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Assessment of peat quality by molecular and bulk geochemical analysis: Application to the Holocene record of the Chautagne marsh (Haute Savoie, France)

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ABSTRACT

Although it is primarily constituted in general from a limited variety of local plants, peat is however sensitive to physicochemical changes in the medium, in particular those induced by hydrological fluctuations. The present study aims at confronting the information on peat quality provided by various families of biochemical components (lipids, lignin, sugars), especially in order to check the validity of a new organic matter (OM) quality indicator, the "R400" index, directly drawn from Rock-Eval pyrolysis. This parameter, which is deduced from the sole S2 pyrolysis peak, is extremely robust. The Chautagne marsh, located between the Le Bourget Lake and the Rhône River lies in a key situation for recording lake level variations and Rhône River floods all along its Holocene filling. The study was conducted on a 6 m long core which comprises 4 m of peat under 66 cm of pedogenetically altered OM-rich sediment, Classical Rock-Eval pyrolysis revealed few qualitative and quantitative OM changes with Total Organic Carbon (TOC) values close to 50% and Hydrogen Index values around 300-350 mg HC g-1TOC in the peat. The R400 parameter remains practically unchanged in the upper unit affected by pedogenesis. It fluctuates however all along the peaty unit together with a progressive downward decrease, ascribable to diagenesis. Molecular analyses show that samples with high R400 values are richer in sugars and in slightly oxidized lignin. These results support the idea that the R400 parameter can be used as an indicator of OM preservation. Since OM preservation is mostly controlled by the water table in peat, the Chautagne marsh records hydrological fluctuations such as those of the Le Bourget Lake water level, all along the Holocene.

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1. Introduction

Peat-forming mires are well-known for their ability to preserve organic matter (OM) derived from local plants or even animal or human bodies. Whatever their type (i.e. rheotrophic or ombrotrophic) their OM preservation ability depends primarily on a high level of the watertable (Moore, 1995; Daulat and Clymo, 1998) and thus on the climate through precipitation and temperature.

Paleoclimatic reconstructions from peat records are most frequently based on the recognition of past vegetation changes after either pollen analysis or the identification and count of organic debris (i.e. plant macrofossils or organic particles observed in palynofacies preparations; Barber, 1981; Chambers et al., 1997; Charman et al., 1999; Hughes et al., 2000; Lavoie and Richard, 2000; Chambers and Charman, 2004; Mighall et al., 2006; van der Linden and van Geel, 2006). Molecular organic geochemistry studies have globally the same aim as paleobotanical approaches through the search of taxon-specific biomarkers belonging to various compound families (fatty acids,

hydrocarbons, carbohydrates...) (Boon et al., 1986; Farrimond and Flanagan, 1996; Kuder and Kruge, 1998; Ficken et al., 1998, Pancost et al., 2002; 2003; Xie et al., 2004; Disnar et al., 2005). Other approaches rely on the recognition of former changes in medium conditions for example by using wetness indices of the original peatforming environment (e.g. testate amoebae identification and count; Booth et al., 2006; Mitchell et al., in press; Laggoun-Défarge et al., 2007) or the extent of humification either directly assessed by the colour of the peat material (Blackford and Chambers, 1993; Briggs et al., 2007) or by the extraction yield of humic substances (Aaby, 1976; Blackford and Chambers, 1995).

The aim of the present study is threefold. Firstly, it aims at comparing the information on the quality of the peat, its preservation and hence its deposition environment provided by different families of biochemicals, namely sugars, lignin and fatty acids. Secondly, this information acquired at the molecular level is used to check the validity of the "R400" parameter, directly drawn from OM characterization by automated Rock-Eval pyrolysis. This new parameter is likely to provide basic but robust information on the degree of preservation of the OM of soils and sediments (Disnar et al., 2003). Thirdly, the variations in the R400 parameter and other classical Rock-Eval parameters through a Holocene peat record are discussed and

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compared with independent records in terms of environmental and climatic variations. The selected study site is the Chautagne swamp, located between the Le Bourget Lake and the Rhône River (Fig. 1), both of them reputed to have been affected by palaeoclimate-driven perturbations during the Holocene (Bravard, 1987; Salvador et al., 1993; Chapron et al., 2002; 2005; Arnaud et al., 2005; Revel-Rolland et al., 2005). As a result, the sedimentary record preserved in this swamp is likely to have recorded past fluctuations in Lake Le Bourget water level, and possibly also major floods of the Rhône River, these two phenomena being primarily climate-driven.

2. Setting

The Chautagne swamp (231.5 m asl) is located in the Rhône floodplain, on the border of Lake Le Bourget, in the French Alps (Fig. 1). This swamp is assumed to have formed at around 11,000–10,000 cal. BP at the extremity of the former great Lake Le Bourget that was dammed by major inputs from the Rhône River which was until then a tributary of the lake (Bravard, 1987). Subsequently, the Savière channel, a relict of the former Rhône inlet, became the outlet of the lake. During the Holocene, the Chautagne swamp received only Rhône inputs during major floods, as the current was reversed in the Savière channel. The Post-Glacial-Holocene evolution of this area is discussed in greater detail below.

3. Materials and methods

3.1. Coring and sampling

In order to obtain a rather large accumulation of peat the coring site was selected close to the Mollard de Vions rock, on its eastern side (Fig. 1). The studied core was drilled in November 2004. In order to

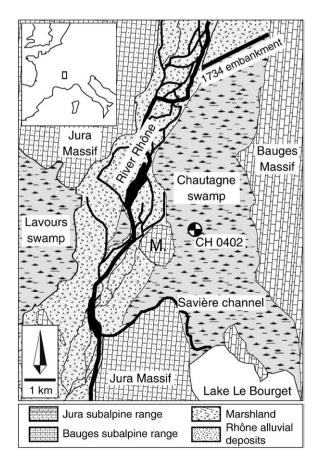


Fig. 1. Location of the Chautagne marsh with indication of the coring site (after Bravard, 1987). M=Mollard of Vions rock.

obtain an unperturbed continuous record, two 50 cm overlapping series of 1 m long sections were retrieved at less than 30 cm apart. The lithology of the CH-0402 composite core obtained is schematically represented in Fig. 2. Three units, numbered 1 to 3 from top to bottom, were distinguished according to lithology. Unit 2 was further divided into 2a and 2b after a major change in OM content at ca. 160 cm depth. This entire peaty unit was brownish and fibrous in aspect, with many rather large plant remains.

3.2. Dating and age model

The age model (Fig. 2) was established from AMS ¹⁴C radiocarbon dates performed on peat samples at the Laboratoire de Mesure du Carbone 14 in Gif-sur-Yvette (Table 1). Samples Sac-A4841 and Sac-A4845 were very probably mixed up, since the corresponding dates agree perfectly with the proposed age model provided that the two samples are swapped. Nevertheless, they are not taken into consideration in the discussion. All calibrated ages were computed according to the 5.0.2 version of Intcal, using the calibration curve of Reimer et al. (2004). Three dates at 2030, 4720 and 7420 yr cal BP, determined from samples taken at 157, 242.5 and 337.5 cm depth respectively, are fully consistent with each other and indicate a mean sedimentation rate of 0.33 mm yr⁻¹ for the whole sub-unit 2b. It can be argued in a first approximation that the top of the core corresponds to Present time. In this hypothesis the sedimentation rate of 0.8 mm yr⁻¹ calculated for the clay-rich interval comprised between 0 and 157 cm depth is higher than that of 0.33 mm yr⁻¹ determined for the underlying peaty unit 2b, in agreement with the difference in lithology of these two sections. A greater sedimentation rate $(0.45~\mathrm{mm}\,\mathrm{yr}^{-1})$ calculated between 337.5 and 457 cm is still in agreement with lithology. The latter rate was arbitrarily applied down to the base of the core at 477.5 cm. Altogether, we consider that the examined sediment record was deposited during three successive sedimentation stages: first with a sedimentation rate of ca. 0.44 mm yr⁻¹ below 337.5 cm, then 0.35 mm yr^{-1} between 337.5 and 157 cm depth, and finally 0.8 mm yr^{-1} between 157 cm depth and the top core. This age model obtained from only four ¹⁴C ages obviously remains to be confirmed but can be judged sufficient for the purpose of this study, especially for the 337.5-157 cm depth section on which we will mainly focus.

3.3. Rock-Eval pyrolysis

Ninety four 1 cm-thick samples were taken at 5 cm apart all along core CH04-02 for Rock-Eval analyses (Fig. 2). The 12.5 uppermost centimetres were not collected because of pedogenic alteration revealed by a granular structure and bioturbation. The analyses were carried out on 100 mg of powdered dry sediments with a "Turbo" Rock-Eval 6® pyrolyser manufactured by Vinci® Technologies. The full description of the method and of the obtained parameters can be found in Espitalié et al. (1985) and Lafargue et al. (1998). Briefly, the samples are first pyrolysed under inert atmosphere (N2), and the residual carbon is subsequently burnt in an oxidation oven. The amount of hydrocarbons (HC) released during pyrolysis is detected by a flame ionisation detector, while online infrared detectors continuously measure the released CO and CO₂. The standard pyrolysis program starts with an isothermal stage of 2 min at 200 °C. The pyrolysis oven temperature is then raised to 650 °C at 30 °C min⁻¹, and held for 3 min at this temperature. The oxidation phase starts at an isothermal stage at 400 °C, followed by an increase to 850 °C at 30 °C min⁻¹ and held at this final temperature for 5 min. Classical Rock-Eval parameters are calculated by integration of the amounts of hydrocarbons (HC), CO and CO2 produced during the thermal cracking of the OM, between well-defined temperature limits. In the present paper, we mainly focus on the following parameters derived from signals recorded during the pyrolysis phase:

 S2 (expressed in mg HC g⁻¹ sample) corresponds to the amount of HC released during pyrolysis;

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