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Maceral composition and molecular markers of two condensed Middle Holocene peat profiles in N Spain

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ABSTRACT

This study deals with the palaeohydrological information obtained from lipids composition and vegetal tissue preservation of two peat cores from Asturias, North Spain. The two profiles differ in the type of peatland (raised bog in La Borbolla and blanket bog in Buelna) and the type of organic matter being more bryophytic in the raised bog and more herbaceous in the blanket bog. The peatlands are located close to the coast on impermeable, old flat erosion surfaces which favoured peat accumulation within a distance of 3.5 km from each other. The accumulation rate varied between 0.05 and 0.07 mm/yr and the records extend from around 9000 to 2500 cal. yr BP.

The main differences between the two peat sites can be summarized as follows: the raised bog has lower mineral matter content and H/C atomic ratio and higher C/N ratio and extraction yields compared to the blanket bog. It has also a higher Tissue Preservation Index for Huminite macerals and increasing Inertodetrinite Index with depth. Regarding biomarkers, the raised bog has a relatively higher concentration of *n*-alkane-2-ones compared to the corresponding *n*-alkane of similar carbon number, higher concentration of medium- vs. high-molecular-weight-methyl-ketones and higher triterpenoids/steroids ratio than the blanket bog.

Alternating humid/dry periods have been recorded in both profiles based on lipid concentrations indicating that the *Sphagnum*-rich intervals in the raised bog are more sensitive than the herbaceous blanket peat record to climatic variations. The main humid intervals identified are dated as 5000–7500 cal. yr BP in the blanket bog and as 6000–3500 cal. yr BP and last 2500 cal. yr BP in the raised bog and correlate with the humid periods traced in other peatlands locations in this region. The transition Middle-to-Late Holocene is characterized by humid conditions in the region which favoured the *Sphagnum* growth in the peats.

The reflectance of huminite in these records appears to be more related with differences in the oxidative conditions than with variation of peat maturity. It is higher in the layers with high mineral matter content at the beginning of organic matter accumulation and also in the upper part of the profile subjected to seasonal desiccation. A more intense biochemical gelification coincides with higher concentration of hopanoids derived from bacteria in the upper part of the profile (acrotelm).

High amount of nonadecan-2-one (K_{19}) and high concentrations of triterpenyl acetates, which are also determined in other peat profiles from Northern Spain are also detected in these profiles. This indicates that the specific conditions required for the formation of these compounds, probably associated to wet temperate climate, dominated throughout the region.

1. Introduction

Since the early work of Blytt (1876) and Sernander (1909), who established a climatostratigraphic division of the Holocene based on alternating dark peat layers containing wood associated to drier and warmer climate, and lighter-coloured, *Sphagnum*-rich horizons indicative of wetter cooler conditions, there has been an increasing number of palaeoclimate studies using peat-bog archives (e.g. Blackford, 2000; Charman, 2002; Barber et al., 2003; Bindler, 2006). The main assumptions on which the peat-based climatic reconstructions rely are: that the vegetation remains are an accurate record of the original vegetation on the mire surface at the time of deposition and that the assemblage composition responds to changes in the water table driven by changing climate. Although any peat deposit can offer palaeoenvironmental information, those with a higher palaeoclimate potential are rain-fed ombrothrophic bogs, the evolution of which is closely linked to meteoric precipitation without any influence from surface water or aquifers (Barber et al., 2003). Both raised bog (Van Geel, 1978; Barber et al., 1994; Gałka et al., 2013) and blanket mire records (Blackford and Chambers, 1991; Chambers et al., 1997; Ellis and Tallis, 2000) have been used

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for palaeoenvironmental studies. Both kinds of deposits, even being essentially ombrothrophic, have a number of peculiarities that should be taken into account when used as archives. Blanket bogs are developed in more open areas and even on gentle slopes that might be responsible for their slightly higher mineral matter contents compared to raised bogs. The latter are typically confined and owe their origin to low relief and impeded drainage, having domed surfaces hydrologically isolated from ground water. High precipitation sustains the blanket bogs that generally have a lower *Sphagnum* contribution than raised bogs. Their overall characteristics may result in different sensitivity to climate variation.

Numerous studies allowed having independent and continuous peat records of climate variability, which have permitted the identification of climate events of different relevance at regional or global scale (Chambers et al., 2010). Efforts focus now in the correlation of different deposits (Mauquoy and Barber, 1999; Hugues and Barber, 2004; Barber and Langdon, 2007; Loisel and Garneau, 2010; López-Días et al., 2013b) and in the refinement of the methodology to make results more comparable (Charman et al., 2009). Many of the palaeoenvironmental studies on peat bogs have been based on palynological profiles, which provide information not only on the peat-forming vegetation in the palaeomire but also on the vegetation in the surrounding area, as pollen and spores are blown by wind. The macrofossil analysis focus on the peat-forming vegetation but it is not always possible to be carried out, when intense humification processes affect the peat. Although peat has been commonly studied using transmitted light (Cohen and Spackman, 1972; Cohen, 1982), reflected light microscopy offers a number of procedures that are very useful for investigating the degree of humification. Koch (1969) distinguished five degrees of humification which can be identified on the basis of their appearance under reflected light microscopy. Esterle (1994) distinguished various types of peat at megascopic and microscopic scale accompanied by chemical signature. Spectral analysis of the fluorescing components (cellulose tissues, some huminites and liptinite components) may provide valuable information not only about the degree of humification but also about the alteration and oxidation processes prior to burial (Hagemann and Dehmer, 1991; Dehmer, 1993). In addition, maceral analysis of peat reflects the degree of preservation of tissues (Sýkorová et al., 2005) and quantifies the impact of wildfires (Glasspool and Scott, 2013).

The Cantabrian region of Spain is the southernmost area in Europe where the climate conditions are adequate for the development of ombrotrophic mires. These have been described in mountainous and littoral locations throughout the Cantabrian region (Fernández Prieto et al., 1987; Pontevedra-Pombal et al., 2006). Organic geochemical studies on Asturian peats have increased in recent years (Ortiz et al., 2010, 2016; López-Días et al., 2010a, 2010b, 2013a, 2013b). This work presents an integrated biomarker and petrographic study of two peat profiles which cover the middle Holocene and the transition to the Late Holocene in the oriental part of Asturias. Both are located very close to each other and can be defined as blanket and raised bogs. Their organic input and the record of arid/humid events are discussed on the basis of preferential lipid concentrations, and degree of preservation of tissues providing an opportunity for discussing the sensitivity of both profiles to palaeoenvironmental variation.

2. Geological setting

The coastal Asturian mires have typically developed on top of a series of sub-parallel, flat, east-west trending ridges ("rasas") over a quartzitic substrate (Mary, 1983). The densest area of littoral mires is located in the eastern part of Asturias close to the boundary with the province of Santander. The flat ridges on which the peat bogs have developed are the result of marine erosion surfaces over the Ordovician quartzite (Mary, 1983). The plane relief and an impermeable surface have prevented drainage, thereby favouring the accumulation of ombrotrophic peat. The studied bogs developed onto two different erosion surfaces situated at different altitudes. La Borbolla is a raised bog (UTM 30 T 365813 4804949) with an extension of 8 ha situated at 227 m above sea level (masl) on a flat surface formed during the Miocene, whereas Buelna blanket bog (UTM 30 T 369898 4805333) is located over a Lower Pliocene erosion surface at a height of 133 masl and covers an area of around 9 ha. A general view of both sites, located within a distance of 3.5 km, is shown in Fig. 1.

The climate in this region is of the Atlantic type with humid temperate winters and occasional droughts in the summer. Identified flora comprises *Sphagnum*, heather: *Erica tetralix* and *Calluna vulgaris*, grass as *Molinia caerulea* and sedges as *Eriophorum angustifolium* and *Carex nigra*. The pollen analysis revealed a significant amount of *Betula*, *Alnus* and *Erica* pollen (Menendez Amor, 1950).

3. Methods

3.1. Sample collection and preparation

A semi-cylindrical peat core sample was taken with a manual Russian probe 5 cm in diameter and 50 cm in length. The sampling site was chosen making transects and selecting the core with the thickest peat layer. The core was then cut into portions approximately 1 cm thick on the same day of collection and kept at −18 °C. The samples were freeze-dried prior to analysis to prevent peat alteration. In general, one out of 4 samples was analysed, except in cases where there was significant variation in the parameters. In this case one out of two samples was selected. Only one sample was analysed from the uppermost and lowermost intervals corresponding to living vegetation and bottom sediment, respectively.

3.2. Radiocarbon dating

Radiocarbon chronology based on Accelerator-Mass-Spectrometry (AMS) ^{14}C dating was performed at the Centro Nacional de Aceleradores, Seville, Spain. Seven samples were analysed from La Borbolla and four from Buelna profiles. Prior to analysis identifiable roots which could belong to various levels of vegetation were removed. The sample was then treated with HCl to eliminate carbonates, NaOH to remove secondary organic acids and finally it was acid rinsed to neutralize the solution prior to drying. AMS results were obtained by reducing the carbon sample to graphite and using the corresponding standards and backgrounds. The conventional radiocarbon age represents the measured radiocarbon age corrected for isotopic fractionation, which was calculated from the $\delta^{13}C$ values. Calibrated dates (2σ) were calculated using the CALIB RADIOCARBON CALIBRATION PROGRAM (Stuiver et al., 2005) version CALIB 6.0 (Reimer et al., 2009) and the calibration curve INTCAL09 (Reimer et al., 2009).

3.3. Elemental analysis and ash yield

The mineral matter content of the samples was calculated as ash yield by heating the samples up to 600 °C under air (100 mL min^{-1}) at a heating rate of 10 °C min^{-1}, after confirming the total absence of carbonates. The carbon, nitrogen and hydrogen contents were determined using a LECO CHN-2000 device. The carbon could be assumed to be organic as no carbonates were detected. Before analysis the samples were ground to 212 μm in an agate mortar.

3.4. Organic geochemical analyses

The samples were ultrasonically extracted for 1 h in dichloromethane/methanol solution (3/1). The sample/solvent ratio was kept at 1:20. After extraction, the solvent solution was filtered and the solvent was removed in a rotary evaporator and then dried under a nitrogen flow. The extracts were analysed using a gas chromatograph (GC) Agilent 7890A attached to a mass spectrometer (MS) Agilent 5975C

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