1979). Most of the published paleoclimate studies conducted in the Western Cordillera have concerned chronology of moraine sequences and Pleistocene equilibrium line altitudes (*e.g.*, Bromley et al., 2011; Dornbusch, 2002, 2005; Engel, 2001; Hastenrath, 1971; Smith et al., 2009; Úbeda et al., 2009). These proxies are incomplete recorders of glaciations and provide only fragmentary evidence of paleoenvironmental conditions. In order to verify further reconstructions based on *Distichia* peat, other continuous long records would be required; *e.g.*, lake sediment cores or ice cores.

Although high-altitude lakes and salt lake basins are abundant in Southern Peru, only a few lakes and bogs have yet been examined in the Western Cordillera. Radiocarbon data and pollen analyses are available from one small bog at the foot of the Ampato volcano (35 km south from the study area) and from Lake Salinas, located 120 km SSE from the area (Graf, 1999; Juvigné et al., 1997). Other published records refer to rodent middens near Arequipa (Holmgren et al., 2001) and in Aricota and Seca lakes in southern part of the Western Cordillera (Baied and Wheeler, 1993; Placzek et al., 2001; Schwalb et al., 1999). The nearest ice cores to the study area were drilled on Nudo Coropuna (~100 km to the W) in 2003 (Thompson and Davis, 2007). As these cores are still being analyzed, only ice cores from Nevado Sajama (~400 km to the SE) represent the semi-arid region of the Western Cordillera.

The oxygen isotopic composition of the ice provides proxy data for T_{air} and precipitation in the last 24 ka (Thompson et al., 1998) and shows a different climate signal than ice cores from Quelccaya and Nevado Illimani in the Eastern Cordillera (Ramirez et al., 2003; Thompson et al., 2000). Whereas the oxygen isotopic composition of ice in the Quelccaya ice cap (~200 km to the NNW) correlates with shifts of the intertropical convergence zone (ITCZ), which controls regional precipitation variability (Peterson and Haug, 2006), the isotopic signal from Sajama is also apparently influenced by Pacific air masses (Bradley et al., 2003). The controversy on coherence of isotope records from these cores persists (Vimeux et al., 2009), and it is unclear which of these records is a more accurate representation of climate conditions in the study area.

The study of *Distichia* peat has great potential to fill the void for terrestrial high-resolution paleoclimate proxies for high altitudes in the South American Andes. However, use of the stable carbon isotope composition of *Distichia* peat as a paleotemperature proxy first requires confirmation of significant correlations between $\delta^{13}C$ and $\delta^{18}O$ of peat-forming plants and T_{air}, as well as proof of good preservation of the relative differences for the $\delta^{13}C$ in peat. These confirmations, together with a quantitative calibration of the $\delta^{13}C$–T_{air} relationship, formed the main objectives of the present study.

2. Material and methods

2.1. Study area and sampling

The study area extended between 15°10′–15°31′S and 71°38′–72°50′W in the Cordillera Chila, the southern part of the Western Cordillera in Peru (Fig. 2). The sampling sites were located along the elevation gradient between the Nevado Mismi peak (5597 m ASL) and the upper Apurimac River (4200 m ASL) (Fig. 3).

The climate in the study area is cold, with rainy austral summers that contribute ~60% of the total annual precipitation. Long-lasting and continuous precipitation occurs between December and March, when a southern shift of the ITCZ enables an increased transport of humid air from Amazonia (Johnson, 1976). The altitude and valley orientation determine the local variations in annual precipitation, which range from 656 to 797 mm in the study area (Supplementary information, Table S1). Snow cover forms sporadically in winter and usually only lasts for a few hours. The mean annual T_{air} decreases with altitude from 6.4 °C at 4220 m ASL to 0 °C at 5150 m ASL. Very small seasonal temperature variations occur in the study area, oscillating around 2.4 °C (Fig. 4). In contrast, diurnal temperature variations are much more pronounced due to sensitivity of the dry alpine environment to solar radiation; these can exceed 30 °C during August and September in the northern lowermost part of the area. Growing seasons are short and lasted only 72 to 77 days during the 2007–2009 periods at the Angostura site. The total number of frost days in 2008 increased with altitude from 260 (Angostura, 4220 m ASL) to 316 days (Bohemia, 5150 m ASL).

The study area belongs to the puna ecoregion, a high Andean grassland classified as dry puna, which represents a transition zone between humid and desert puna (Molina and Little, 1981). The puna zones are located above 3500 m ASL and extend widely from central Peru, across the Bolivian Altiplano, to northern Chile and Argentina (Baied and Wheeler, 1993). The dry puna ecosystem in the present study is dominated by grasses (*Calamagrostis*, *Agrostis*, *Festuca* and *Stipa*) with occasional scattered dwarf shrubs (*Lepidophyllum quadrangulare*, *Margyricarpus sp.*) and cushion plants on inundated bottoms of valleys (*Distichia*, *Oxychloe*, *Plantago*, *Carex*, and *Juncus*). One of the most characteristic species of the puna is Yareta (*Azorella compacta*), which overgrows stones and forms dense cushions.

Within the puna zone, the high Andean cushion bogs, locally called “bofedales”, are quite unlike *Sphagnum* bogs of temperate zones. They are formed by cushions of unique southern hemisphere plants characterized by vegetative organs that grow close to the ground (*i.e.*, chamaephytes) (Bosman et al., 1993). The genus *Distichia* (*Juncaceae*) dominates bogs characterized by fresh or low salinity waters, whereas *Oxichloe andina* (*Juncaceae*) prevails within highly saline environments (Squeo et al., 2006). The *Distichia* genus includes one species widespread from Colombia to northern Argentina species (*D. muscoides*) and two species with more geographically restricted

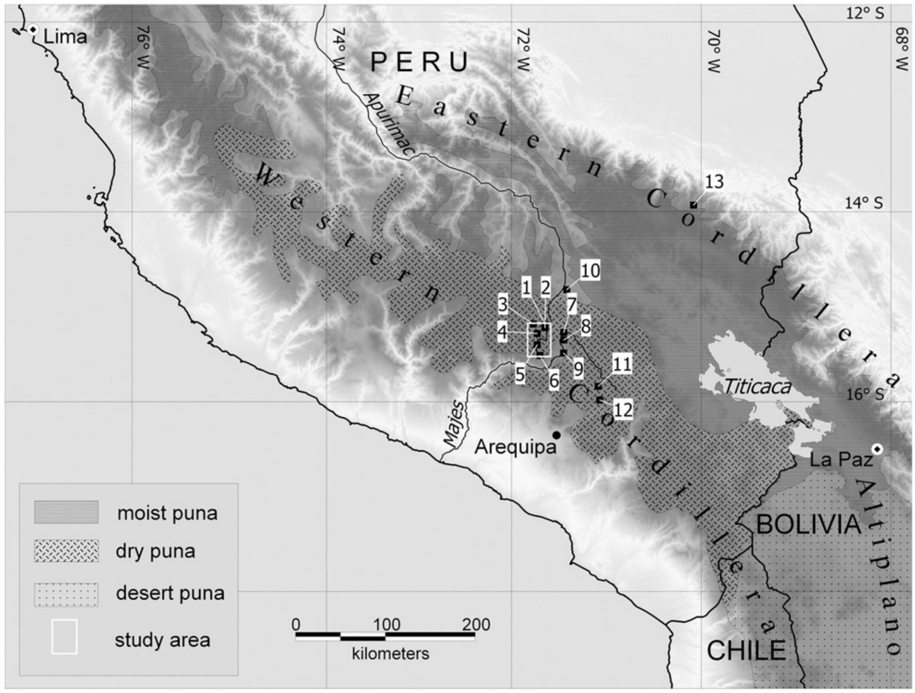

Fig. 2. Location of the study area within high Andean grassland (Puna) in Southern Peru. Distribution of puna after Olson et al. (2001), topography based on USGS (2004) dataset and state boundaries adopted with permission from sample data of Pitney Bowes Business Insight. Numbers 1 to 13 indicates locations of meteorological stations used for calculation of the elevation temperature gradient (see Supplementary information for details about stations).

distribution in Ecuador (*D. acaulis*), and in Bolivia and northern Chile (*D. filamentosa*) (Balslev, 1996).

The species examined in the present study was *Distichia muscoides*, a dioecious (individual plants are either male or female) semiaquatic plant locally called "champa" (Fig. 1). Growing in dense cushions, this species is well adapted to diurnal freeze–thaw cycles. *Distichia* reaches the altitudinal vegetation limit between 3500 and 5100 m ASL, where it frequently forms large bogs or carpets on riverbanks or lakeshores. It has 3–7 mm long distichous leaves, inserted densely along the stem, giving this species its name. *D. muscoides.* As one of only a few species found near the highest limits of vegetation, it is capable to survive the extremes of diurnal freezing and thawing that occur when growing in sunny places (Buffen et al., 2009). In the water-rich conditions of the bofedales, the growth of *Distichia* as a peat forming plant is limited mainly by the T_{air} and photoperiod, with little growth evident during the cold dry season.

Samples of *Distichia* plants and peat were collected between 4356 and 5049 m ASL in ~100 m altitudinal intervals from eight locations with similar hydrological and morphological conditions within the mires (see Fig. 3 and Supplementary information for details). Short 15 cm-deep cores were sampled from eight locations using a spade and knife, and then were divided into three subsamples: A — fresh green plants (~0–2 cm); B — slightly decomposed dead plant matter of yellowish color (~2–7 cm); and C — peat, decomposed organic matter (~7–15 cm). Each sample ~250 g was homogenized and used as a whole for further treatment and analyses.

2.2. Air temperature and precipitation data

Data from the Angostura meteorological station (4220 m ASL) and from the Bohemia site (5150 m ASL) were used to determine the relationship between stable isotope composition of *Distichia* peat and T_{air} (see Fig. 3 for locations). Mean daily temperature (T_{day}) for the Angostura station were derived from temperatures recorded regularly at 7 AM, 1 PM, and 7 PM using the equation $T_{day} = (T_{7AM} + T_{1PM} + 2\ T_{7PM})/4$. Temperatures at the Bohemia Lake site have been recorded at hourly intervals for three years (2007–2009) using a Minikin (EMS Brno) air temperature sensor with accuracy of ±0.2 °C, and T_{day} was calculated as an arithmetic mean of hourly observations. Because T_{air} may be considered as the main limiting factor for the growth of *Distichia* in the given hydrologic conditions, temperature thresholds were used to assess the length of the growing season. Mean T_{air} and a vertical temperature gradient were calculated for the austral spring, which is the warmest season in the study area. As an alternative, the temperature calculations were made for periods beginning and terminating with five consecutive days with $T_{day} \geq 5$ °C (Frich et al., 2002). In order to validate results based on a relatively short measurement period (2007–2009), a vertical temperature profile was calculated for the wider area using T_{air} records from high-altitude meteorological stations, which were up to 160 km far from the study area (see Supplementary information, Tab. S1). Since most organic matter is produced during the warmest period, the temperature gradient calculated for the austral spring was used to determine the mean spring T_{air} at sampling sites along the altitudinal transect (Supplementary information, Tab. S2).

Precipitation records are available for five meteorological stations in the study area, including Angostura, and for six other high-altitude stations in its close proximity (see Figs. 2 and 3, and Supplementary information, Tab. S1). The amounts of precipitation were recorded at 7 AM and 7 PM, relating to the preceding 12-hour periods. Because the length of precipitation records varies among the stations, data were normalized for the 1965–2000 period using a normal-ratio method (Chow, 1964). The mean annual long-term precipitation was correlated with relevant elevations of meteorological stations, in order to reveal the possible relationship between precipitation and altitude. The weather stations did not record relative humidity.

2.3. Stable isotope analyses

Dried 5 g samples from each of eight sampling points along altitudinal transect (A — plants, B — decomposed plants, and C — peat) were powdered and the stable carbon, nitrogen, and oxygen isotope

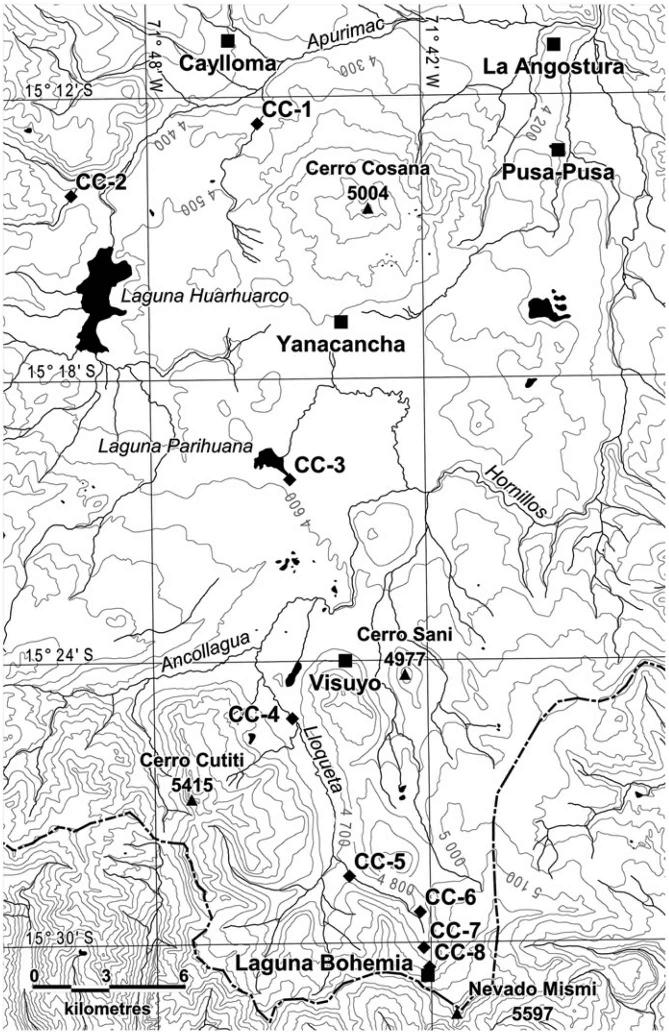

Fig. 3. The location of *Distichia* plants and peat sampling sites (diamonds) and meteorological stations (squares) in the study area.

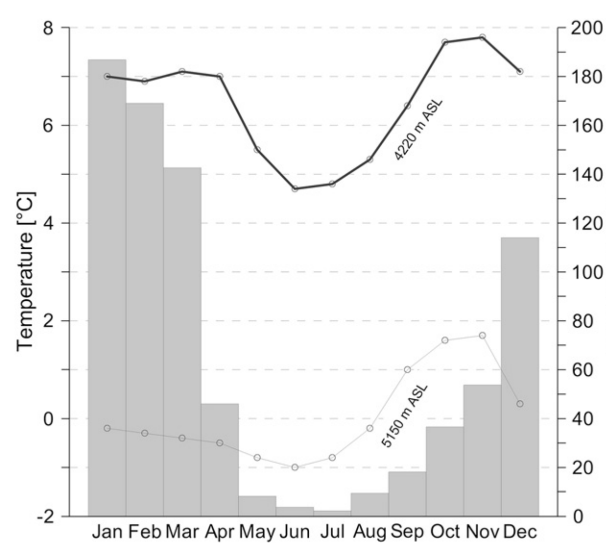

Fig. 4. Mean monthly temperatures and precipitation in the study area at Angostura station 4220 m ASL (bars and thick line) and mean monthly temperatures at the Bohemia site 5150 m ASL (thin line).

compositions were analyzed in the organic matter (Engel et al., 2010). The analyses of stable carbon and nitrogen isotope composition were carried out in a continuous flow system using an elemental analyzer (Thermo Flash EA 1112) coupled with a Thermo Delta V Plus an isotope ratio mass spectrometer (IRMS). Stable oxygen isotope composition was analyzed using a high temperature conversion elemental analyzer (TC/EA Thermo-Finnigan) coupled with a Thermo-Finnigan Delta^{Plus}XL IRMS (Skrzypek et al., 2010a). All stable isotope results are presented as a δ-values, defined traditionally in parts per thousand (‰), as a relative difference between the isotope ratio of the sample and the standard. The δ-values were normalized according to multipoint normalization (Paul et al., 2007), based on international standards (NBS19, LSVEC, USGS24 and NBS22 for δ^{13}C; N1, N2, and N3 for δ^{15}N and IAEA601, IAEA602, IAEA CH6, and IAEA C3 for δ^{18}O) provided by International Atomic Energy Agency from Vienna, using approach proposed by Skrzypek et al. (2010b). The uncertainties associated with stable isotope analyses (1σ standard deviation) calculated based on long term-monitoring of laboratory reference materials were as follows: 0.10‰ for δ^{13}C, and δ^{15}N, 0.30‰ for δ^{18}O and are within a commonly accepted range of precision (*e.g.*, Brand et al., 2009; Coplen et al., 2006). All stable isotopes analyses were performed by first author in the West Australian Biogeochemistry Centre, the node of the John de Laeter Centre of Mass Spectrometry/School of Plant Biology, The University of Western Australia. The correlation coefficient factors (R and R^2) were calculated within the 95% confidence level, and the statistical significance of regression was assessed based on a p-value for the F-test as a part of ANOVA analysis. As statistically significant the relationship with $p \leq 0.05$ were considered.

3. Results and discussion

3.1. Vertical temperature and precipitation gradients

Mean T_{air} of the spring season (2007–09), the warmest period in the study area, varied substantially between the Angostura (4220 m ASL) and Bohemia (5150 m ASL) sites, resulting in a seasonal vertical temperature gradient of 0.67 °C/100 m (Supplementary information Tab. S1 and Fig. S1). The vertical temperature gradient (0.69 °C/100 m) based on annual T_{air} in the Angostura and Bohemia sites was similar to that calculated for the spring season and was only slightly lower than the gradient calculated for high-altitude meteorological stations in the vicinity of the study area (0.71 °C/100 m, $R = 0.99$, $p < 0.01$), based on linear regression. Thus, the vertical gradient derived from measurement over 2007–2009 in the study area seems to be fairly reliable. According to data from all of the monitored mountain stations, the decrease in temperature between 4220 and 5150 m ASL was nearly linear (Supplementary information, Fig. S1).

In contrast to temperature, we did not observe any significant correlation between the amount of precipitation and altitude ($R = 0.02$, $p = 0.95$) for eleven meteorological stations at elevations between 3810 m ASL (Sibayo) and 4620 m ASL (Visuyo) in the study area (Supplementary information Tab. S1 and Fig. S2). The lack of correlation between altitude and amount of precipitation may result from complicated local weather patterns that are governed by seasonal changes of ITCZ and interannual variations in sea surface temperatures in both Atlantic and Pacific regions (*e.g.*, Cook, 2009). This controversy regarding coherence of moisture origin was also raised based on data from stable isotope measurements in ice cores (Bradley et al., 2003; Vimeux et al., 2009; Vuille et al., 2003).

3.2. Altitude effects on the stable isotope composition of Distichia plants and peat

The stable carbon, nitrogen, and oxygen isotope compositions analyzed along altitudinal transects varied in the range expected for

C3 plants and a peat bog environment (Supplementary information, Tab. S3). The observed $\delta^{13}C$ values ranged from −27.44 to −22.53‰, $\delta^{15}N$ between −1.93 and 4.06‰, and $\delta^{18}O$ between 12.26 and 19.51‰.

3.2.1. The stable carbon isotope composition of Distichia peat

Strong and statistically significant correlations between the $\delta^{13}C$ value and altitude were observed for all three subsamples (living plants: R = 0.92; decomposed plants: R = 0.92; peat: R = 0.86; $p < 0.01$), confirming that factors associated with altitude had a significant influence on the stable carbon isotope composition (Fig. 5). The relationship was similar for layers A (living plants) and B (decomposed plants) with observed differences, 0.38 and 0.36‰/100 m, within the range of analytical uncertainty ±0.10‰. The observed relationship differed for the lowermost layer C (peat, 0.65‰/100 m), which may suggest a secondary influence of decomposition on the $\delta^{13}C$ value. Nevertheless, in all three layers, $\delta^{13}C$ became progressively more positive as altitude increased. The similarity in direction for all three trends in $\delta^{13}C$ change suggests that the relative differences in stable isotope compositions of the original peat-forming plants were reasonably well preserved in the peat. A similar range of altitudinal $\delta^{13}C$ gradients has been observed along slopes for mosses and *Sphagnum* peat in European bogs (0.7 to 0.8‰/100 m for moss and 0.20 to 0.25‰/100 m for peat) in earlier studies (Skrzypek et al., 2010a; Skrzypek and Jędrysek, 2005).

Although various factors can influence the $\delta^{13}C$ value (Farquhar et al., 1989; O'Leary, 1981), in certain ecosystems and locations, many of these factors are nearly constant or their differences are negligible for certain sites/plants (Skrzypek et al., 2007a, 2010a). All samples in the present study were collected from ecosystems with similar pools of nutrients and water availability (see Supplementary information). Therefore, three major factors associated with altitude could be considered to control differences in plant $\delta^{13}C$ value along altitudinal transects: pCO_2, precipitation/RH and T_{air}.

In general, increases in altitude and associated with decreases in pCO_2 and increases in $\delta^{13}C$ of the atmospheric CO_2 (Keeling, 1958). However, this effect has only a minor influence on the plant $\delta^{13}C$ value (*e.g.*, <0.1‰/100 m for *Sphagnum*, according to Ménot and Burns, 2001) in comparison with the overall range of altitudinal $\delta^{13}C$ gradients (Skrzypek et al., 2010a). Therefore, even if this effect is observed and cumulated with other primary effects, its influence is very limited. In contrast, temporal variability in pCO_2 (Figge and White, 1995; White et al., 1994) can be much greater than what is observed along altitudinal transect (Ménot and Burns, 2001). Therefore, when peat cores are studied, use of the approach proposed by McCarroll and Loader (2004) for pCO_2 correction will improve precision of the reconstructions.

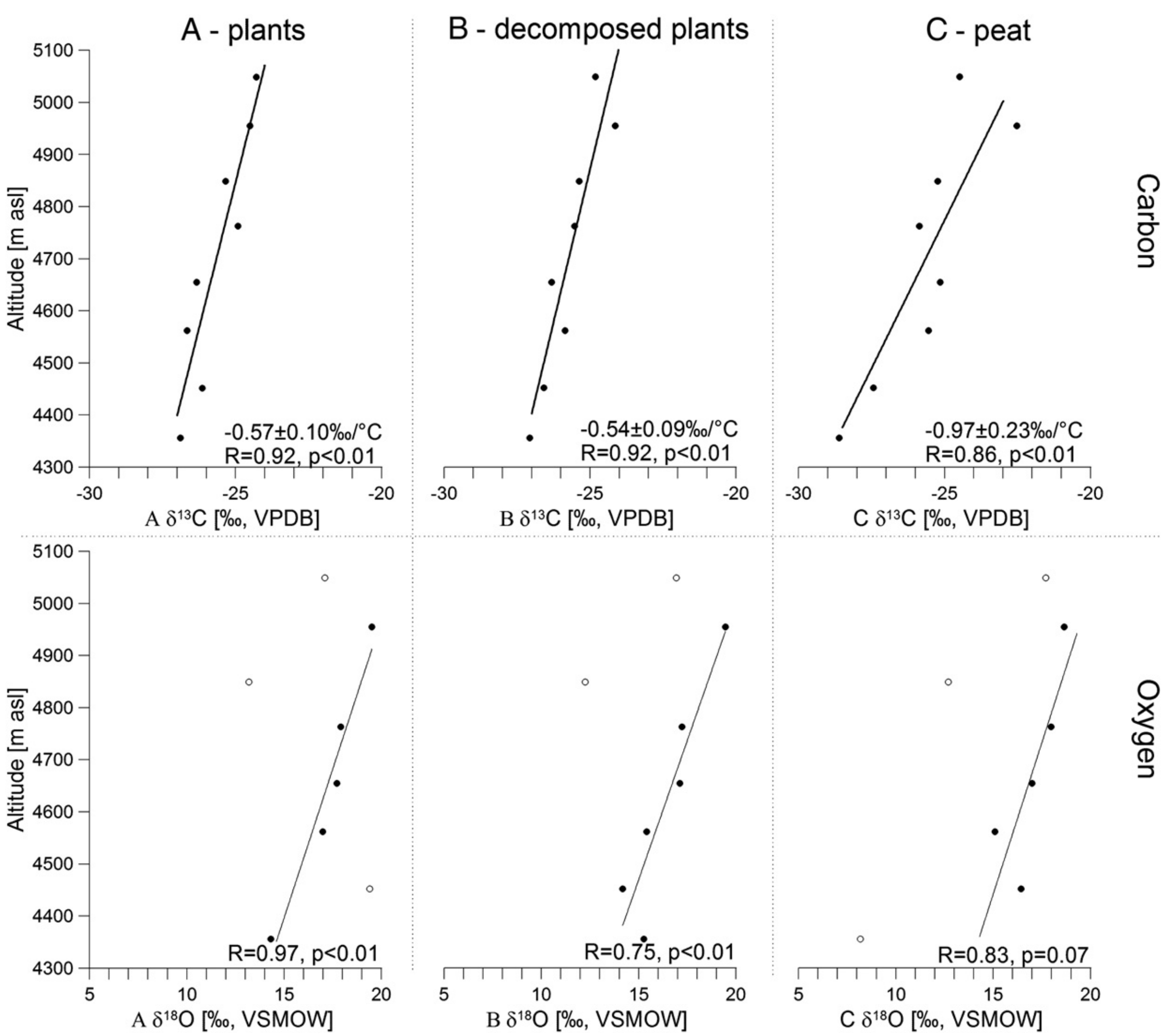

Fig. 5. Correlations between altitude and stable carbon and oxygen isotope compositions, along the altitudinal transect: A — green living plants, B — decomposed plants, and C — peat. Analytical uncertainties: 0.10‰ for $\delta^{13}C$, 0.30‰ for $\delta^{18}O$.

The differences in moisture gradients associated with the amount of rainfall during growing seasons can be viewed as a second factor that influences moss $\delta^{13}C$ values (*e.g.*, Andersson and Schoning, 2010; Loisel et al., 2009; Nichols et al., 2009). However, moss grows only if the minimum amount of water is available; a significant drop in ground water level limits assimilation, thereby reducing or interrupting organic matter production. Moreover, as Skrzypek et al. (2007a) reported, T_{air} frequently correlates with RH and precipitation. Therefore, distinguishing which of these two factors has a primary influence on $\delta^{13}C$ could be challenging. For this reason we attempted to link the amount of precipitation (apart from T_{air}) and $\delta^{13}C$ in the present study. The total annual precipitation data for the study area showed no significant relationship with altitude ($p=0.95$). Based on the field study data, no evidence was observed to indicate progressive changes in water availability/stress along the altitudinal transect. Consequently, we did not observe any correlation between $\delta^{13}C$ and the amount of precipitation.

The correlations between the calculated T_{air} and the measured $\delta^{13}C$ values (*Fq* factor) were as statistically significant as those between altitude and $\delta^{13}C$. The $\delta^{13}C$ value along the altitudinal transect increases when temperature decreases, at about -0.57 ± 0.10‰/°C for living *Distichia* plants, -0.54 ± 0.09‰/°C for decomposed plants, and -0.97 ± 0.23‰/°C for peat (Fig. 5). A similar range of values, varying from -1.0 to -2.4‰/°C, has been reported for other plants (*e.g.*, Griensted et al., 1979; Leavitt and Long, 1986; Lipp et al., 1991; Robertson et al., 1997; Skrzypek et al., 2007a,b; Smith et al., 1973; Troughton and Card, 1975). However, opposite trends ($+0.33$‰/°C) have also been reported for some species and locations (Lipp et al., 1991). The orientation of trends observed in this study, as well as the calculated *Fq* values, are in good agreement with those previously reported for *Sphagnum* peat, at -0.5 to -0.6‰/°C (Skrzypek et al., 2010a; Skrzypek and Jędrysek, 2005). Likewise, Ménot and Burns (2001) observed up to -0.4‰/°C in *Sphagnum*, but the temperatures were not measured precisely at the sampling places. However, in two separate studies, Ménot and Burns (2001) and Ménot-Combes et al. (2004) noted the same negative relationship between $\delta^{13}C$ and T_{air} (as temperature decreases, $\delta^{13}C$ increases) as we observed here for *Distichia*.

The value of -0.97 ± 0.23‰/°C obtained in this study for *Distichia* peat subsamples fell within the previously reported range for other plants, and the calculate change in $\delta^{13}C$ per 1 °C can be used to estimate relative paleotemperature changes recorded in *Distichia* peat from the Andes.

3.2.2. The stable oxygen isotope composition of Distichia peat

The stable isotope composition of oxygen in plant organic matter primarily reflects the composition of the water source available for plants during photosynthesis (Aravena and Warner, 1992; Epstein et al., 1977). For mosses, Zanazzi and Mora (2005) found strong correlation between the $\delta^{18}O$ value of cellulose and the $\delta^{18}O$ of the pond water at the growth site: for *Sphagnum*, the $\delta^{18}O$ values of cellulose were higher by about $+27$‰ compared to water (by $+24.6$‰ according to Aucour et al., 1996). A similar range of oxygen isotope fractionation has been observed for vascular plant tissues (Aucour et al., 1994) and wood (Epstein et al., 1977).

The $\delta^{18}O$ values in *Distichia* observed along altitudinal transect varied between 14.3 and 19.5‰ for living *Distichia* plants (Fig. 5, A) and, similarly, between 15.1 and 18.6‰ for peat (Fig. 5, C), when outliers, as discussed subsequently, are excluded (Supplementary materials Tab. S3). Taking into account the fractionation of $+27$‰ (Zanazzi and Mora, 2005), the $\delta^{18}O$ values of water available for plants had an approximate range between -7.5 and -12.7‰. The isotope monitoring of precipitation was not conducted at any of the stations in the study area; however, the computed range is relatively close to the range of $\delta^{18}O$ in precipitation estimated for this region, at -14.0‰ for the highest sampling point at 5049 m ASL, to -12.7‰ for the lowest sampling point at 4356 m ASL (waterisotopes.org, Bowen et al., 2005). More importantly, this range of $\delta^{18}O$ values and direction of trends estimated for precipitation is opposite to those observed in plants and peat (Fig. 3). In general, lower $\delta^{18}O$ values in precipitation are expected to be found at higher altitudes.

Overall, $\delta^{18}O$ values in plants collected at different altitudes are likely to follow the isotope composition of the local sources of water. Therefore, the value primarily depends on the isotope composition of precipitation, but also can be driven by several factors in addition to T_{air}, such as humidity and evaporation. These additional factors may contribute significantly to the final isotopic composition of the water available for plants and may diminish the general pattern resulting from precipitation (Aucour et al., 1996; Różanski et al., 1993). These complex and variable influences on plant $\delta^{18}O$ are reflected by statistically insignificant relationships along our altitudinal transect, if all sampling points are taken into account. However, two outliers can be identified (4452 for A and 4356 for C, see Supplementary information), as these do not follow the linear regression characteristics of well-preserved samples (discussed in the next paragraph, Fig. 6). Even if these two points are omitted, $\delta^{18}O$ for a further two locations (at 4849 and 5049 m ASL) still did not follow the general trend for all three subsamples (A, B, and C), despite being confirmed as well preserved (as discussed in Section 3.3, Fig. 6). In all likelihood, these two points were regression outliers resulting from a contribution of significant amounts of water from higher altitudes to these sites. After exclusion, in total, of 2 to 3 outlier points, the linear regressions consisted only of 5–6 points (see Fig. 5). Nevertheless, these are worth reporting because the relationships between $\delta^{18}O$ and altitude are quite similar for plants and peat (0.82 for A, 0.44 for B and 0.60‰/100 m for C) and the correlations are significant for A and B ($p<0.01$), although not for C ($p=0.07$). However, this trend in $\delta^{18}O$ along the transect was opposite to that generally observed in mountains, where T_{air} is the main factor governing the stable isotope composition of precipitation (lower $\delta^{18}O$ values at lower temperatures) (Dansgaard, 1964; Różanski et al., 1993). The opposite trend and relatively lower change in $\delta^{18}O$ per each 100 m was reported by Ménot and Burns (2001), for *Eriophorum* (-0.2‰/100 m) and *Sphagnum* (-0.3‰/100 m) from the Swiss Alps.

The positive trend ($+0.8$ to $+0.6$‰/100) observed in the Andes could be explained by higher evaporation rates and lower RH at higher altitudes. Assuming that the RH in our study area is lower at higher altitudes, this trend would be in agreement with the trend reported by Aucour et al. (1996): an increase of 0.1 to 0.5‰ per 1% RH decrease. However, we do not have sufficient meteorological evidence, such as RH, to support this hypothesis.

Thus, these complex factors are likely to be more significant contributors to stable oxygen isotope composition of water available to plants in the studied region than are precipitation and temperature themselves. These factors might include the different origin and trajectory of the moisture-bringing air masses that contribute to precipitation at different altitudes, RH, a rainout effect, or different proportions between rain/dew and rain/snow (Aravena et al., 1999; Aravena and Warner, 1992). This feature, together with the inconsistency in results (several outliers), precludes recommendation of the use of $\delta^{18}O$ of *Distichia* for direct paleotemperature reconstructions, despite the quite good preservation of the original plant oxygen isotope composition in *Distichia* peat. A similar conclusion was drawn by Daley et al. (2010) and Tillman et al. (2010a) for *Sphagnum* mosses, who stated that $\delta^{18}O$ is better correlated with bog surface wetness than with temperature (Price et al., 2009).

3.2.3. The stable nitrogen isotope composition of Distichia peat

In the case of mires, the plant nitrogen stable isotope composition represents a value that reflects a mixing ratio between three main sources of nitrates and ammonia: *e.g.*, rainwater, surface and

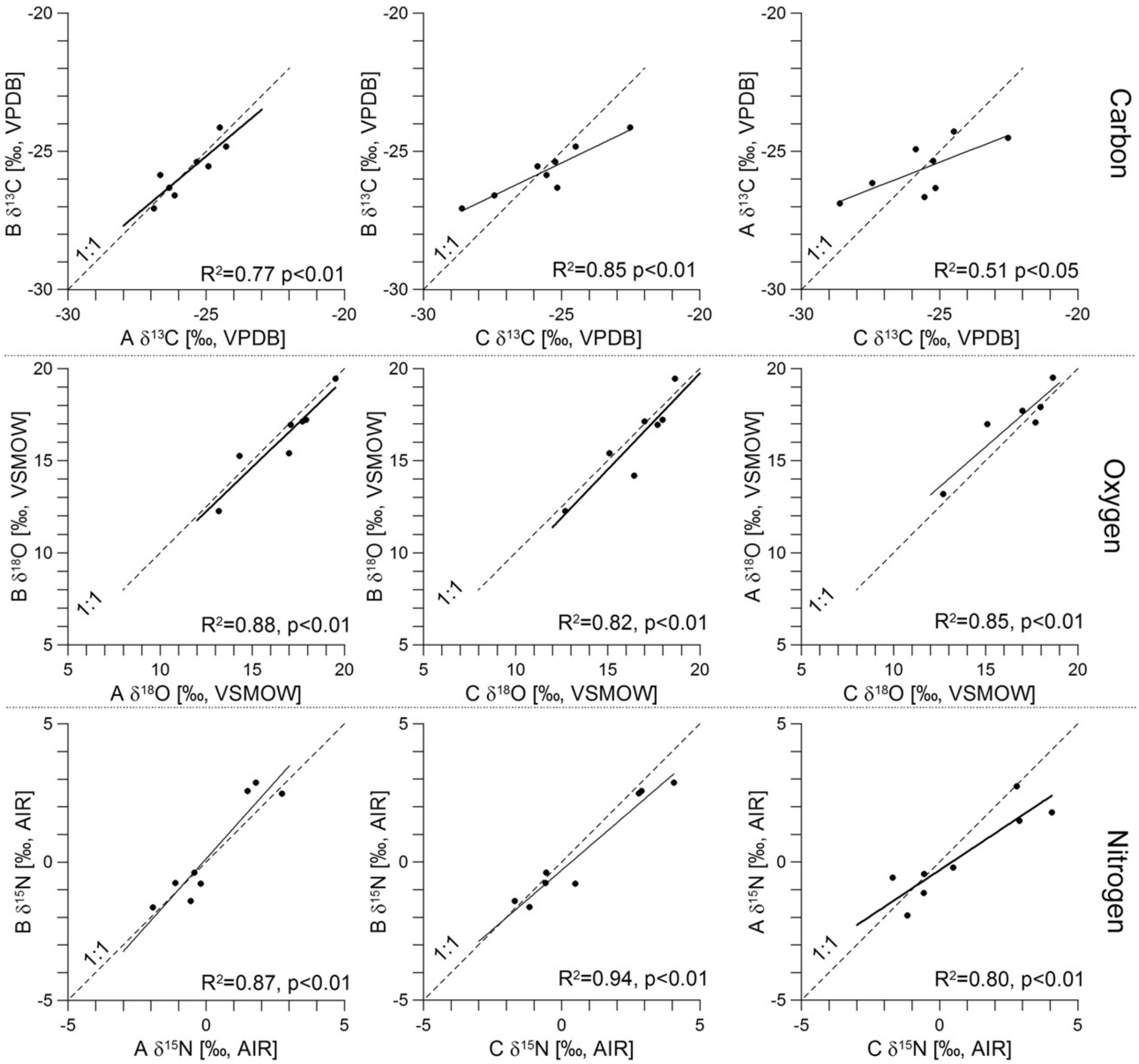

Fig. 6. Correlations for $\delta^{13}C$, $\delta^{18}O$ and $\delta^{15}N$ for the pairs of plant–peat samples along the altitudinal transect: A — green living plants, B — decomposed plants, and C — peat.

groundwater and plant preferences in uptake of NO_x, NH_4 or amino acids (Asada et al., 2005; Bragazza et al., 2006; Breeuwer et al., 2009). Indeed, most water sources that supply mires on high-mountain slopes originate from direct infiltration of precipitation and partially from shallow circulation in underlying weathered bedrock. In our study area, an additional source for nitrogen is associated with grazing animals (llamas). Since pristine areas like the Cordillera Chila have a minimum amount of nitrogen associated with industrial pollution, no altitude effect in the $\delta^{15}N$ value was observed along the altitudinal transect. In general, $\delta^{15}N$ is not particularly suitable for direct paleoclimate reconstructions, although it could be valuable for verifying the stage of preservation of the organic matter in peat (Engel et al., 2010; Skrzypek et al., 2010a). In theory, samples at higher altitudes could be better preserved due to the lower temperatures. Therefore, $\delta^{15}N$ should increase with altitude decreases, since bacteria are more active at higher temperatures and would likely be more efficient at removing ^{15}N over ^{14}N (Skrzypek et al., 2010a). However, this expected correlation was not observed for plants ($p = 0.21$) and decomposed plants ($p = 0.13$). A slight trend was observed for peat, but this was also not statistically significant ($p = 0.18$, see Tab. S3 in Supplementary information). Despite, $\delta^{15}N$ does not provide direct information about paleoclimate, but it still can be useful for verification of preservation of $\delta^{13}C$ in peat (Engel et al., 2010) as discussed in Section 3.3.

3.3. Preservation of plant isotope signatures in peat

The observed strong and significant correlations between altitude/temperature and $\delta^{13}C$ for *Distichia* plants and peat would be useful for paleoclimate reconstruction studies, provided that the original isotope compositions of the peat-forming plant are well preserved in the resulting peat. Therefore, in the next step, we tested the preservation of the relative differences in primary stable isotope compositions by analyzing regressions for pairs of subsamples (A–B, B–C, and A–C) collected along the altitudinal transect, following the approach developed by Skrzypek et al. (2010a) and Engel et al. (2010) for *Sphagnum* peat samples. The strong and significant correlations between $\delta^{13}C$ of *Distichia* plants and decomposed plant subsamples (A–B, $R^2 = 0.77$ $p < 0.01$), between decomposed plants and peat (B–C, $R^2 = 0.85$ $p < 0.01$), as well as between plants and peat (A–C, $R^2 = 0.51$ $p < 0.05$) confirmed that the $\delta^{13}C$ of plants can be predicted based on the $\delta^{13}C$ of peat (Fig. 6). Therefore, the relative differences in $\delta^{13}C$

plants are well preserved in the relative differences in $\delta^{13}C$ of the peat. However, the slopes (A: 0.84, B: 1.30 and C: 1.77) were different from each other (Fig. 6), indicating a secondary influence of decomposition. This was also the reason why the calculated *Fq* values for correlations between T_{air} and $\delta^{13}C$ were different for A (alive plants; -0.57 ± 0.10‰/°C), B (decomposed plants; -0.54 ± 0.09‰/°C) and C (peat; -0.97 ± 0.23‰/°C). Nevertheless, the same trend is observed and the correlations are strong and statistically significant for all cases of $\delta^{13}C$ (Fig. 5).

In addition to carbon, the nitrogen and oxygen stable isotope compositions and C:N ratios were also quite well preserved in peat. The correlations between all pairs of subsamples, A–B, B–C, and A–C, were significant and strong (for $\delta^{15}N$ all $R^2 > 0.80$ and all $p < 0.01$; for $\delta^{18}O$ all $R^2 > 0.82$ and all $p < 0.01$, Fig. 6). Since different mechanisms govern carbon and nitrogen assimilation by plants and since these elements originate from different macroelement pools (*e.g.*, atmospheric for CO_2 and water for NO_x/NH_4), no direct relationship exists between the stable carbon and nitrogen isotope composition. For this reason, in principle, no primary relationship should be observed between $\delta^{13}C$ and $\delta^{15}N$ (Engel et al., 2010; Skrzypek et al., 2010a). On other hand, decomposition usually has simultaneous influences on both carbon and nitrogen stable isotope composition. Therefore, the lack of significant correlations between $\delta^{13}C$ and $\delta^{15}N$ pairs observed for A ($R^2 = 0.12$, $p = 0.39$), B ($R^2 = 0.21$, $p = 0.25$) and C ($R^2 = 0.17$, $p = 0.36$) indirectly confirms the good preservation of relative differences in primary stable isotope compositions of plants in peat (one sample from 4356 m for C:N and $\delta^{15}N$ regression was excluded as unrepresentative, due to very high mineral addition to the sample C = 4.2% and N = 0.2%). This conclusion was also supported by the lack of significant correlation between $\delta^{15}N$ and C:N ratios, as well as $\delta^{13}C$ and C:N ratios, but with exception of peat subsamples (C). The correlation between $\delta^{13}C$ and C:N ratio in peat samples was significant ($R^2 = 0.85$, $p < 0.01$), which may suggest a partial influence of decomposition on peat $\delta^{13}C$ values. However, as the C:N ratio showed significant correlation with altitude ($R^2 = 0.66$, $p = 0.03$) and temperature ($R^2 = 0.78$, $p = 0.03$), the correlation between $\delta^{13}C$ and C:N could, in part, represent a propagation of the primarily good and more significant correlations of $\delta^{13}C$ with altitude and temperature ($R^2 = 0.73$ $p < 0.01$).

We can evaluate which of these two factors (T_{air} or decomposition) had a primary influence on $\delta^{13}C$ (and hence was responsible for the significant correlation between $\delta^{13}C$ and $\delta^{15}N$) because the decrease in decomposition rate and the decrease in T_{air} with altitude compensate for each other. Progressive organic decomposition and preferential removal of more ^{12}C over ^{13}C depends on T_{air}, and therefore each is more characteristic of lower altitudes. Consequently, more advanced decomposition would result in a higher $\delta^{13}C$ in peat (more ^{12}C removed) at lower altitudes (warmer), while slower decomposition would generate lower $\delta^{13}C$ values (less ^{12}C removed) at higher altitudes (colder/better preserved peat). As a result, any correlation between $\delta^{13}C$ of peat *versus* altitude would be negative if the $\delta^{13}C$ was primarily influenced by decomposition. In contrast, higher T_{air} of the growing seasons at lower altitude would result in lower $\delta^{13}C$ values of peat-forming plants, while lower T_{air} at higher altitudes would result in higher $\delta^{13}C$. Therefore, the correlation between $\delta^{13}C$ of plants and altitude is positive if the $\delta^{13}C$ is primarily influenced by T_{air}. Since we observed a positive correlation between $\delta^{13}C$ and altitude for peat along our transect (higher $\delta^{13}C$ values at higher altitude), T_{air} seems to be the major factor controlling $\delta^{13}C$. Moreover, in *Distichia* plants (where, by definition, decomposition had no influence, as the samples were living plants), the altitudinal trend in $\delta^{13}C$ was similar to that observed for $\delta^{13}C$ in peat (Fig. 5). This provides additional confirmation that the influence of decomposition should be considered as a secondary factor that only slightly modifies the relative difference in the $\delta^{13}C$ value in overall well-preserved peat.

4. Conclusions

Our study demonstrates how the $\delta^{13}C$ value variation in *Distichia* peat can be interpreted. Overall, the relative differences in the $\delta^{13}C$ value of *Distichia* plants were well preserved in peat and the $\delta^{13}C$ value of *Distichia* peat represented a good predictor of mean T_{air} for growing seasons. The 1 °C decrease in mean T_{air} during the growing season resulted in a ~0.97‰ increase in the $\delta^{13}C$ value of *Distichia* peat. Consequently, the quantified *Fq* factor (-0.97 ± 0.23‰/°C) could be use as a paleoclimate proxy for estimation of the relative paleotemperature variations in the Peruvian Andes, based on the stable carbon isotope composition in peat cores. On the other hand, the stable nitrogen and oxygen isotope compositions of the *Distichia* plant, although also quite well preserved in peat, were found to be unsuitable for paleotemperature reconstructions, since factors other than temperature exerted the prevailing influences on their δ-values along altitudinal transects.

As a next step, the proposed new proxy can be applied to *Distichia* peat cores to be collected from various locations in the Andes mountains in order to establish a new peat-based high-resolution (<50 years intervals) paleotemperature history of the region for at least several thousands of years. Once this reconstruction will be completed, the final verification procedure will be a cross-correlation with other existing proxies and models in order to confirm the validity of the proposed approach and its accuracy.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.epsl.2011.05.002.

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