Water balance over the last 20,000 yrs in North-Eastern Brazil. Insights from the dD variations of fatty acids from a lacustrine series (Lagoa do Caçó).

Jérémy Jacob

Jérémy JACOB
Institut des Sciences de la Terre d'Orléans (UMR 6113 du CNRS), France
Host Laboratory: Brown University, Providence, RI, USA
Supervisor: Dr. Y. Huang

Water balance over the last 20,000 yrs in North-Eastern Brazil.
Insights from the δD variations of fatty acids from a lacustrine series (Lagoa do Caçó).

In spring 2003, I received the EAOG Travel Scholarship so as to complete bulk and molecular organic analyses performed during my PhD, in the Earth Science Institute of Orléans (ISTO, France), on a sedimentary core drilled in Lagoa do Caçó (Maranhaõ State, NE Brazil). With the agreement of Pr. Yongsong Huang, I spent one month and a half (from April to May) at Brown University (Providence, RI, USA). The EAOG award covered my return air fare and living expenses while in Providence. During this period, we extracted, separated, quantified and measured the isotopic composition ($\delta^{13}C$ and δD) of sedimentary lipids in 31 samples belonging to this lacustrine series. We mainly focused on fatty acids (FA) due to their easy isolation from the total extract. I present herein the scientific context in which this Travel Scholarship was undergone and some key results that concern the hydrogen isotopic composition of higher plants derived FA and their use as proxy of water balance in a tropical setting.

Aim of the study
The main purpose of my thesis was to use organic markers and their isotopic ratios to describe past environments and past climates in recent lacustrine series. This work was undertaken as part of a larger framework that intends to document paleoclimates in tropical South America since the Last Glacial Maximum (LGM). Results from Rock-Eval pyrolysis, bulk isotope measurements and palynofacies analyses realized on a six meter core in Lagoa do Caçó indicated that the sediment recorded major climatic fluctuations during the last 20,000 yrs (Jacob et al., 2004a). Additionally, the molecular investigation of these sediments allowed us to identify several higher-plant biomarkers (Jacob et al., 2004b, Jacob et al., submitted). One of the original aims of the EAOG-sponsored study was to test whether the hydrogen isotopic composition of single molecules could account for paleoclimatic proxies in tropical setting. Recently, Huang et al. (2002) have demonstrated that the hydrogen isotopic signal preserved in phytoplanktonic lipids extracted from lacustrine sediments, is a efficient tool for estimating past temperature changes at mid- to high latitudes. Although it is now admitted that the tropics have been subjected to temperature fluctuations (Stute et al., 1995), this zone appears buffered relative to this parameter. Conversely, the moisture balance (precipitation intensity and seasonality, precipitation/evaporation ratio (P/E)) that is the major component of local climate regimes still needs to be better documented and quantified. The data presented herein suggest that the two periods of dryness that affected the eastern border of Amazonia at the end of the LGM and during the Younger Dryas (YD), are well recorded in the δD of the nC_{30} fatty acid. These observations are substantiated by comparison with independent results.

Settings
Lagoa do Caçó is located in north-eastern Brazil (Maranhaõ State), about 80km from the Atlantic coast and close to the Equator (2°58'S, 43°25'W and 120 m above sea-level).

Figure 1: Location of Lagoa do Caçó, present day position of the ITCZ during austral summer (January) and winter (July) and main ecosystems encountered in north-eastern Brazil.

The local present-day climate is tropical humid with pronounced seasonality. Precipitation, which annually reaches 1750mm on average, mostly occurs during the rainy season, from November to May. The mean annual temperature is 26°C. The vegetation in the watershed pertains to a large cerrado (shrub savannah) corridor inserted between the dry caatinga (savannah) ecosystem to the east and the rainforest to the west. Lagoa do Caçó is therefore in a sensible position to track changes in vegetation distribution related to climate variations. Furthermore, this lake is located where the InterTropical Convergence Zone (ITCZ), that is the major control on precipitation distribution, presently enters the continent and shifts from its winter to summer position. The lake (ca. 2.5 km² surface area) occupies a former river valley within a dune field dating back to Pleistocene times. The maximum water depth is 10m during the wet season (austral summer) and 9m during the dry season (austral winter). The organic matter preserved in the sediments is mainly terrestrial in origin as attested both by bulk and molecular analyses (Jacob, 2003; Jacob et al., 2004a; Jacob et al.2004b; Jacob et al., submitted).

Methods

Core 98-3 (6m long), which was collected in 1998 in the middle of the lake (10m) with a vibracorer, was kept frozen until analysis. Thirty one 1cm long samples were selected for this study on the basis of a previous Rock-Eval screening (Jacob et al., 2004a) and various molecular investigations (Jacob et al., 2004b; Jacob et al., submitted). The samples were then oven-dried at 50°C for 12 hours before crushing. The method allowing the extraction, separation and measurement of the isotopic composition of individual FAME has been detailed elsewhere (Huang et al, 2002). The accuracy of hydrogen isotope measurements was evaluated using four *n*-alkane (C_{16}, C_{18}, C_{20}, and C_{30}) standards with offline measured δD values. The reported δD values for fatty acids methyl esters were corrected by mathematically removing the isotopic contribution from added hydrogens during methylation (δD = -123 ‰

VSMOW for methanol). The precision of the GC-TC-IRMS was routinely verified by triplicate analyses. The average precision (31 samples, 18 compounds) for δD is 3.88 ‰. This relatively poor precision can be explained by the weak abundance of several compounds that have nevertheless been measured. The precision is much better for more abundant compounds (1.94 for nC_{28} and 2.54 ‰ for nC_{30} FA).

Results

In order to directly interpret the paleoenvironmental and paleoclimatic information brought by compound specific measurements, the δD of selected even FA was plotted against time in Figure 2, according to an age model based on six AMS dates (Jacob et al., 2004 -b). For convenience, the δD values (‰ VSMOW) are given as ‰ (per mil) and yrs cal BP as yrs. nC_{28}, nC_{30} and nC_{32} FA are relatively enriched by ca. 40 ‰ in deuterium in the 20-17 kyrs time interval compared to younger samples (average -157 compared to -128 ‰, respectively), the highest values being recorded around 17,000 yrs. A smaller increase in δD by ca. 15 to 20 ‰ is also observed around 12-13 kyrs for nC_{30} and nC_{32} FA and coincides with the YD event.

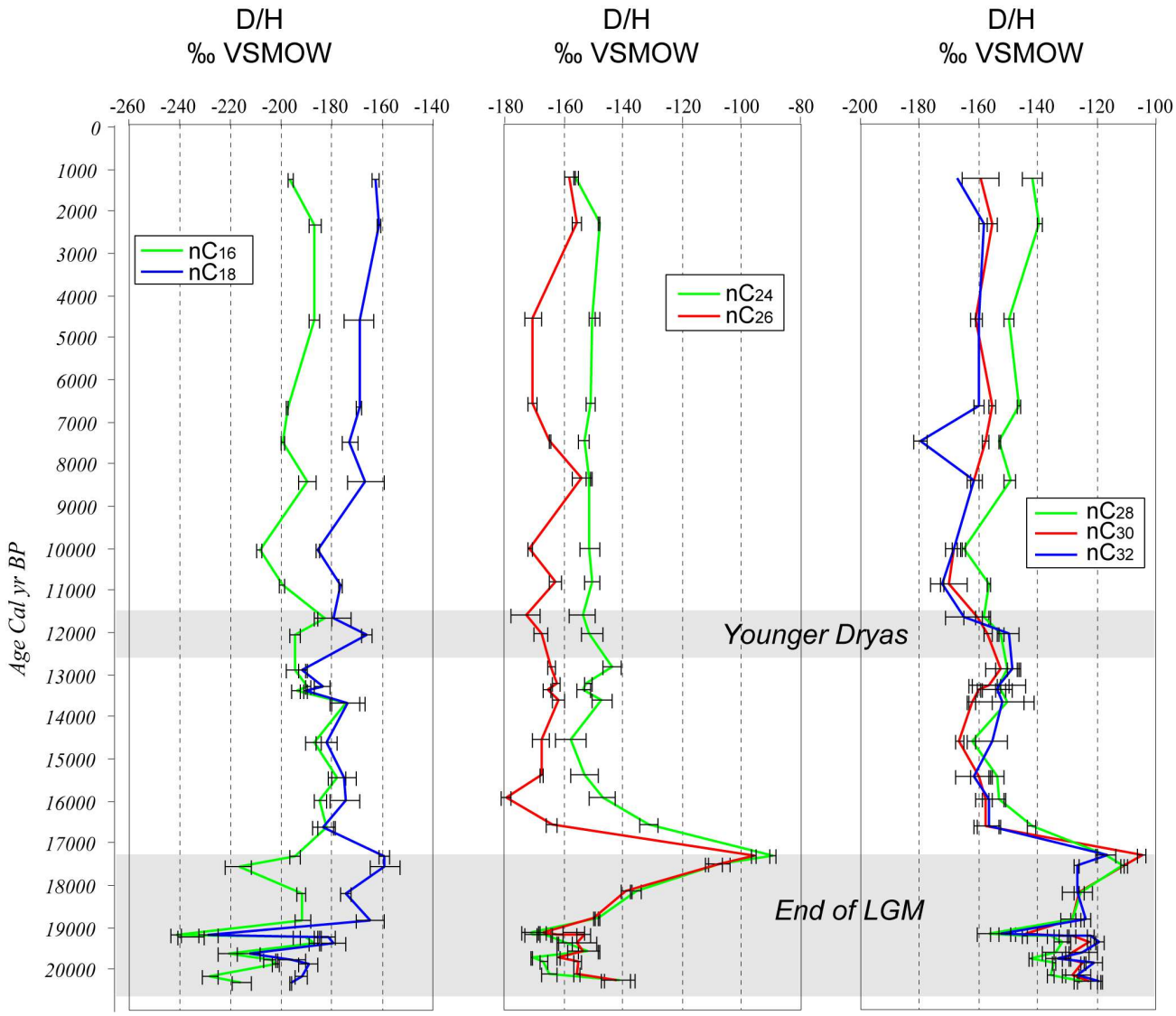

Figure 2: δD variations along age for selected even FA.

Significance of the δD of FA

The H isotopic composition of short chain FA cannot be used as a proxy of the isotopic composition of precipitation because of the diverse origins these compounds have in this lake. Contrastingly, the δD of long chain FA appears to contain clue paleoclimatic information.

There are many parameters that control the δD composition of sedimentary lipids. The temperature and composition of the source of precipitation, the distance from the source, the altitude and temperature at the precipitation site can all affect the isotopic composition of precipitation waters (von Grafenstein, 2002). Then, δD is altered by evaporation during runoff, within soils or a lake water reservoir. When water is used for biosynthetic purposes, H suffers other fractionation effects, related to the metabolism and the physiology of the considered organism (see Sessions et al., 1999). Only the temperature, the amount and the seasonality of precipitation and the intensity of evaporation (and evapotranspiration) could be invoked as a control on the δD of waters in the study setting. In fact, the δD of tropical precipitation depends more on the amount of precipitation and average humidity than on temperature, compared to mid and high latitudes (Dansgaard, 1964). Fewer precipitation and enhanced evaporation (i.e. dryer conditions) cause deuterium enriched environmental waters, and conversely. Contrary to the δD of phytoplanktonic lipids, the δD of terrestrially derived lipids is affected by evapotranspiration and cannot be used as a proxy of the δD of sole precipitation (Sauer et al., 2001 and Huang et al., 2002). Therefore, the δD of lipids isolated from terrestrial higher plants can account for the balance between precipitation and evaporation-evapotranspiration. High figures of δD for nC_{28}, nC_{30} and nC_{32} FA at the end of the LGM are accordingly interpreted as a reduced balanced between precipitation and evaporation. This interpretation also accounts, to a lesser extent to the less negative δD values recorded during the YD.

Variations in the hydrological balance since the end of the LGM in North-Eastern Brazil

Comparison of the δD variations of the nC_{30} FA along Lagoa do Caçó's sedimentary record with previous results, confirms the hypothesis that the δD of terrestrially-derived *n*-alkyl lipids could be used as a proxy of moisture availability in tropical settings. The presence of onocerane I in some levels of the sediments of Lagoa do Caçó have been attributed to the former presence of a plant well-adapted to semi-arid climates in the lake watershed (Jacob et al., 2004). As a matter of fact, the highest abundances of onocerane I coincides with the highest enrichment in deuterium of the nC_{30} FA, at the end of the LGM and during the YD. Increased dryness at these times is also evidenced by palynological results. The AP/NAP ratio, which illustrates the relative abundance of arboreal plants compared to non-arboreal plants (i.e. forest against savannahs in tropical ecosystems), is very low in the 20-17 kyrs time interval. Palynological results indicate sparse vegetation, typical of semi-arid climate at this time. From 17 to 13 kyrs, humid forest developed on the lake surroundings as a consequence of moister conditions. During the YD, the forest is replaced by open vegetation, as supported by the decrease of the AP/NAP ratio. Then, the conditions tend to those prevailing today.

Controversies recently arose concerning the effective dryness that affected tropical South America during the LGM and the consequences on the rainforest ecosystems. This question is of multiple interests because the rainforest plays a crucial role in CO_2 and CH_4 cycling. The "refuge" hypothesis, first emitted by Haffer (1969), attributed the present biological disparities in the Amazonian rainforest to a fragmentation into patches of humid forest separated by corridors of savannas, due to severe dryness at this time. The numerous evidences for this assumption have been strongly denied by Turcq et al. (2003). Although the lake is only on the border of the present day Amazonian rainforest, our data suggest that the

climate was drastically dryer at the end of the LGM in the region. As a consequence, its reduction at its eastern border is most probable. These sole results cannot account for a global reduction of the rainforest surface. They should be completed by other studies on the present borders and within the rainforest. This study also confirms a relative dryness in the region during the Younger Dryas cold reversal, as defined in the Northern Hemisphere.

Conclusion and perspectives

These results expand the possibilities afforded by δD measurements in paleoclimatic studies. The δD of terrestrially derived biomarkers could be used as an estimate of moisture availability for plants, a key climatic parameter in the Tropics. In order to get more quantitative paleoclimatic information, it is necessary to calibrate the δD signature of higher plant lipids on the present day vegetation in the area.

The maximum of deuterium enrichment of the nC_{30} FA and the highest abundance of onocerane attributed to the YD, are recorded around 13,000 yrs cal BP in core 98-3 while the lower AP/NAP ratios are found around 12,000 yrs cal BP in core 97-1. A possible sedimentary hiatus around 17,000 yrs cal BP, not taken into account in the age model of core 98-3, could account for this discrepancy when compared to core 97-1. We are currently performing additional AMS dating in order to better constrain the age model for the Lateglacial / Younger Dryas period.

The next step of this ongoing study will be to compare the isotopic ($\delta^{13}C$ and δD) composition of more specific biomarkers (pentacyclic triterpenes and their derivatives) that are abundant in the lipid extracts of the sediments from Lagoa do Caçó. The first aim is to better characterize the sources of these molecules and their degradation pathway. This study also aims at measuring δD on specific biomarkers (possibly a single source species for pentacyclic triterpene methyl ether, Jacob et al., submitted), in order to constrain any δD variation that could be due to differing metabolisms.

Acknowledgements

Pr. Huang is greatly acknowledged for housing me during one month and a half and making his well-furnished laboratory fully available for this study. I also thank him for the many discussions we had during my venue of which this report is a preliminary proof. Dr. Disnar is acknowledged for improvement of the English version. I would also like to thank Dr. van Grass for being so fast in making the funds available, Pr. Michaelis for being so patient in receiving this report and, of course, the EAOG for giving me this great scientific and human opportunity.

References

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16, 436-468.

von Grafenstein, U. (2002). Oxygen-isotope studies of ostracods from deep lakes. The Ostracoda: Applications in Quaternary Research. Geophysical Research Monograph 131, 249-266.

Huang Y., Shuman B., Wang Y., and Thompson Webb III (2002). Hydrogen isotope ratios of palmitic acid in lacustrine sediments record late Quaternary climate variations. Geology 30, 1103–1106.

Jacob, J. (2003). Enregistrement des variations paléoenvironnementales depuis 20000 ans dans le Nord Est du Brésil (Lac Caço) par les triterpènes et autres marqueurs organiques. Thèse de Doctorat, Université d'Orléans, 296p. http://tel.ccsd.cnrs.fr/documents/archives0/00/00/29/42/index_fr.html

Jacob, J., Disnar, J.R., Boussafir, M., Sifeddine, A., Albuquerque, A.L.S. and Turcq, B. (2004a). Major environmental changes recorded by lacustrine sedimentary organic matter since the Last Glacial Maximum under the tropics (Lagoa do Caçó, NE Brazil). Palaeogeography, Palaeoclimatology, Palaeoecology 205, 183-197.

Jacob, J., Disnar, J.R., Boussafir, M., Ledru, M.-P., Sifeddine, A., Albuquerque, A.L.S. and Turcq, B. (2004b). Onocerane attests to dry climatic events during the Quaternary in the Tropics. Organic Geochemistry 35, 289-297.

Jacob, J., Disnar, J.R., Boussafir, M., Sifeddine, A., Albuquerque, A.L.S. and Turcq, B. (submitted). Pentacyclic triterpene methyl ethers in recent lacustrine sediments (Lagoa do Caçó, Brazil). Organic Geochemistry.

Sauer, P.E., Eglinton, T.I., Hayes, J.M., Schimmelmann, A. and Sessions, A.L. (2001). Compound-specific D/H ratios of lipid biomarkers from sediments as a proxy for environmental and climatic conditions. Geochimica et Cosmochimica Acta 65/2, 213-222.

Sessions, A.L., Burgoyne, T.W., Schimmelmann, A. and Hayes, J. (1999). Fractionation of hydrogen isotopes in lipid biosynthesis. Organic Geochemistry 30, 1193-1200.

Stute, M., Forster, M., Frischkorn, H., Serejo, A., Clark, J.F., Schlosser, P., Broecker, W.S. and Bonani, G. (1995). Cooling of tropical Brazil (5 °C) during the last glacial maximum. Science 269, 379-383.

Turcq, B., Cordeiro, R.C., Sifeddine, A., Simoes Filho, F.F.L., Albuquerque, A.L.S. and Abrao, J.J. (2002). Carbon storage in Amazonia during the LGM: data and uncertainties. Chemosphere 49, 821-835.

Haffer, J. (1969). Speciation in Amazonian forest birds. Science 165, 131-137.