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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)

Jean-Robert Disnar^a, Jérémy Jacob^a, Mayssa Morched-Issa^a, Nathalie Lottier^a and Fabien Arnaud^b

^aISTO, UMR 6113 du CNRS, Université d'Orléans, 1A rue de la Férollerie, 45071 Orléans cedex 2, France

^bEDYTEM, UMR 5204 du CNRS/Université de Savoie, Campus Savoie Technolac, F-73376, le Bourget du Lac, France

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.

Keywords: Peat; Paleohydrology; Carbohydrates; Lignin; Rock-Eval pyrolysis

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] and [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] and [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], [Pancost et al., 2003], [Xie et al., 2004] and [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 peat-forming environment (e.g. testate amoebae identification and count; [Booth et al., 2006], [Mitchell et al., in press] and [Laggoun-Défarge et al., 2007]) or the extent of humification either directly assessed by the colour of the peat material ([Blackford and Chambers, 1993] and [Briggs et al., 2007]) or by the extraction yield of humic substances ([Aaby, 1976] and [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 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], [Chapron et al., 2005], [Arnaud et al., 2005] and [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 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 ^{14}C 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 mm 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 ^{14}C 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 (N_2), 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 CO_2 . 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 CO_2 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;
- S3CO (in mg CO g^{-1} sample) corresponds to the amount of CO released before 500 °C during pyrolysis. This is to avoid interference from the contribution of inorganic CO released at higher temperature (Espitalié et al., 1985);
- S3CO₂ (in $\text{mg CO}_2 \text{ g}^{-1}$ sample) corresponds to the amount of CO_2 released before 400 °C during pyrolysis. This is to avoid interference from the contribution of inorganic CO_2 released at higher temperature;
- TPS2 is the temperature of the pyrolysis oven recorded at the top of peak S2, which thus corresponds to the optimum release of hydrocarbons during pyrolysis. In order to ensure consistency with previous versions of the Rock-Eval apparatus, the TpS2 is converted into the well-known Tmax;
- TOC is the Total Organic Carbon, i.e. the sum of all the carbon moieties (HC, CO and CO_2) attributed to the OM and integrated during pyrolysis and the subsequent oxidation stage;
- HI corresponds to the quantity of HC released during pyrolysis relative to TOC, namely S2/TOC expressed in mg HC g^{-1} TOC.
- OICO₂ corresponds to the quantity of pyrolysed CO_2 relative to TOC, i.e. S3CO₂/TOC expressed in $\text{mg CO}_2 \text{ g}^{-1}$ TOC. This oxygen index was determined with earlier versions of the Rock-Eval pyrolyser and is thus often named OI. The Rock-Eval 6 device also allows the following two oxygen indexes (not used in the present study) to be determined:
- OICO corresponds to the quantity of pyrolysed CO relative to TOC, i.e. S3CO/TOC, in mg CO g^{-1} TOC;
- OIRE6 corresponds to the quantity of oxygen released as CO and CO_2 during pyrolysis, relative to TOC. It is expressed in $\text{mg O}_2 \text{ g}^{-1}$ TOC.

The R400 parameter (Disnar et al., 2003) is defined as the ratio between the area of the S2 peak integrated up to 400 °C normalized to its total surface (Fig. 3).

3.4. Carbohydrate analysis

Neutral sugar analyses were carried out in 2 steps following a procedure adapted from previous work ([Bethge et al., 1966], [Oades et al., 1970], [Modzeleski and Laurie, 1971] and [Cowie and Hedges, 1984]). The first step, which comprises a phase of soaking with 24 N H₂SO₄, allows the hydrolysis of both cellulose and hemicellulose(s). The second step, consisting of the same procedure without the 24 N H₂SO₄ pre-treatment, yielded only hemicellulose “H” monomers. Consequently, the cellulose content was calculated by subtraction of the results obtained in the first step from those obtained in the second step.

The operating procedure for total sugar analysis can be summarized as follows: 1 ml of 24 N H₂SO₄ was added to 100 mg of dried sediments in a SVL® Pyrex® tube. After 12 h of contact at room temperature, the solution was diluted to 1.2 M H₂SO₄ with pure water. The tubes were tightly closed under vacuum (see Appendix A) and heated at 100 °C for 4 h. After cooling, deoxi-6-glucose (400 µg in solution in water) was added as an internal standard. The samples were subsequently neutralised with CaCO₃. The precipitate was removed by centrifugation and the supernatant was evaporated to dryness. The sugars were then dissolved in methanol and the solution was purified by centrifugation. After introduction of the alcoholic solution in another vessel, the solvent was evaporated under vacuum. The sugars were then dissolved in pyridine, trimethylsilylated (Sylon BFT, Supelco; 1 h at 60 °C) and immediately analysed using a Perkin Elmer gas chromatograph fitted with a 25 m × 0.25 mm i.d. CPSil5CB (0.25 µm film thickness) column and a FID detector. The temperature program began at 60 °C, then the oven temperature was raised at a rate of 30 °C min⁻¹ up to 120 °C, maintained at this temperature for 1 min, then raised again to 240 °C at 3 °C min⁻¹ and finally at a rate of 20 °C min⁻¹ up to 310 °C where it was maintained for 10 min. The injector split was off at the start time and turned on after 2 min. The injector was maintained at 240 °C, and the detector at 300 °C. A mixture of eight monosaccharides (ribose, arabinose, xylose, rhamnose, fucose, glucose, mannose, and galactose) was used as an external standard for compound identification through peak retention times and for individual response coefficient determination. Since each sugar gives several peaks corresponding to the different possible epimers (up to 5; Bethge et al., 1966), quantifications of a given compound were made on the greatest of those peaks that were not affected by any coelution. Replicate analyses gave an analytical precision between 10% and 15%.

3.5. Thermochemolysis (lignin and fatty acids)

When checking different thermochemolysis methods, Challinor (1998) compared the results of experiments carried out at 770, 510 and 358 °C and concluded that “temperature has a small influence on the product distribution” and that “the methylated polyol products are produced in greater abundance at the lower temperature”. Despite these conclusions he chose to operate at 770 °C “that is the standard temperature for conventional pyrolysis”. Recently Klingberg et al. (2005) tested lignin pyrolysis in the 310–710 °C range and also concluded that the highest yield of monomers was obtained at 310 °C. Previously, Hatcher et al. (1995) compared the results of analysis of lignin in decomposing wood by thermochemolysis with TMAH at 250 °C and those of conventional analysis after lignin saponification in presence of CuO, also at 250 °C. We chose to operate at this mild temperature of 250 °C in order to obtain biological components unaltered by too high an operating temperature and unmixed with a large variety of pyrolysis products.

Briefly, 50 to 100 mg of dried and crushed peat were introduced in SVL® screw-cap glass tubes (18 cm long; 18 mm external ϕ). The peat material was successively wetted with 100 μ l of standard solution (heptylbenzoic acid 21 μ g/100 μ l MeOH) and 100 μ l tetramethyl ammonium hydroxide solution (TMAH; 25% in MeOH). The tubes were placed open in an oven at 75 °C for 3 to 5 h to evaporate the excess methanol, then cooled and closed under vacuum (see Appendix A). Then they were placed vertically in a sand bath heated at 250 °C and left for 20 min. After cooling in ambient air, they were opened and 1.5 ml diethylether was introduced to extract the pyrolysis products. After evaporation of the ether, the extracts were diluted in 50 or 100 μ l CH₂Cl₂ and analysed by GC-MS on a TRACE-PolarisGCQ. The gas chromatograph was fitted with a Rtx-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μ m film thickness) with 5 m of guard column. The GC operating conditions were: temperature held at 40 °C for 1 min, then increased from 40 to 120 °C at 30 °C min⁻¹, 120 to 300 °C at 3 °C min⁻¹, with final isothermal hold at 300 °C over 30 min. The sample was injected splitless, with the injector temperature set at 280 °C. The carrier gas was helium. The mass spectrometer was operated in the electron ionisation (EI) mode at 70 eV ionisation energy and scanned from 50 to 600 Da.

4. Results and discussion

4.1. Rock-Eval pyrolysis

The variations in the main Rock-Eval pyrolysis parameters with depth are shown in Fig. 2. TOC contents are about 10% in Unit 1 with Tmax values around 430 °C. This unit has clearly been affected by pedogenesis. This is not evidenced by HI values, which remain at normal levels (ca. 250 mg HC g⁻¹ TOC) for an immature type III OM (i.e. derived from ligno-cellulosic material), but by rather high OI values (ca. 250 mg CO₂ g⁻¹ TOC). Taken together these HI and OI values indicate that the OM of this unit has not been extensively altered but has nevertheless suffered notable oxidation. Unit 1 is not considered extensively in the following.

Unit 2a is characterized by TOC values around 20% and lower Tmax values than in the overlying Unit 1 (330 against 430 °C; Fig. 2). In this mixed organo-mineral section, high OI values (ca. 150 vs. ca. 100 mg CO₂.g⁻¹ TOC) are accompanied by relatively high HI values (ca. 350 vs. ca. 300 mg HC g⁻¹ TOC). These figures could be explained by a combination of factors such as the burial of notable amounts of oxidized organic material (responsible for the rise of OI) together with hydrogen-rich biological remains. This latter point is supported by the HI value of about 450 mg HC g⁻¹ TOC, recorded at about 1.6 m depth (together with Tmax values reaching 430 °C).

TOC contents reach as much as 50% in Unit 2b and show few marked variations. Tmax also remains constant around 330 °C except for the 370–460 cm interval at the base of this unit where it alternates between 330 and 430 °C (Fig. 2). Within this specific interval, TOC values irregularly decrease to reach values close to 20% at its base. The very high TOC contents (up to about 50%) found in a large part of Unit 2b are typical for mineral-poor peat material. The uniform distribution of such high TOC values on a large interval also suggests rather stable environmental (i.e. mostly hydrologic) conditions during peat deposition. In contrast, the variable and lower but still high TOC contents (20 to 50%) observed in the lower and upper parts of Unit 2b indicate that initial and final peat growth conditions were perturbed by detrital inputs from the Rhône River. In contrast to the TOC record, HI and OI values display few changes all along Unit 2b. For example, the marked TOC fluctuations recorded at the

base of this unit are accompanied by very limited OI and even more limited HI changes. In summary, the marked environmental changes that occurred during the deposition of Unit 2b and that are revealed by changes in lithology and TOC contents are not accompanied by significant OM quality changes as revealed by OI and HI indexes.

The R400 parameter represents the part of the S2 peak produced below 400 °C compared to the total S2 peak ($R400 = S2_{<400} / S2$; Fig. 3). The part of the S2 signal produced below 400 °C mostly results from the thermal decomposition of biological components (especially cellulose and lignin), whereas the higher temperature (> 400 °C) signal is more particularly due to geopolymers (e.g. humic substances; Disnar et al., 2003). Hence, high R400 values are recorded for samples containing well-preserved OM whereas low R400 values correspond to more degraded OM.

In Unit 1 affected by pedogenic alteration, R400 values remain at ca. 0.4 (Fig. 2). They increase downwards in Unit 2a to reach a maximum value of 0.58 at ca. 1 m depth, before decreasing progressively down to ca. 160 cm depth. In Unit 2b R400 values show marked fluctuations and are always higher than 0.4 except in the lowermost section where values approaching 0.4 (i.e. identical to those found in Unit 1), are recorded again. When examined more closely, the R400 vs. depth curve delineates a general decreasing trend with more or less regular fluctuations of less than one meter amplitude (Fig. 2). The R400 general decreasing trend in the peaty Unit 2b can be attributed to normal diagenesis that primarily affects labile biochemicals with time. Conversely, the subtle variations in OM quality that are only depicted by the R400 parameter in Unit 2b, whereas HI and OI indices remain constant, can be either interpreted as variable OM inputs or varying preservation conditions. Previous macrofossil analyses (J. Shultz, unpublished results) revealed that all the examined peat derives from typical marsh plants such as the Cyperaceae that cover it at the present time. No notable change in the peat-forming plants can therefore be adduced to explain the R400 variations. In contrast, lithology and TOC changes in the core clearly evidence marked changes in the depositional environment. In the following sections we report results of analyses of various biochemical components aiming at verifying whether the variations in the R400 parameter are indeed related to OM compositional changes not depicted by the OI and HI indices.

4.2. Carbohydrates

The main results of carbohydrate analysis are presented in Fig. 4 and Fig. 5 and in Table 2. If one excludes the two uppermost samples that have undergone pedogenic alteration and the deepest one that has been notably altered ($HI < 250 \text{ mg HC g}^{-1}\text{TOC}$), most of the analysed samples contain rather high carbohydrate amounts. Up to $90 \text{ mg g}^{-1}\text{TOC}$ are recorded in four of the peat samples analysed, and more than $160 \text{ mg g}^{-1}\text{TOC}$ in six of them (Fig. 7). These amounts are much lower than those found in most terrestrial plants in which carbohydrates are the dominant constituents, under the form of the structural polymers cellulose and hemicelluloses. Nevertheless, together with recent findings on modern peat material (Comont et al., 2006) and even lacustrine sediments (Ogier et al., 2001), the presence of such amounts of neutral sugars released by peat hydrolysis contradicts the widely accepted idea that carbohydrates are labile compounds which undergo rapid consumption in the sedimentary environment, peatbogs included (e.g. Pancost et al., 2002). In this respect, the present observation provides further evidence that carbohydrates can be preserved in sediments for thousands of years without any discernible diagenetic evolution.

The cellulosic/total sugar ratio varies between 0.14 and 0.55, the greatest changes being displayed by adjacent samples taken from the thick peat Unit 2b, taken between 303 and 348 cm depth (Fig. 4). In the absence of any marked change in plant source material over the whole section, the change in the proportions of cellulosic and hemicellulosic carbohydrates can most probably be imputed to differential consumption of these two kinds of polymers.

If one first excludes the three extensively altered samples (i.e. the two upper ones and the deepest one) and secondly the ubiquitous glucose (cellulosic plus hemicellulosic), the dominant hemicellulosic sugar is xylose, followed by arabinose. Xylose alone or with other monomeric compounds (arabinose, glucose...) can form various hemicellulosic polymers (xylanes, arabinoxylanes, glucuronoxylanes...) particularly abundant in higher plants (Aspinall, 1983). Accordingly, in the peat-forming environment the major bryophyte hemicellulose monomers are mannose (polytric) or galactose and rhamnose (sphagna) ([Popper and Fry, 2003] and [Comont et al., 2006]) whereas xylose – accompanied by arbinose – is predominant in sedges ([Wicks et al., 1991] and [Bourdon et al., 2000]). The high proportions of these two sugars in all the analysed samples (except those taken in the upper section affected by pedogenesis) are consistent with macrofossil analyses, showing that Chautagne peat derives from typical marsh plants such as sedges, without any noticeable change during the whole record (J. Schultz, unpublished data).

4.3. Lignin and fatty acids (thermochemolysis)

An example of the distribution of compounds obtained by thermochemolysis in the presence of TMAH is shown on the chromatogram in Fig. 6. The identity of the major compounds is mentioned in Table 3. For all analysed samples, the compound distributions are dominated by two series of products, firstly a series of phenolic moieties (methylated by the TMAH) and secondly a series of fatty acid methyl esters (FAMES). The hydroxyl and carboxylic groups of all compounds released by thermochemolysis are methylated (i.e. etherified and esterified, respectively) but for reasons of simplicity they are designated by the name of their non-methylated counterpart in the following discussion.

Lignin yields comprised between 4 and 20 $\mu\text{g g}^{-1}\text{TOC}$; i.e. in the same range as those obtained on various plant materials, including *Juncus*, a typical marsh plant (Hatcher et al., 1995). Syringic over Vanillic (S/V) ratio values are comprised between 0.45 and 0.93 (Table 4), which is consistent with an inheritance of angiospermous OM, gymnosperm tissues being devoid of S units (Hedges and Mann, 1979). This conclusion is consistent with carbohydrate analyses. Macrofossil investigations also revealed that most of the non-amorphous OM debris originated from monocotyledon rootlets, another part of the particulate material being fragments of leaves of various typical bog plants (sedges, rushes...; J. Schultz, unpublished data). These observations are also consistent with notable Cinnamic over Vanillic ratio (C/V) values ranging from 0.9 to 4.7 (Table 4; Fig. 7), which indicate that the OM derives at least partly from non-woody tissues of angiosperms or more specifically from non-woody monocotyledons such as the marsh plants of the *Juncus* and *Cyperus* genera, the lignin of which is known to be rich in cinnamyl derivatives ([Clifford et al., 1995] and [Bourdon et al., 2000]).

C/(V + S) ratios range from 0.6 to 2.4 (Table 4). These rather high values indicate that the analysed material was rather well-preserved. In contrast to syringyl and vanadyl (or guaiacyl) units which are linked together by resilient $\beta\text{-O-4}$ to form the lignin backbone, cinnamic units

are peripheral to this structure to which they are linked by rather labile ester bonds (Dence and Lin, 1992). These features explain why cinnamic units can be released rather easily, for example during early diagenesis (Bourdon et al., 2000) or more generally thanks to intensive microbial activity.

The correlation between $C/(V + S)$ and S/V ratios ($r^2 = 0.76$; Fig. 7) might reflect another alteration process involving the loss of an original methoxyl group on syringyl moiety resulting in the corresponding vanillyl counterpart ([Hedges et al., 1988] and [Goñi et al., 1993]). Another common lignin degradation process is the apparent production of vanillic and syringic acids (Vac and Sac) at the expense of the corresponding aldehydes, thus entailing an increase in the corresponding Ac/Ald ratio values. In fact, Vac and Sac formation primarily results from the oxidative cleavage of the C3-alkyl side chain of the lignin monomeric units that can be realized by white rot fungi ([Hedges et al., 1988] and [Higuchi, 1990]). However, except for the sample taken at 222.5 cm depth, which has a very high Ac/Ald ratio value, those of the other samples remain in the same range (i.e. between ca. 2.5 and 4.5) throughout the core (Table 4). We can thus hypothesize that the conditions particularly favourable to fungi development were reached only once during the deposition of the studied section (from the small number of samples analysed). These conditions were probably fulfilled during a marked lowering of the water table entailing a drying of the surface peat layer. In contrast, the two other lignin alteration processes (loss of cinnamic units on the one hand and of methoxyl groups on the other hand) might have been caused by less drastic environmental conditions, for example, a rather low level of the water table favouring aerobic microbial activity such as that observed in the case of drainage.

The other major compounds released in notable amounts by thermochemolysis are regular fatty acids (Table 3 and Table 4). The distribution of these compounds extends at least from the n -C₁₆ to the n -C₃₀ and is highly dominated by the even-numbered homologues (Fig. 6). Classically the even-numbered high molecular weight fatty acids (C₂₀₊) are believed to be typical of higher plants and more precisely of their epicuticular waxes (Eglinton and Hamilton, 1967). In contrast, their lower homologues (C₂₀₋, i.e. mainly the n -C_{16:0} and n -C_{18:0} FA) are ubiquitous. In lake sediments the latter are assumed to be derived from autochthonous production because those derived from terrestrial plants are rather easily degraded in soil litters ([Marseille et al., 1999] and [Disnar et al., 2005]). In peat they can be inherited from all the peat-forming plants, i.e. from aquatic plants with a possible contribution from diatoms and from microorganisms that proliferated during early diagenesis ([Bourdon et al., 2000] and [Disnar et al., 2005]). In addition, the C₂₀₋ produced *in situ* are rather easily degraded during early diagenesis, as compared to their high molecular weight counterparts (Stefanova and Disnar, 2000 and references therein). For these various reasons, the classical C₂₀₋/C₂₀₊ fatty acids ratio must be considered with caution and used as an indicator of diagenesis rather than of source material in peat samples. The weak opposite correlation between the C₂₀₋/C₂₀₊ and the S/V ratios (Fig. 8) shows increasing lignin alteration with increasing proportions of low molecular weight fatty acids inherited from microorganisms, and thus, with increasing early diagenetic alteration.

5. General discussion

5.1. R400 significance and relation with OM composition and alteration

Rock-Eval pyrolysis has rather frequently been used for paleoenvironmental reconstructions from peat and recent sediment records (e.g. Talbot and Livingstone, 1989; [Sifeddine et al.,

1995], [Sifeddine et al., 1998] and [Lüniger and Schwark, 2002]). However, these applications were based only on the classical parameters TOC, HI and OI. Until recently little attention was paid to the shape of the pyrolysis signal S2 except in some specific applications (e.g. Disnar and Trichet, 1984). However, an evolution in the shape of the pyrolysis S2 peak with increasing humification is straightforward along soil profiles (Disnar et al., 2003). This evolution is typified by a change in the shape of the S2 peak which usually presents several shoulders in soil or recent sediment samples and by a displacement of the major component towards higher temperatures with increasing maturity (humification or diagenesis). Accordingly, this displacement is accompanied by a stepwise change in the temperature of maximum production of hydrocarbonaceous compounds (T_{peak}), measured at the apex of the S2 signal. The rationale for this evolution is the progressive disappearance of the labile biological components, which are predominant in the litter, and an increase in the proportions of rather refractory geopolymers (i.e. humic substances) at depth. Despite an overlap, these two types of compounds are pyrolysed before and after 400 °C, respectively (in standard analysis conditions; see Section 3). This basic observation explains and justifies the determination of the R400 parameter, which simply represents the proportion of labile components in the studied OM (Disnar et al., 2003; Fig. 3). Sebag et al. (2006) went further in the analysis of the S2 peak in demonstrating that, for almost all types of soils, the S2 curve can be deconvoluted in four gaussian elementary curves named F1 to F4. F1 and F2 account for labile components and F3 and F4 for refractory geopolymers. Sebag (2002) applied S2 decomposition to a peat deposit located near the Seine River, in the vicinity of its estuary, and interpreted the observed variations in terms of watertable level changes. The same approach was first applied to the presently studied Chautagne CH04-02 core (C. Thibault, unpublished Master's dissertation). However, because this calculation is time-consuming and tedious we decided to use the R400 parameter, which is easily calculated from the Rock-Eval device output and moreover very robust. As a matter of fact, in contrast to TOC, OI and HI which rely on the recording of several analytical signals by at least two detectors (one FID and one IR cell; see Section 3), the calculation of the R400 uses only the S2 signal (Fig. 3). R400 should therefore not be affected by any Rock-Eval malfunctioning and could even be measured accurately without any calibration of the FID detector. To our knowledge this study is the first application of the R400 parameter.

As illustrated in Fig. 9a, R400 values and total carbohydrate contents are significantly correlated ($r^2 = 0.81$). This result was expected given the observations on which the R400 parameter is based and the important role played by carbohydrates in plant material. r^2 is lower for the R400-Total lignin correlation (0.38; Fig. 9b) and even lower for the R400-Total fatty acids correlation (0.29; Fig. 9c). Put very simply, the agreement of our molecular data with R400 values decreases in the following order: carbohydrates > lignin > fatty acids. In fact, this order also roughly represents the relative abundance of these compounds in plants. This observation is straightforward for carbohydrates that constitute by far the major part of plant material in the form of structural and storage components (cellulose, hemicelluloses, pectines and starch), even if they are preferentially used over lignin in anaerobic environments ([Young and Frazer, 1987] and [Beguín and Aubert, 1994]). Despite much lower amounts in our peat samples than in the original plant material, carbohydrates remain in sufficiently high amounts to contribute significantly to the labile biopolymer fraction that decomposes before 400 °C upon pyrolysis, and thus contribute to high R400 values. In contrast, lignin is much less abundant than carbohydrates and suffered little degradation. The loss of peripheral lignin units (cinnamic acids) or functional groups (methoxyls) as well as those of fatty acids can only play a limited part in bulk OM properties, in proportion to their limited contribution to the peat material.

5.2. Paleoenvironmental record and significance of the R400 parameter

After the Rhône bypassed Lake Le Bourget at the beginning of the Holocene (see Section 2 “Setting”), the river detrital inputs progressively filled in the glacial depression upstream of the Chat mountain (Bravard, 1987; Fig. 1). The immediate consequence of this was a continuous rise in the Rhône riverbed, which controls the hydrology of Lake Le Bourget and of the Chautagne swamp. This functioning necessarily entails that the water level fluctuations in the lake and the swamp can only be straightforwardly compared to paleoenvironmental records pertaining to this very peculiar hydrological system. Some records fulfilling this requirement are displayed in Fig. 10 where they are compared with the variations in TOC and R400 values with time in the Chautagne swamp record. Lake Le Bourget water level variations during the last 4500 years were reconstructed by Magny and Richard (1985) after the study of shallow-water sediment cores. The Rhône River hydrological activity (reconstructed by Arnaud et al., 2005 after Bravard, 1996), provides additional information but on an even shorter time span (Fig. 10). The only hydrological record that covers a similar time span as that of the Chautagne swamp in the study area comes from Le Bourget Lake filling. Over the Holocene, the amount of detrital input (attested by titanium concentration) carried by the Rhône River within the autochthonous carbonated sediments of the lake is indicative of the recurrence of Rhodanian floods and, by extension, of precipitation over the Alps ([Chapron et al., 2005] and [Arnaud et al., 2005]). Because of these rather scarce data the following discussion is limited to the most salient points, leaving a more detailed analysis of lake Le Bourget water level fluctuations to a further approach.

Consistently with previous estimates of the initiation of the Chautagne swamp (Bravard, 1987), the base of peat Unit 2b is dated back to the Early Holocene (10060 ± 160 cal BP at 4.57 m depth). Then, from this event and thus during all the Holocene, both the Chautagne swamp and lake Le Bourget received only Rhône river inputs during major floods, the current being then reversed in the normal outlet of the lake, the Savière channel (see Section 2 “Setting”). This common history of the swamp and of the lake is fully reflected by their respective fillings despite contrasted lithologies (Fig. 10). To the TOC-free basal Unit 3 of core CH04-01 corresponds the lowermost section of lake Le Bourget core LDB04 characterized by high and highly fluctuating Ti contents typical of Rhodanian input (Fig. 10). Both these sections were certainly emplaced contemporaneously in the paleogreat lake Le Bourget, when the river was still directly flowing into the lake, and thus before the initiation of the Chautagne swamp peat accumulation. After this event and during the entire time span covered by Unit 2b, a marked change in the environment with the establishment of quiet sedimentation conditions is depicted by peat accumulation at Chautagne and by the simultaneous deposition of Ti-poor lake sediments typical of autochthonous carbonate production. Large TOC fluctuations at the base of Unit 2b indicate that quiet sedimentation conditions did not establish suddenly in the marsh but were for some time still perturbed by incursions of the Rhône River. Despite these inputs of inorganic material and other similar inputs that also occurred near the top of Unit 2b, the peat material of the whole section remained rather homogeneous and well-preserved, as depicted by rather low OI and high HI values (about $150 \text{ mg CO}_2 \text{ g}^{-1} \text{ TOC}$ and $300 \text{ mg HC.g}^{-1} \text{ TOC}$, respectively). In addition to notable fluctuations further discussed hereafter, R400 parameter values also register a general downward decrease all through Unit 2b that may be ascribed to normal diagenetic alteration (see Section 4.1) The shorter range variations of the R400 parameter all along Unit 2b, i.e. between ca. 10,000 and 1000 cal BP, exhibit minimum values around 8500, 7000, 4500 and 2150 cal BP. While the latter minimum which corresponds to the limit between Units 2b and 2a is also well documented by marked variations of other Rock-Eval parameters (TOC, HI

and OI; see hereafter), the other minima are not. However, their significance in terms of OM alteration is confirmed by molecular analysis data, namely by particularly low carbohydrate contents (Table 2; Fig. 4). These low R400 values are thus very probably related to low levels of the water table during peat deposition.

The marked R400 parameter lowering that occurs at the top of Unit 2a (~ 2150 cal. BP) precludes a marked lowering in TOC values accompanied by a simultaneous rise in HI and OI values as well as minerogenic contribution. A simultaneous change in both these parameters is unexpected and contradictory. The rise of HI up to a value exceeding 450 mg HC g^{-1} could tentatively be explained by a notable input of lacustrine OM whereas the high OI values could be attributed to a contribution of oxidized peat-forming material. However, it can be speculated that such features might have resulted from a rise in the water table and in local hydrodynamic conditions simultaneously entailing: (1) a perturbation in the growth of the peat-forming plants and in the preservation of their remains but with (2) a simultaneous stimulation of the lacustrine production because of a greater water depth and nutrient input from the Rhône. Nevertheless, this explanation remains only tentative in the absence of other indications. R400 reaches a maximum at around 100 cm depth before decreasing with other parameters towards the top of Unit 2b.

The rather continuous peat accumulation all through Unit 2b is consistent with the irregular but progressive rise of the water level in the swamp and the lake consequential to the rise of the Rhône riverbed after it changed channel at the beginning of the Holocene (see here above). This rise, with marked irregularities, is also documented by Magny and Richard (1985) for the ca. 4500–2000 cal BP time span (Fig. 10). In a similar way the clay-rich peaty Unit 2a might have been deposited during the following high lake level period (Magny and Richard, 1985) which corresponds to several intervals of high activity of the Rhône successively during the Roman and the High Middle Age wet periods, and even more recently during the Little Ice Age (Arnaud et al., 2005). Nevertheless we shall not expand on this point since this latter period might more precisely correspond to the deposition of Unit 1 latter affected by pedogenic alteration.

6. Conclusions

In contrast to widely held ideas carbohydrates (cellulose and hemicelluloses) are preserved in high proportions at the molecular level in peat and, additionally, survive long term diagenesis, i.e. at least several thousands of years. Degradation of the peat material is simultaneously expressed by carbohydrate consumption and lignin alteration, but limited to the loss of peripheral components and functional groups (i.e. cinnamic units and methoxyls, respectively) for lignin. These two processes are probably operative in environmental conditions only slightly unfavourable to peatification. In contrast, the oxidative cleavage of the lignin polymer entailing the formation of vanillic and/or syringic acids more probably requires more severe biodegradation possibly triggered by a lowering in the watertable (e.g. during a drought).

R400 is a robust and sensitive indicator of OM quality in peat and recent sediments since its changes are effectively accompanied by compositional OM changes (carbohydrates and other biochemical contents; see here above), not indicated by significant change in the Rock-Eval OI and/or HI indexes. Its evolution all through the peat section penetrated by the studied CH04-02 core is also overall consistent with the major hydrological events that affected the study area, since and including the change of channel of the Rhône at the beginning of the Holocene. In full agreement with the information brought by the lake Le Bourget sediment

filling, the study of the Chautagne peat record reveals rather quiet sedimentation conditions from the beginning of the Holocene up to around 2000 yr cal BP and much more perturbations afterwards.

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Appendix A

The tube containing the material to be analysed with the reagents is placed vertically, cap unscrewed, in the device schematized in Fig. 11. The Teflon lined u-shaped open cap at the bottom of the device is fastened tightly. Then the vacuum pump is turned on. Once the air inside the device and the reaction tube is evacuated, the reaction tube is pushed firmly against the rubber stopper and turned to screw until closed.

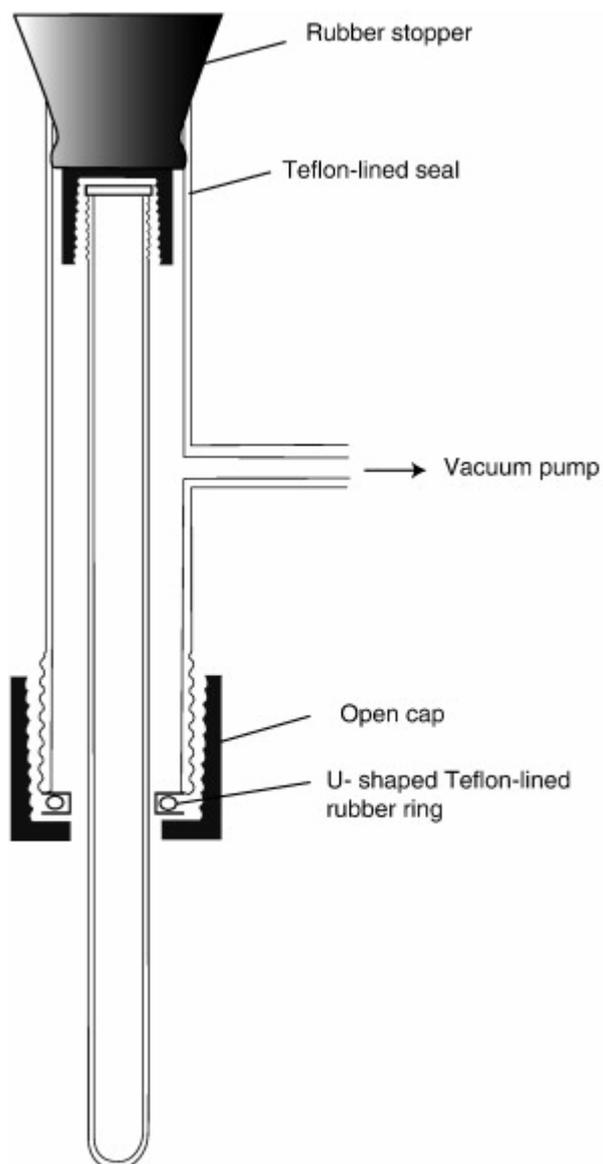


Fig. 11. Device used to evacuate the air inside the samples tubes previous to hydrolysis (carbohydrate analysis) or thermochemolysis.

Figures and Tables

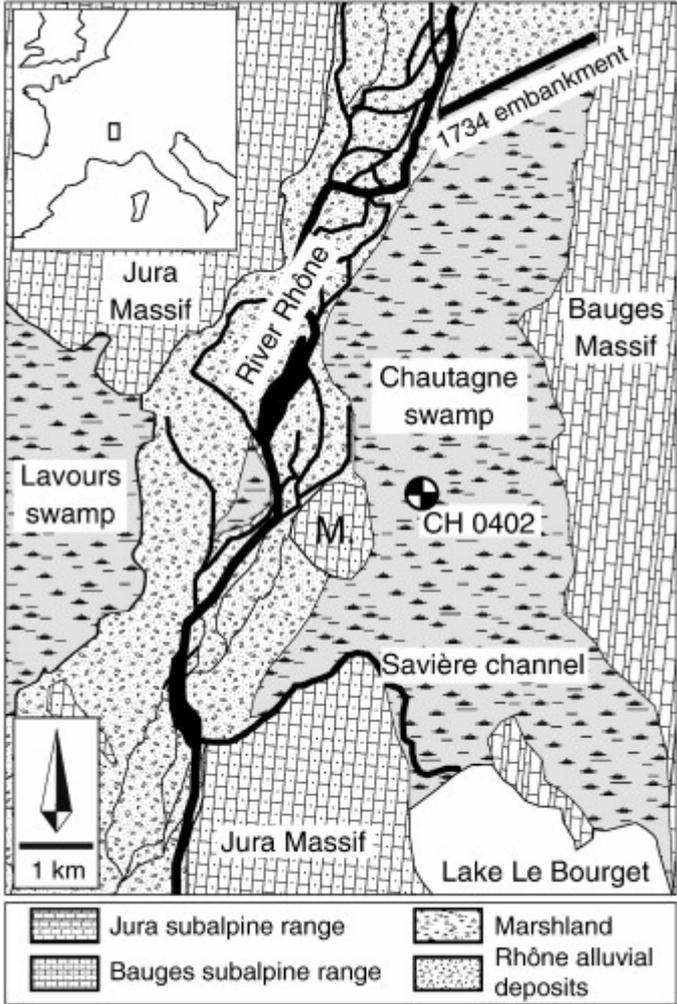


Fig. 1. Location of the Chautagne marsh with indication of the coring site (after Bravard, 1987). M = Mollard of Vions rock.

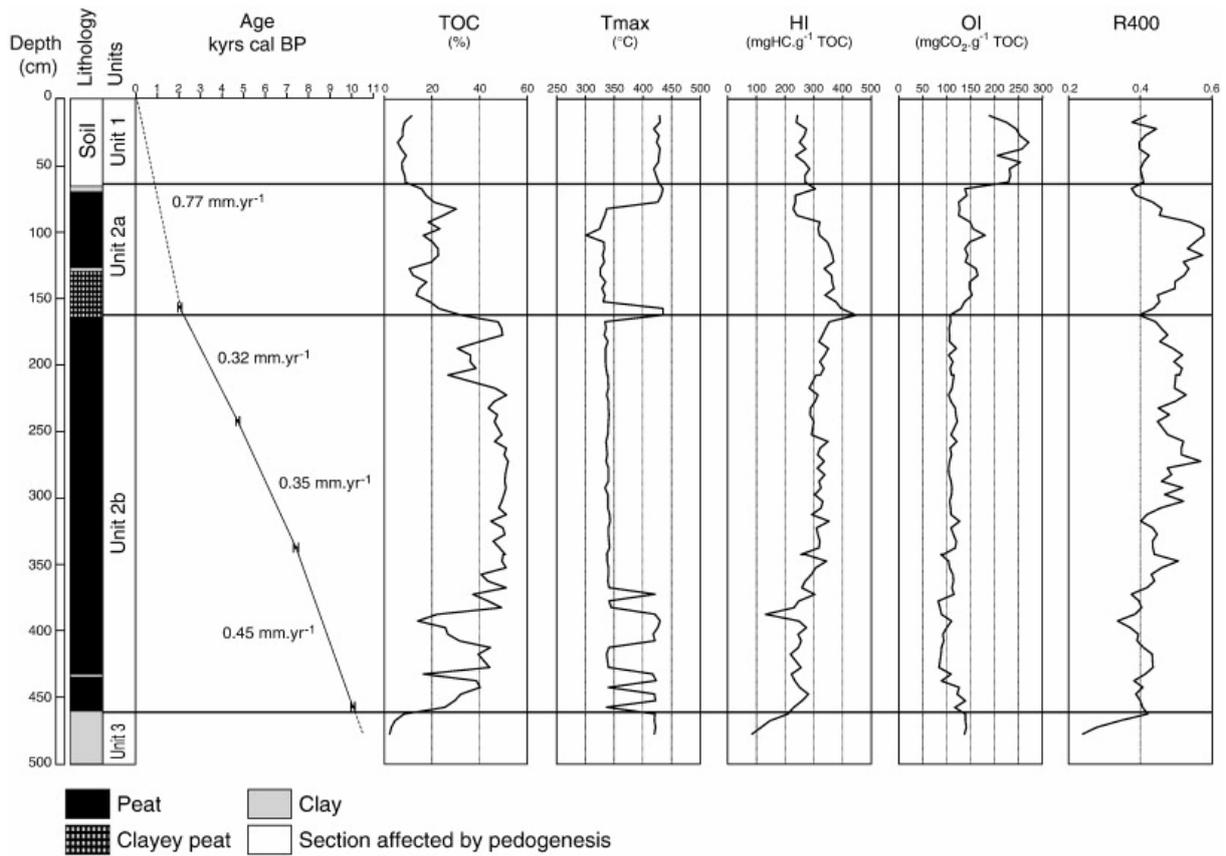


Fig. 2. Lithology of the studied core section (Chautagne core CH04-02), age model and evolution of Rock-Eval parameters (TOC, IH, IO, TpS2, R400) with depth.

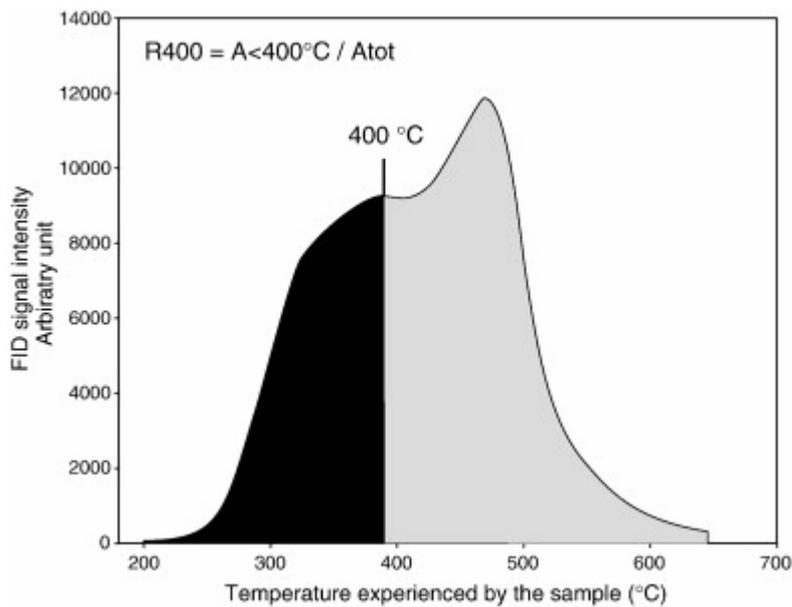


Fig. 3. Example of S2 peak produced by RE pyrolysis of an immature OM-containing sediment (or soil) with indication of the mode of calculation of the R400 parameter (details in Disnar et al., 2003).

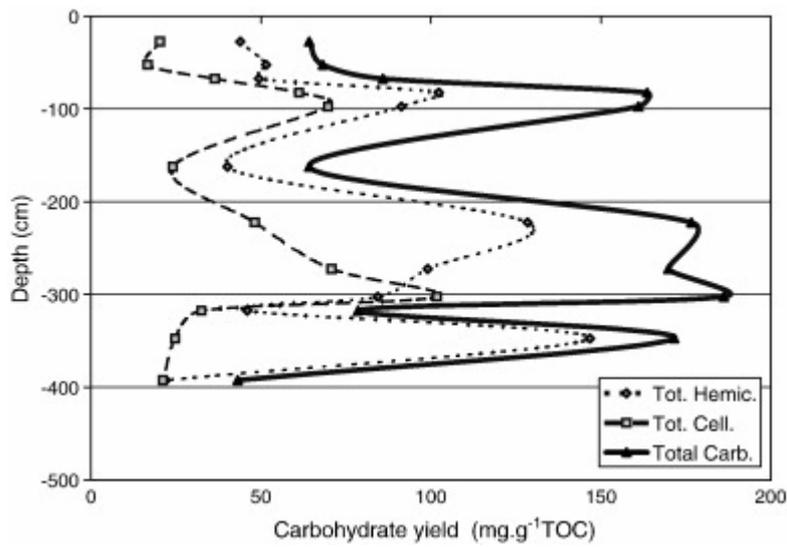


Fig. 4. Depth profiles of cellulosic, hemicellulosic and total (cellulosic + hemicellulosic) carbohydrate yields ($\text{mg g}^{-1} \text{TOC}$) in the Chautagne swamp (core CH04-02).

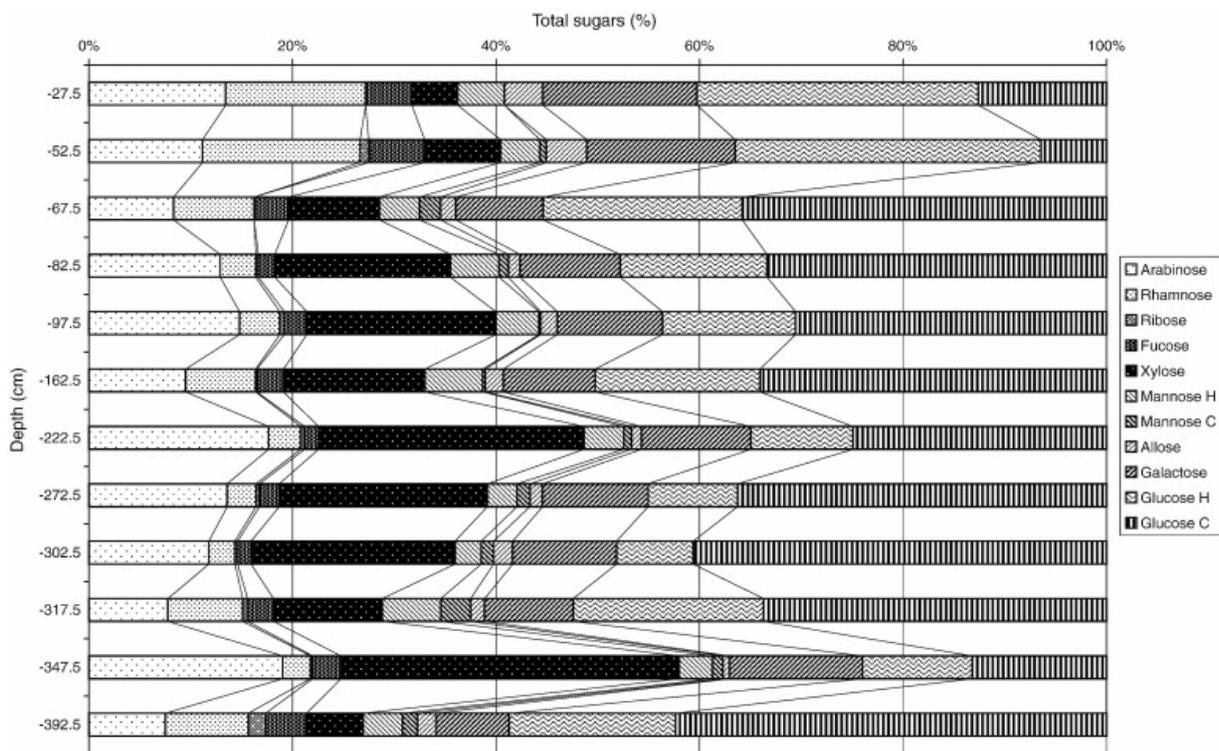


Fig. 5. Individual carbohydrate distribution in the analysed Chautagne peat samples (arabinose, rhamnose, ribose, fucose, xylose, mannose, allose, galactose, cellulosic (C) and hemicellulosic (H) glucose in wt.%).

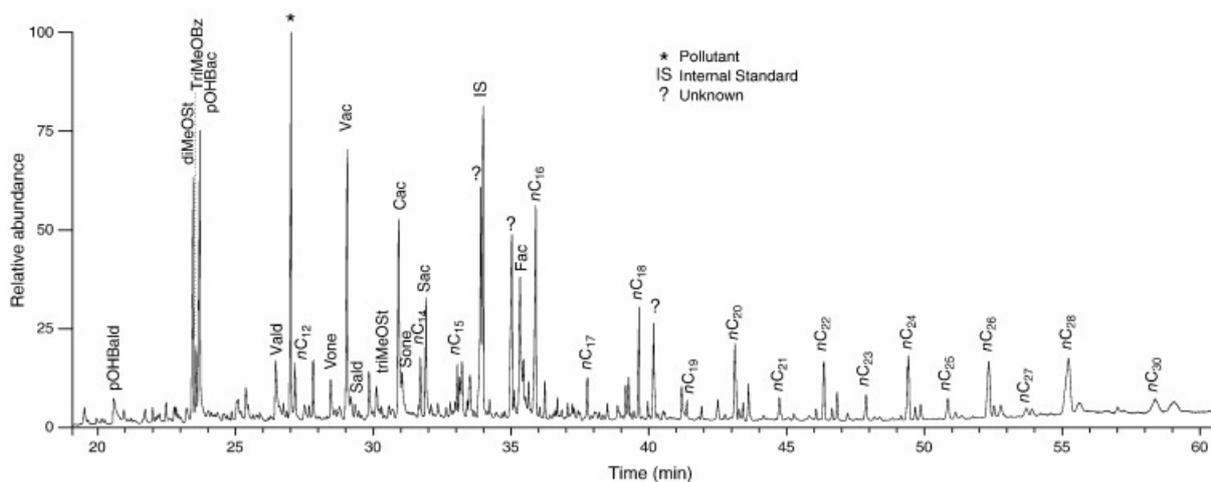


Fig. 6. Example of partial reconstituted Total Ion Current (TIC) chromatogram of the products of thermochemolysis with TMAH, of a peat sample from the Chautagne swamp (core CH04-02, sample CH12 taken at 67.5 cm depth). Fatty acid methyl esters (FAMES) are designated by their carbon number. The main other compounds identified are listed in Table 3.

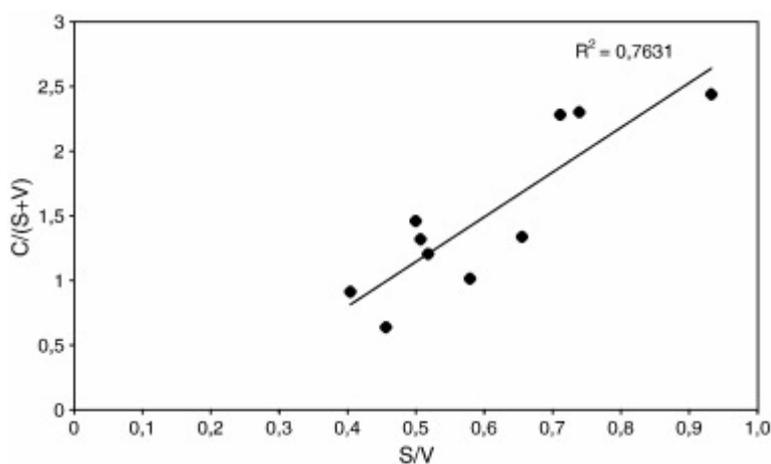


Fig. 7. Coumaric (C) over vanillic (V) plus syringic (S) vs. syringic over vanillic ratio (S/V) correlation.

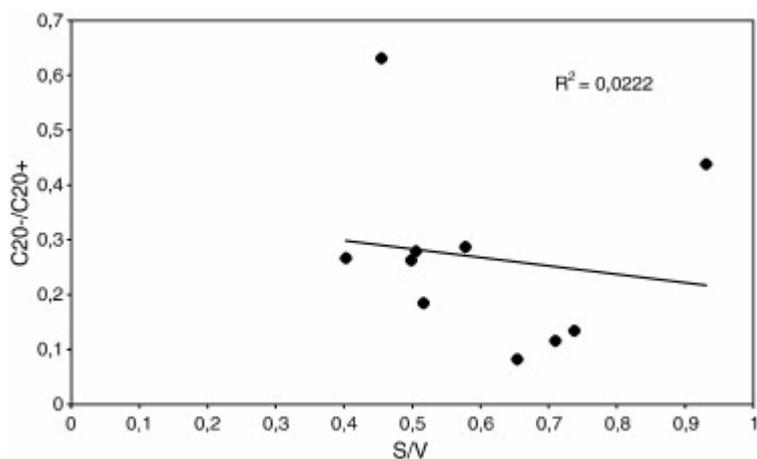


Fig. 8. (C_{20-}/C_{20+}) FAMES vs. S/V ratio.

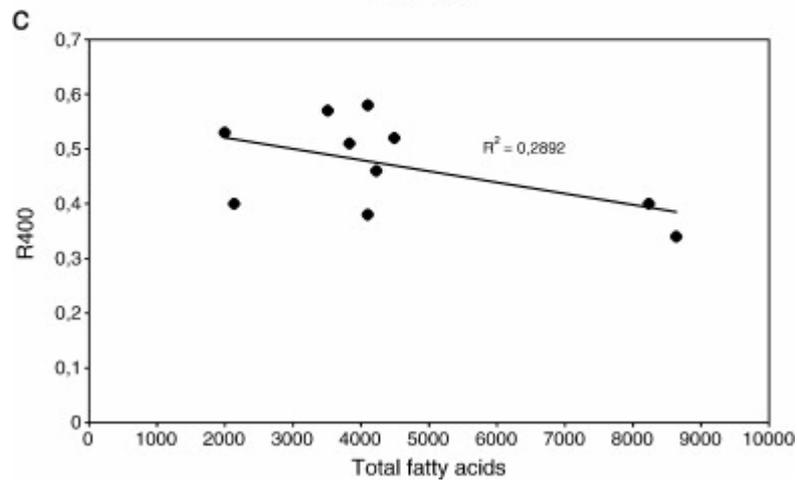
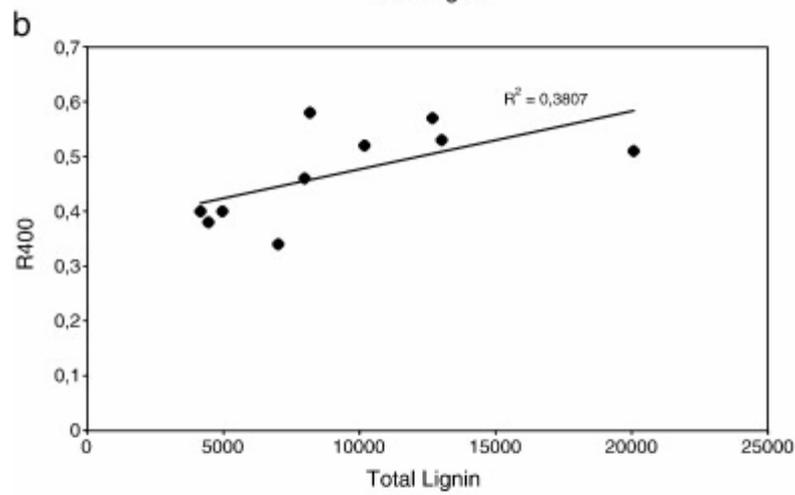
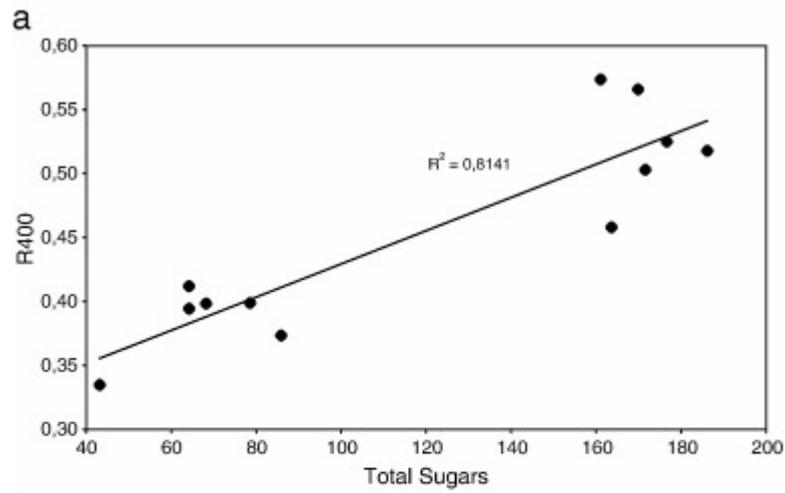


Fig. 9. a, b and c: R400 vs. total carbohydrates; R400 vs. total lignin; R400 vs. total fatty acids.

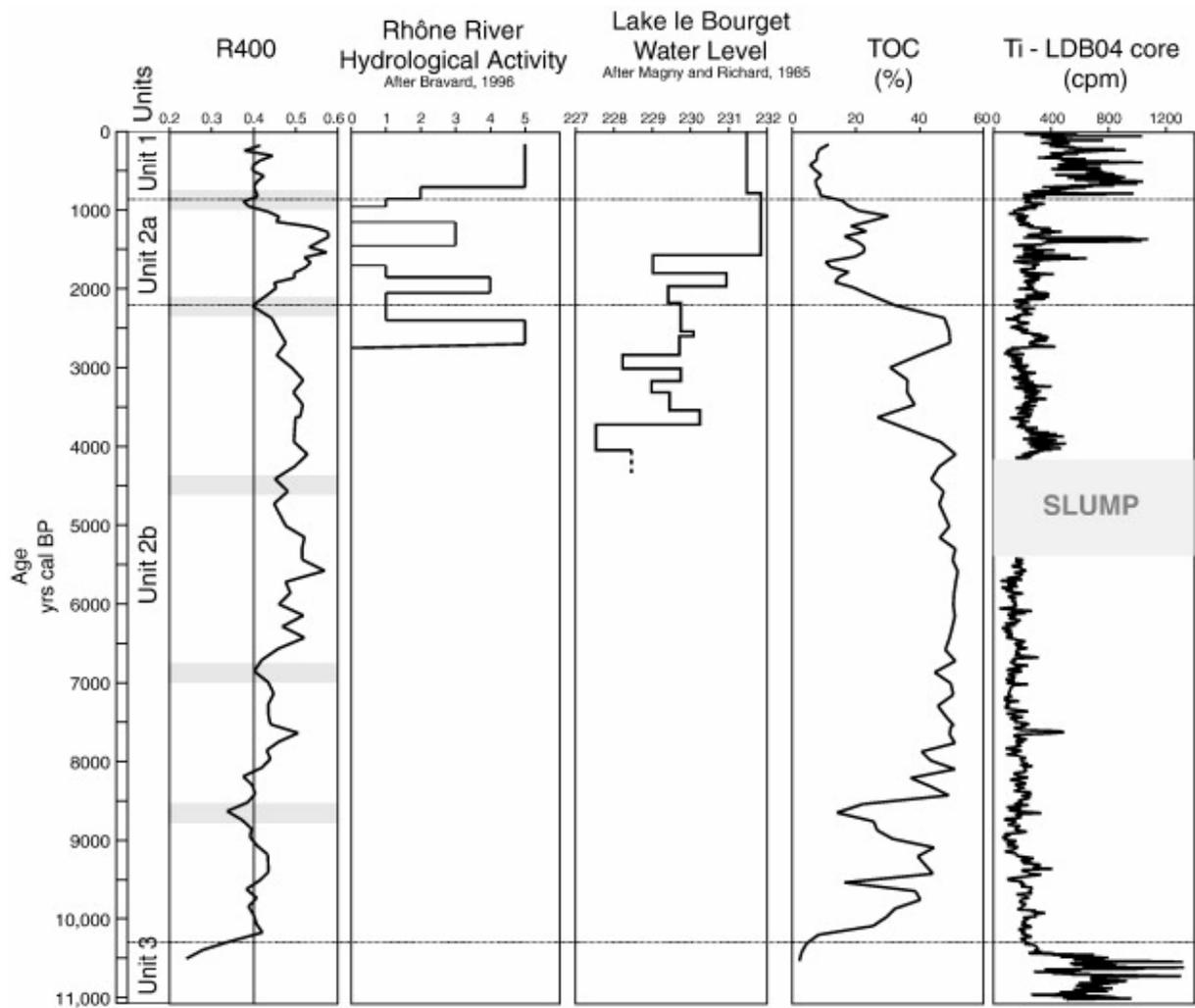


Fig. 10. Evolution of R400 and TOC contents (%) in core CH04-02, compared to other regional and global proxy records: Rhône River hydrological activity (after Bravard, 1996); Lake Le Bourget water level fluctuations (after Magny and Richard, 1985); Ti contents in lake Le Bourget sediments (LDB04 core; F. Arnaud, unpublished report).

Table 1. : ^{14}C dates used for the establishment of core CH-0402 age model

Lab number	Sample	Type	$\delta^{13}\text{C}$	^{14}C age yr BP	Age cal BP
SacA4841	CH0402-78	Peat	- 26.10	6890 \pm 40	7740 \pm 85
SacA4842	CH0402-157	Peat	- 36.00	2055 \pm 30	2030 \pm 85
SacA4843	CH0402-242	Peat	- 26.20	4175 \pm 35	4720 \pm 110
SacA4844	CH0402-337	Peat	- 24.60	6515 \pm 40	7420 \pm 95
SacA4845	CH0402-412	Peat	n.d.	965 \pm 30	860 \pm 70
SacA4846	CH0402-457	Peat	- 26.25	8940 \pm 45	10,060 \pm 150

(*) erroneous dates not taken into consideration; n.d. = not determined.

Table 2. : Cellulose and hemicellulose yields and individual sugar distribution in the analysed Chautagne peat samples (a) total sugar abundance (in mg g^{-1} dry sample); (b) distributions of hemicellulosic sugars (arabinose, rhamnose, ribose, fucose, xylose, mannose, allose, galactose and cellulosic (C) and hemicellulosic (H) glucose in wt.%)

Hemicellulosic sugars									Total hemicellulosics	Total cellulotics	Total sugars
Arabinose	Rhamnose	Ribose	Fucose	Xylose	Mannose	Allose	Galactose	Glucose			
%	%	%	%	%	%	%	%	%	mg g^{-1}	mg g^{-1}	mg g^{-1}
8.8	18.8	–	5.8	6.4	6.7	2.6	10.5	40.4	3.4	1.6	4.9
11.2	14.4	1.1	7.3	7.9	5.1	2.2	11.0	39.8	3.9	1.2	5.1
14.4	11.9	–	5.2	15.5	6.8	1.3	10.9	34.0	7.8	5.7	13.5
19.4	5.3	0.4	2.2	27.6	7.6	0.7	13.7	23.0	30.9	18.5	49.4
19.5	7.0	0.8	3.0	25.1	7.5	0.9	13.2	23.1	21.3	16.2	37.5
15.2	9.1	–	3.1	22.2	9.1	1.1	14.4	25.9	13.0	7.8	20.8
24.3	4.1	0.4	1.6	35.9	5.4	0.7	13.9	13.8	65.8	24.7	90.4
21.8	4.3	0.5	3.3	35.1	5.0	0.6	14.3	15.1	51.4	36.7	88.2
20.4	4.7	0.3	2.9	33.9	5.7	0.7	14.8	16.6	41.6	50.2	91.8
13.2	9.0	0.8	2.3	18.3	9.8	1.2	13.3	32.0	20.6	14.6	35.1
22.3	3.2	0.2	3.3	38.8	3.8	0.6	15.3	12.6	72.4	12.2	84.6
13.0	16.0	–	6.5	10.9	7.6	1.4	12.5	32.1	3.1	3.0	6.0

Table 3.

Identity of the major compounds released by thermochemolysis with TMAH of peat samples from the Chautagne swamp (FAMEs excluded)

Compound name	Abbreviated name
p-Hydroxybenzaldehyde ME	pOHBald
Dimethoxy-2,3-styrene	diMeOSt
Trimethoxy-1,2,4-benzene	triMeOBz
p-Hydroxybenzoic acid MEMe	pOHBac
Vanillin ME	Vald
Ionol (contaminant)	(ionol)
Acetovanillone ME	Vone
Vanillic acid MEMe	Vac
Syringaldehyde ME	Sald
Trimethoxystyrene	triMeOSt
Coumaric acid MEMe	Cac
Syringic acid MEMe	Sac
n-alkanol?	?
p-Heptylbenzoic acid Me (Internal standard)	IS
Hexadecenol?	
Ferulic acid MEMe	Fac

ME = Methyl ether; Me = Methyl ester.

Table 4. : Main results from the thermochemolysis + GC-MS analysis of samples from the Chautagne swamp

Spl.	Depth	TOC	R400	C	V	S	Lignin	S/V	Ald	Ac	Vald/Vac	Sald/Sac	Ac/Lig	Ac/Ald	C/ (S + V)	FAME C20-	FAME C20+	FAME tot	FAME C20-/C20+
	Cm	%		$\mu\text{g g}^{-1}$ TOC	$\mu\text{g g}^{-1}$ TOC	$\mu\text{g g}^{-1}$ TOC	$\mu\text{g g}^{-1}$ TOC		$\mu\text{g g}^{-1}$ TOC	$\mu\text{g g}^{-1}$ TOC						$\mu\text{g g}^{-1}$ TOC	$\mu\text{g g}^{-1}$ TOC	$\mu\text{g g}^{-1}$ TOC	
1	67.5	15.69	0.38	1725	1871	851	4447	0.45	689	1826	0.30	0.56	0.41	2.65	0.63	1585	2513	4098	0.63
2	82.5	30.16	0.46	4730	2169	1081	7980	0.50	854	2146	0.50	0.24	0.27	2.51	1.46	878	3344	4222	0.26
3	97.5	23.28	0.58	4641	2347	1186	8174	0.51	957	2322	0.53	0.24	0.28	2.43	1.31	895	3206	4100	0.28
4	162.5	32.36	0.40	2086	1310	757	4153	0.58	348	1582	0.22	0.21	0.38	4.54	1.01	1836	6396	8232	0.29
5	222.5	51.25	0.53	9228	1962	1827	13,018	0.93	386	3054	0.08	0.17	0.23	7.91	2.44	608	1388	1996	0.44
6	272.5	51.9	0.57	8811	2263	1607	12,682	0.71	991	2622	0.56	0.20	0.21	2.65	2.28	364	3146	3510	0.12
7	302.5	49.26	0.52	7089	1776	1311	10,176	0.74	717	2185	0.48	0.31	0.21	3.05	2.30	532	3958	4490	0.13
8	317.5	44.66	0.40	2360	1853	747	4960	0.40	517	1879	0.33	0.09	0.38	3.63	0.91	449	1685	2134	0.27
9	347.5	49.34	0.51	11,467	5202	3403	20,072	0.65	2453	5693	0.53	0.31	0.28	2.32	1.33	291	3538	3829	0.08
10	392.5	14.03	0.34	3825	2101	1086	7011	0.52	844	2079	0.54	0.23	0.30	2.46	1.20	1346	7291	8637	0.18

Sac, Sald & S = Syringic acid, aldehydes and Total, respectively; Vac, Vald & V = Vanillic acid, aldehydes and Total, respectively; C = cinnamic acids [= coumaric (Cac) + ferulic acids (Fac)]; L = total lignin (= sum of V, S and C); Ac, Ald = sum of S & V acids, aldehydes, respectively.

AcetovanilloneME (Vone) and acetosyringoneME (Sone) are both present in all samples but at very low levels. In contrast to Vone that was taken into account in V and Lig calculation, Sone, which only forms a shoulder on the cinnamic acid peak, was omitted.